IVAM UvA BV

Nano in Furniture

State of the art 2012

Fleur van Broekhuizen
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Colophon

Title:	Nano in Furniture -State of the art 2012
Authors:	F.A. van Broekhuizen (IVAM UvA BV, NL)
Steering group:	R. Gehring (EFBWW), C. Ravazzolo (EFIC), M. Eirup (EFIC), B. de Turck (UEA), R. Rodriguez (UEA), U. Spannow (BAT, DK), J. Waage (FNV Bouw, NL) and J. Moratalla (AIDIMA, Es)

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More information about the report can be obtained from:

IVAM UvA BV

Amsterdam-NL

Tel: +31 20 525 5080

www.ivam.uva.nl

Email: office@ivam.uva.nl

1 Introduction

Within the European Social Dialogue, the EFBWW (European Federation of Building and Wood Workers), EFIC (European Furniture Industries Confederation) and UEA (European Furniture Manufacturers Federation) have taken the initiative to commission IVAM UvA BV to investigate the current awareness amongst stakeholders and to make an overview of actual nano-products at the European Furniture market. The report "Nano in Furniture, state-of-the-art 2011, Executive Summary" summarizes the findings of this study that are described in detail in the main report below.

Four questions are central in this work:

- What type of nanomaterials are being used in furniture products?
- What are near future perspectives for using nanomaterials in furniture products?
- What health and safety issues may play a role for workers at the workplace?
- What would a safe workplace look like?

In section 1.1 the current definition and scope of this study will be outlined. Section 2 summarizes different nanomaterials that could be of value for the furniture industry. In section 3, the current market perspective is outlined, including the drivers and barriers encountered. Section 4 then presents health and safety consideration when working with nanomaterials and nano-products in furniture, including the most important routs of exposure, typical exposure scenario's and approaches for working safely. Section 5 does present the current issues regarding the traceability of nanomaterials and the regulatory actions taken in different European member states in order to improve this traceability throughout the product-value chain.

1.1 What is a nanomaterial?

Nanotechnology is considered to be an enabling technology and involves the studying, modification, manipulation or design of processes, substances, materials or products at the nano-scale (which runs between 0,0000001 m and 0,000000001 m). This study focuses on (possible) applications of nanomaterials for furniture products. It does not focus on nanotechnological applications to optimize assessor products for furniture manufacturing like furniture engineering equipment, equipment for quality control, lubricants, air filters or cleaning agents.

Asking the furniture industry which nanomaterials they use is not just a simple question with one straight answer. As only in October 2011 the European Commission adopted an official definition of a nanomaterial, speaking about nanotechnology used to be (and still is) difficult and a lot of misunderstanding between people arises because they mean different things when they say *'nanomaterial'* or *'nano-product'*. Just to give an example: The term *nano-product* is used for products containing nanoparticles like *nano*-TiO_2, which are prepared as nanoparticles (particles with a size range between 1-100 nm in two (nanorods or tubes) or three (spheres) dimensions) and have true new physical and chemical characteristics, and for products like nano-emulsions of i.e. water and wax (for example particular wood coatings which only show improved suspension stability and wood coverage due to the smaller wax particles) that do contain nano-sized wax-droplets of wax-like character. For the first type of products the term nano-product is mostly appreciated. For the second however, this term is much more questioned and rejected by some. As a consequence, it remains a challenge speaking the same language when talking about nano-particles (even among scientists).

On the 18th of October 2011, the European Commission adopted the following definition:

> ***A nanomaterial is a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm. In specific cases and where warranted by concerns for the***

environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%.

A year earlier (5th Oct. 2010), the Australian Government did adopt a slightly different working definition of a nanomaterial, applying to any new chemical that is brought to the market, being:

> ***… industrial materials intentionally produced, manufactured or engineered to have unique properties or specific composition at the nanoscale, that is a size range typically between 1 nm and 100 nm, and is either a nano-object (i.e. that is confined in one, two, or three dimensions at the nanoscale) or is nanostructured (i.e. having an internal or surface structure at the nanoscale)"***
>
> Noting that:
> - intentionally produced, manufactured or engineered materials are distinct from accidentally produced materials;
> - 'unique properties' refers to chemical and/or physical properties that are different because of its nanoscale features as compared to the same material without nanoscale features, and result in unique phenomena (e.g. increased strength, chemical reactivity or conductivity) that enable novel applications;
> - aggregates and agglomerates are considered to be nanostructured substances;
> - where size distribution shows 10% or more of a substance (based on number of particles) is at the nanoscale, NICNAS[1] will consider this substance to be a nanomaterial for risk assessment purposes.

However, in contrast to some other industries like i.e. the paint and lacquer industry, the chemical industry or the plastics industry, the furniture industry isn't a large user of raw nanomaterials. When it would use a nanomaterial, this use is most likely in the form of an ingredient that was put in i.e. a paint, lacquer, textile or composite material by their supplier. The furniture industry therefore doesn't typically work with a nanomaterial, but with a product containing a nanomaterial. In this study therefore the nano-product is the central focus being:

- A ***product*** where one deliberately puts in a nanomaterial to influence its properties -

Wherever possible in this document, the nanomaterials described for furniture are assessed along the European definition of October 2011.

1.2 Different nanomaterials

Nanomaterials are defined as materials that are deliberately designed in a size-range between 1 and 100 nm in 1, 2 or 3 dimensions.

A one dimensional nanomaterial can be a nano-thin sheet of material, like graphene, or a nano-thin coating on the surface of a substrate, like an infra-red reflecting window. It may also be thin platelets of nano-clay that are added to a plastic to reduce the gas permeability of plastic soda bottles to elongate the consumption period of the soda, or that may be used in the near future to reduce the flammability of foams or composite material.

A two dimensional nanomaterial can be tubular or cone like materials. These can be a nano-rod, a single walled nano-tube (SWNT) or a multi walled nano-tube (MWNT), with their main difference being that rods are non-hollow whereas tubes are. A single walled tube thereby consists of only a one layer wall whereas MWNT have walls consisting of multiple layers of material. Another two dimensional nanomaterial may be a surface that is designed like a mountain landscape with nano-sized cones or fillies. Or the mirror-image of this: a surface designed with nano-sized holes or pores.

A three dimensional nanomaterial may be globular or ellipsoidal in shape, rectangular, triangular or any other form with a size between 1 and 100 nm in three directions. These are normally addressed as nanoparticles. However, a three dimensional nanomaterial may also be a metal with an internal

[1] The National Industrial Chemicals Notification and Assessment Scheme (NICNAS)

organization in the nano-range, or a foam or insulation material with an internal foam structure with nano-sized bubbles.

Besides the man-made engineered nanomaterials, the world is full of natural nanomaterials, produced by i.e. volcano eruptions, forest fires, crystallizing salts or erosion processes. In the work environment, one can additionally encounter engine generated nanoparticles, which are ultra fine particles produced by all sorts of engines when these operate, and process generated nanoparticles, nanoparticles that are formed during processes like sanding, spraying, sawing or drilling and that consist of the material that is being worked-on. Together, these nanoparticles make up for the background concentration of nanoparticles (or nanomaterials) present at the workplace better known as Ultra Fine Particles (UFPs). All these nanoparticles have in common that they are not engineered with a specific functionality and that they are largely heterogeneous with respect to their chemical composition, size and shape. Consequently these show a broad range of reactivity and toxicity that has been studied for years under the heading of i.e. UFP research. These background nanoparticles are not the subject of this study. However, increasing knowledge on nano-specific characteristics of engineered nanomaterials does hint to suspect that also the engine and process generated nanoparticles should deserve further attention in the assessment of health and safety practices at the workplace.

1.3 The fate of nanomaterials

Central in the health and safety debate on nanomaterials is the question of fate:

What happens to the nanomaterial once it is applied and what happens to its nano-specific character?

When addressing this question in the context of health and safety concerns, it can be broken down in two other questions:

- What happens with the nano-specific toxicity profile during the materials life cycle?
- What happens with the nano-specific exposure profile during the materials life cycle?

If there is a specific nano-hazard but no exposure, there isn't an overall risk to deal with, and if there isn't a hazard anymore because of nanomaterial modification along the application phase, then exposure can be large without the arising of longer a nanomaterial related risk to be concerned about. What is special about nanomaterials is that they earn an important part of their behavior from "*being nano-sized*". This implies that in their design, the size (and shape) parameter is tuned to reach an optimal performance. It also means that once nanomaterials:

1. react chemically to form new products,
2. melt,
3. dissolve, or
4. degrade (biologically or though wear processes)

then these nanomaterials loose part of their nano-typical character or functionality. Either, they become "*normal chemicals*" when they dissolve or degrade, they become part of a larger structure when they melt or they change structure and shape completely when they react chemically.

When assessing possible health and safety issues related to the application of a nanomaterial in furniture, it is not only the 'ingredient' so to say that should be taken into account but more importantly also the chemical fate of the nanomaterial in its application and the fate of the furniture product and the fate in the body of the persons exposed. One example: in a number of coatings, nano-SiO_2 is added to obtain a higher surface strength. The nano-SiO_2 polymerizes, which means that after hardening exposure to nano-SiO_2 during working-on, handling or use of the finished product is unlikely. During the actual coating activity, exposure could occur to nano-SiO_2 embedded in the liquid coating, but only during the coating preparation, direct exposure of workers to the plain nanomaterial could be expected when the worker does add this material to the coating formulation.

In section 5.1, health and safety considerations of nanomaterials will be discussed in more detail as well as their exposure scenarios in section 5.2. However as the perception of (future) potentials and health and safety issues of nanomaterials are so closely entwined, it is important to realize that a nanomaterial doesn't have to be a static "thing" but that it may evolve in a same way as any other substance or material evolves starting as raw material and ending up as waste. And that also its toxicity may evolve from a potentially hazardous raw material to a non-toxic consumer product to hazardous waste again, like for example batteries.

2 Market perspectives

For its research and development on new materials and products, the furniture sector has always lived on the fruits of the research and development activities of other industries. One of the most recent technological developments is the ability to observe, monitor and influence materials (and their behavior) down to the nanometer detail. In practice, this means one can follow (or steer) what goes on at a size range that is about 10.000 times smaller than the thickness of a human hair. For industry at large, but also for the furniture industry in particular, this ability has enormous implications for the future of furniture materials; on its quality and functionalities but also on its environmental and health performance.

Though the Internet houses a lot of information on potentials of nanotechnology for furniture, the market penetration in actual furniture products seems small and is difficult to deduce. First field experience seem to suggest main application areas in the field of coatings, nanocoatings, with a market size that is probably no larger than 1% of all "non-nano" coatings applied anno 2011.All other materials seems to be only sporadically applied, and most often only on specific customer demand. A small questionnaire set out in France by FCBA[2] in the context of this project showed a mix of furniture manufacturers already using nanomaterials in their products and intending to continue this use, Furniture manufacturers that were currently looking into the possibilities of using nanomaterials but did not yet use any and Furniture manufacturers that were not using nanomaterials and were not planning to start using them in the near future. According to an inventory conducted in 2010 by the Dutch Association of Furniture manufacturers (the Centrale Bond for Meubelproducenten, CBM) and SHR (Stichting Hout Research), the use of nanocoatings in furniture at that moment in time was only small, reserved for very specific applications like anti graffiti coatings for street furniture.

Sketching this picture it is important to highlight some of the factors that do strongly color the current activity in the furniture sector. These can be summarized by the single term *Traceability*, or better: the lack thereof, which results from:

- the absence of an EU (or internationally) agreed definition of a nano-product
- the absence of nano-dependent notification (or communication) requirements
- the pioneering phase of nanomaterial R&D and the Intellectual property rights (IPR) involved
- the world wide social debate on health and safety issues and related uncertainties

As there is found a high level of ignorance with respect to the availability or use of nanomaterials, a lot of secrecy about the actual uses or R&D activities and a large reluctance for furniture companies to expose themselves as nanomaterial-users, the traceability of nanomaterials in the furniture chain is an important weakness. It is a weakness with respect to the market activities described in this report, but even more importantly, it is a weakness for the furniture sector itself because only when you are aware that you use nanomaterials at your workplace or in your products, you are able to decide on the appropriate measures you have to (or don't have to) take to assure workplace or consumer safety. It is therefore also one of the main points that should deserve further attention by the different Social Partner Organizations involved. The issue of tracing nanomaterials through the value chain of a furniture product will be discussed further in section 3. In sections 4.1 and 4.2 different materials and products are summarized that already have, or might have the potential of becoming more widely used in the furniture sector in the near future. Since it in this project appeared impossible to estimate current market seizes, it has been indicated for which materials actual market examples have been found.

Despite the difficulty encountered to identify positive applications of nanomaterials in furniture products, more transparent information was obtained from a number of European furniture companies, raw material manufacturers, intermediate product manufacturers and independent research institutes

[2] FCBA French technological institute for Forestry, Cellulose, Construction Timber and Furniture

that do collaborate with furniture companies was highly valuable to gather better insight in the present status of nanomaterials and their use in furniture products.

2.1 Companies contacted in the context of the study

Insight in the current and near future market for nanomaterials to be used in furniture was obtained by conducting a series of interviews with furniture manufacturers, research and development (R&D) institutes and suppliers to the furniture industry. The companies and institutes approached were very collaborative to provide insight in their own market regarding nanomaterials. However, many of these companies appreciated confidentiality with respect to their identity. It was therefore decided not to mention those companies by name and present their information and views anonymously.

In summary, the following organisations collaborated in the study:

Furniture companies	11 (in 5 different EU Member States)
Suppliers to Furniture companies	8 (in 4 Member States)
R&D Institutes for the Furniture sector	5 (in 3 Member States)
R&D Institutes and Universities	4 (in 4 Member States)

Two of these furniture companies volunteered in the exposure cases described in more detail in section 6.3.

2.2 Current market drivers

Like other sectors , the furniture sector does strive at minimizing material use, minimizing waste and optimizing energy consumption while improving the product performance. Nanomaterials can play an important role in achieving these goals. In the near future, using nanomaterials in furniture may lead to for example a reduced need for adhesives, functional textiles or smart furniture. Examples of smart furniture are furniture that heats itself (when it's cold), becomes opaque (when the sun is shining intensely), changes color upon demand, or signals you (when you run out of food supplies).

Areas where nanomaterials already can be of added value are for example places where service and maintenance of the furniture is an important factor of expenditure like in (residential) offices, hospitals or other public spaces. In those places, additional costs of the furniture due to the use of more expensive materials are balanced by a less intense and thereby less expensive service and maintenance required.

Other areas where nanomaterials could further optimize furniture performance today is in street furniture and garden furniture. In these subsectors nanomaterials may show added value in the reduction of corrosion, erosion, UV-degradation processes, they may prevent for algae growth or the attack by other organisms such as woodworm or termites, they may improve the vandalism resistance of materials and introduce an easy-to-clean effect and finally may allow for the construction of more light furniture structures.

In direct contact, market players in the furniture industry do present their sector as relatively conservative that is looking critically at the possible advantages of nanomaterials for their products. With respect to the introduction of nanomaterials, the top four of most important reasons for product optimization and innovation are:

1. better cost-performance ratio;
2. consumer comfort, health and safety;
3. worker health and safety;
4. environmental protection.

In this list, nanomaterials are treated no different than other materials. In discussion with the various stakeholders contacted in the context of this study, 10 to 5 years ago, nanomaterials were advocated as the most important innovation that would color furniture R&D in the years to come and a significant market share was expected at around the time we live in now. High expectations were launched. However, as a consequence of the economic crisis that attacked Europe in the last years, much less money was available for companies (also in the furniture sector) to invest in R&D on possible applications of nanomaterials for furniture and developments are now seen to proceed much slower than anticipated. And a lot of the R&D that was undertaken did not result in mature market products because the material performance appeared less than expected.

In similarity with i.e. the construction sector or the textile sector, first advances of nanomaterials in furniture products are found in the field of coatings and coating-type applications. Potentials of product innovation can be expected in the area of:

- easy-to-clean surfaces
- stronger, more durable materials
- more light materials
- novel flame retarding methods
- anti-bacterial products
- more sustainable furniture design and production processes

However, a number of barriers are to be dealt with before the market can make large scale use of these potentials.

2.3 Limiting factors for nano in Furniture

Though the potentials of nanomaterials for furniture may be promising, a large scale introduction of nanomaterials in furniture products is being hampered by a number of barriers. The most important factors that limit application at this moment in time are summarized below.

2.3.1 Costs versus benefits

The cost-performance relation is the most important first condition that is to be met before a furniture manufacturer decides on applying a (new) nanomaterial. It is also this criterion that is difficult to pass for many nanomaterials at this moment in time.

Since most nanomaterials are produced as low volume substances, costs per mass are still relatively high, compared to the alternatives they should substitute. Even, if nanomaterials have the clear potential to improve an end-product, they might still be too expensive to use in a furniture product. For a furniture product, this cost issue becomes much more apparent than in a sector like electronics, where memory capacity and processing speed are benefitting enormously from nanotechnological developments and where customers easily pay for stronger though lighter processors. In contrast, for a furniture product it is much more difficult to convince a customer on the added value of, for example, a nano-textile or a nano-coating if the traditional materials were already good enough.

At this moment, market growth is being observed in the application of bactericidal and easy-to-clean furniture in places like medical centers or saunas to prevent infection and outbreaks of multi resistant bacterial strains like the MRSA bacterium. This is one of the first examples where an added value clearly shows (see also section 4.2.3 and 4.2.6). One other type of product that slowly gains more market share are the scratch resistant coatings and lacquers that are currently used on furniture in expensive yachts, but may equally become recognized for use in kitchen furniture, high gloss table tops, wooden cabinets or other pieces of furniture where scratches, or fingerprints are easily visible (and intolerable; see also section 4.2.1). A third type of product that has been described in literature for some time now but appeared to be too expensive in relation to the traditional products already at the market, are the UV-protecting coatings to protect materials from erosion by sunlight. Because of the steady increase in the yearly production volumes of the nanomaterial involved, these coatings now are on the edge of become economically interesting alternatives to existing UV-protection methods (see section 4.2.4).

2.3.2 Long term performance

Many nanomaterials still have to prove their long-term durability and resistance against the normal erosion and usage processes. This experience will grow naturally with time, but at this moment this is still a factor leading to some reluctance of furniture manufacturers to substitute their well known materials with new (more expensive) nanomaterials with a still uncertain long term performance. For one range of nano-products, the anti-graffiti coatings, Solid Försäkring AB[3] in Helsingborg offers the certification of quality of performance. This certification takes into account not only the nano-content of the product but also its performance over time, supporting potential users in the decision making on possible applications of this type of product. Two other certifications schemes are CENARIOS and the Hohenstein Quality Label for Nanotechnology and Quality Seal Nano Inside. **CENARIOS** [4] is a risk management and monitoring system and the products that pass the evaluation are certified by the TUV-SUD. Acquiring certification involves a lot of work which is comparable to ISO9000. The clear advantage of having this certificate is the positive communication to the customer, being a sign of Corporate Social Responsibility. It is uncertain how many products have been certified. **The Hohenstein Quality Label** [5], certifies textiles only. The label is given only to those textiles in which the nanomaterial adds a demonstrable new function to the textile without having any adverse effect on the textile fibre. At the same time, the label includes parameters like quality, resistance to wear and wear comfort. The label is thereby of use to consumers and downstream users to decide on the added value of the “nano” to the textile. Up to 2009, 4 companies did file for this label.

2.3.3 Customer behavior

An important factor in the success of a new product in furniture is the actual behavior of the customer. For example, if the life time of a product is extended from 25 to 40 years but fashion causes the customer to buy new furniture every 10 years, the quality improvement remains unobserved and only a small number of customers shall be willing to pay any extras.

Another example is the cleaning behavior of customers. The average customer is used to clean their furniture on a regular basis with water and some form of detergent. When this is no longer needed, this would reduce the environmental load of the life cycle of the furniture product by reducing water consumption and detergent uses. However, where this type of novelty might work very well in office spaces or public buildings, it may turn out that private users would still prefer to conserve their traditional sense of cleanliness and would continue cleaning with detergents. Eventually it may be the case that a customer rather continues regular washing of textile than to rely on technology keeping the textile clean. This latter argument was brought forward by a textile company, stating that in the design of hospital furniture they often did show their customer the novel potentials of bactericidal textiles, but that in the end, most hospitals did decide on using (the less costly) traditional fabrics they were familiar with but that needed relatively more service and maintenance.

2.3.4 Health and safety concerns

Independent on whether it concerns workers, customers or the environment, present uncertainties regarding the health and safety issues of nanomaterials are one of the most important concerns of

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[3] http://www.solidab.se/

[4] http://www.innovationsgesellschaft.ch/en/index.php?page=336

[5] http://www.hohenstein.de/en/certification/hohenstein_quality_label/hohenstein_quality_label.xhtml

furniture manufacturers. Their concerns relate to risks of exposure to nanomaterials during application, use and in the end-of-life and the consequent health and safety hazards for those involved. Uncertainty relates to:

- Which toxicity assays do correctly quantify the acute and chronic toxicity profile of a specific nanomaterial?
- How does this profile look like?
- What are the health hazards of a specific nanomaterial in the product?
- What are the risks of exposure for the worker, the customer or the environment?
- At what daily dose should one start to take measures to prevent exposure?
- How does the employer determine this dose?
- How does the employer protect his workers correctly?
- How does the furniture maker prove and describe the risks associated with the product?

Uncertainty on health and safety is also a reason for confidentiality surrounding an application, resulting in only little transparency of nano-information on commercialized nano-products. And, according to one furniture company interviewed in the project, it even influences the desire to know and become informed on the nanomaterials used in the product. This because as soon as you know that you use or have used nanomaterials in your product, what should you do with this information? Should you take your products off the market? Should you inform your customers in some way or another, and what should you tell them? Should you substitute this nanomaterial or modify the production process?

These are very essential questions that are in no way specific for the furniture sector but that are playing at all levels through-out society and will be addressed in further detail in section 3.

3 Traceability of nanomaterials and nano-products and regulatory actions

Tracing nanomaterials through the supply chain of furniture faces great difficulties. Whereas the raw material manufacturers generally have a good idea about the nanomaterials they product, their direct customers have much less knowledge on the nanomaterials they might use in their products. Following this chain one step further, one may reach a typical furniture manufacturer that buys paints, lacquers, adhesives, textiles and all other sorts of materials for use in the final furniture product. By 2012, the situation is that only a very limited amount of furniture manufacturers are informed by their supplier about the presence of nanomaterials in their products.

Legislation on chemicals aims to provide a high level of protection for human health and the environment. The onus thereby has been put on industry to ensure the safety of the substances they manufacture, use or place on the market. Currently, however, many products incorporate nanomaterials without a proper assessment of the safety and risks of their nano-specific features, even though there is generally agreed knowledge that the smaller the particle the higher the surface reactivity and the higher the risk. Several initiatives for a voluntary reporting in some of the Member States failed to motivate the industrial players to report whether they use nanomaterials to enhance the performance of their products.

Given this situation, it is the demand of many stakeholders to be able to recognize a nanomaterial or nano-product in order to perform one's own risk assessment and to formulate one's own risk management strategy. In order to stimulate the development of an adequate risk assessment system for nanomaterials and nano-products, various European and national initiatives used the precautionary principle to design a safe workplace for working with nanomaterials and nano-products. Based on this principle, a diversity of tools has been developed to support employers, employees and consumers in assessing uncertain risks of nanomaterials and nano-products and performing risk management (see also section 6).

However, for the application of these tools, the issue of traceability has to be resolved (how to recognize a nanomaterial or nano-product?). Irrespective the type of stakeholder (being for example policy makers, medical staff, car refinishing and maintenance workers, construction workers, occupational health executives or scientific researchers, consumers), they all struggle with the same problem:

"before I can assess the need for possible precautionary measures, I have to know whether or not I am dealing with a nanomaterial or nano-product".

3.1 Initiatives of Regulation on Nanomaterials and Nano-products

Like any other chemical substance in Europe, the registration, evaluation, authorization and restriction of nanomaterials is regulated under REACH[6]. REACH provides an over-arching legislation applicable to the manufacture, placing on the market and use of substances on their own, in preparations or in articles. Nanomaterials are covered by the definition of a "substance" in REACH, even though there is no explicit reference to nanomaterials. The general obligations in REACH, such as registration of substances manufactured at 1 ton or more and providing information in the supply chain apply as for any other substance. The European Commission report *Nanomaterials in REACH* (2008) provides an overview on how exactly REACH impacts on the regulation of nanomaterials[7].

The other important regulation in place for normal substances and mixtures is the Chemical Labeling and Packaging directive CLP[8]. Nanomaterials that fulfill the criteria for classification as hazardous

[6] http://ec.europa.eu/enterprise/sectors/chemicals/reach/index_en.htm
[7] http://ec.europa.eu/enterprise/sectors/chemicals/files/reach/nanomaterials_en.pdf
[8] http://ec.europa.eu/enterprise/sectors/chemicals/classification/index_en.htm

under the CLP directive must be classified and labeled. Many of the related provisions, including safety data sheets and classification and labeling apply already today, independently of the tonnage in which the substances are manufactured or imported. Substances, including nanomaterials, meeting the classification criteria as hazardous must have been notified to ECHA by 3 January 2011. The European Commission report *Regulation, Classification, Labeling and Packaging of nanomaterials under REACH and CLP* (2009) provides an overview of the impact of REACH and CLP on nanomaterials[9].

Over the past years, three working groups studied the further requirements for regulating nanomaterials within REACH. Their conclusions are summarized in three REACH Implementation Plans: RIPo1, RIPo2 and RIPo3. A new European initiative, NANOLEGS is currently developing an advice on where existing regulation needs further specification for nanomaterials and to develop guidance on the bridging of regulatory gaps.

A first concrete initiative of France to make the reporting of the use of nanomaterials in products obligatory, is initiated within the context of the French environmental legislation *Lois Grenelle* [10]. Its first phase has passed the notification, the second phase of the law is subject to European notification until June 2012. The law obliges all producers, importers or distributors of nanomaterial substances in France to declare what these substances are and what they are used to. Article 185 of Law No 2010-788 of 12 July 2010, Grenelle Law 2, specifies the mandatory reporting scheme. Conditions for application of the declaration of substances with nanoparticle status defined by Articles L. 523-1 to 5. It will enter into force as of 1 January 2013, reporting over all substances produced, imported or distributed in 2012. The regulation applies to Chemical products, biocides and substances with nanoparticle status (Article 1) when produced, imported or distributed in France for 100 grams or more per year. Other countries like Denmark, Italy, Germany and Belgium are considering also to develop some form of nanomaterial notification scheme to get better insight in their national market. The Italian initiative asks for organisations to voluntarily notify their MNMs whereas, like the French initiative, those of Belgiun and Denmark are mandatory (Pineros Garcet 2012)[11]. Mandatory reporting as from January 2013 is expected in Denmark and first registration is expected in 2014. The information to be declared set out below:

- identity of registrant (incl. industry/business category);
- product information (use category, amounts produced, content of nano); and
- information on nanomaterial(s) (chemical and physical characterization).

In Belgium the database of nanomaterials and articles that use nanomaterials in their manufacture, placed on the Belgian market is expected in 2013. In this case the information to be declared is:

- registrant ID, professional clients ID;
- nanomaterial(s) characterisation, quantities sold, foreseen uses, commercial name of the substance, mixture, or product; and
- characterisation: possibility of providing only the registration number received from the provider.

The Italian inventory is also expected to enter into force in 2013, but details of the information requirements were not available at the time of writing.

[9] http://ec.europa.eu/enterprise/sectors/chemicals/files/reach/nanos_in_reach_and_clp_en.pdf

[10] http://www.nanonorma.org/

[11] Pineros Garcet JD (2012), Developments in different EU Member States for mandatory or voluntary national nanomaterials registration systems, *On behalf of the FR-BE-IT-DK nanodatabases harmonization group,* 7th Joint US/EU Conference on Health and safety at work, Brussels, 11th July 2012

3.2 Initiatives of Voluntary Reporting on Nanomaterials and Nano-products

One of the first initiatives to identify nanomaterials in products was the Voluntary Reporting Scheme (VRS), developed by the British Department for Environment, Food and Rural Affairs (DEFRA). It was aimed at collecting data concerning free engineered nanomaterials from manufacturers, commercial users, research and the waste industry. For the purposes of the collection, the VRS used a very narrow definition of nano with the following criteria: the material is engineered deliberately (*i.e.* not material that is created naturally or unintentionally as a by-product of other processes); the material shows in two or more dimensions an extension of up to 200 nm, or is in two or more dimensions roughly within the nanoscale; the material "is free within any environmental media at any stage of a products life cycle". During the period of data collection (September 2006 – September 2008) only twelve completed responses were submitted. Therefore this voluntary scheme must be deemed as little successful.

Another initiative in this context comes from Swiss retailers organizations that in 2008 developed a Code of Conduct[12] as a voluntary instrument for retailers. The Code obliges retailers to take a responsible approach to nanotechnology products. The retail trade undertakes to provide consumers with full information on nanotechnology and to label as such only those products that really do have nanotechnology-based components or modes of action. It is however not clear whether this initiative was brought into full operation for the Swiss consumer market, and if so whether this initiative was successful. The willingness of companies to voluntarily report their MNMs seems to be dependent on the type of company, with smaller and younger innovative companies tending to keep nano-information confidential[13].

Recently an adaption on the format of the Safety Data Sheet (SDS) for chemical substances was published by the European Chemical Agency[14]. Adaptations in section 3 and 9 are proposed. Section 3 of the safety data sheet describes the chemical identity of the ingredient(s) of the substance or mixture, including impurities and stabilizing additives. In this section appropriate and available safety information on surface chemistry shall be indicated. It should be noted that the term "surface chemistry" as used is intended to refer to properties that may arise as a result of the particular surface properties of a (solid) substance or mixture (e.g. due to having certain dimensions in the nano-range). The second adaptation concerning "nano" refers to section 9 concerning:

(a) appearance: the physical state (solid (including appropriate and available safety information on granulometry and specific surface area if not already specified elsewhere in the safety data sheet), liquid, gas)
(b) the color of the substance or mixture as supplied shall be indicated. Here properties of nanomaterials should be taken into account such as size and size distribution, shape, porosity, pour density, aggregation/agglomeration state, morphology, surface area (m^2/mass), surface charge/zeta potential and crystalline phase.

By end of 2012, it is not clear whether info on the SDS on new nano-products will be reported according to this guidance. One important remaining barrieris the fact that the threshold concentration above which a nanomaterial should be included in the SDS has not been defined yet. This means that to date it is unclear how a nano-product should be defined. The expectation is that it may take a long while to settle for this discussion. The call of the Netherlands Government upon the European Commission to give high priority to find agreement on a definition for nanomaterials in REACH, to generate an overview of nano-products in Europe and to develop suitable instruments for risk analysis

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12 IG DHS code of conduct for nanotechnologies. 18.4.2008

13 Kuzma, J, A. Kuzhabekova: Nanotechnology, voluntary oversight, and corporate social performance: does company size matter? *J Nanopart Res 13:1499–1512*, (2011).

14 ECHA 2011. Guidance on the compilation of safety data sheets Version 1.0 – September 2011. http://guidance.echa.europa.eu/docs/guidance_document/sds_en.pdf

was supported by France, Sweden, Italy, Belgium and Austria. But so far little movement is observed at the European level.

Besides these more regulatory oriented voluntary initiatives, many web-based initiatives are being developed that aim at forming databases of nanomaterials and products containing nanomaterials available at the market. Most of these databases aim at a public of consumers. Manufacturers of nanomaterials or nano-products are invited to add their products to the database, including comments on their nano-specifics. One of the oldest examples of such a website is that of the American Woodrow Wilson institute[15]. More recent examples are Nanowerk[16], Nanodaten[17] (both of German origin) and the Danish database Nanodatabasen[18]. None of the databases is specific for furniture.

3.3 Difficulties in chain communication

Within Europe, but also world-wide, there is an enormous problem with respect to "sharing information about nanomaterials" through the value chain of the product in which the nanomaterial is used. This is not at all specific for the furniture industry but is also observed in sectors like the paints and lacquers industry, the construction sector, the food industry or the automotive industry.

Until recently, one of the reasons behind this was the lack of a commonly agreed definition of a nanomaterial. Without a definition there is simply nothing solid to communicate about. Another important reason is that there is still no binding regulation in The European Union that describes what should be communicated and what not. Voluntary schemes that tried to tackle this failed or were only of little success.

Consequently, the communication of information on nanomaterials in products through the value chain is a mess:

1. Products are marketed for their "*nanotechnology*" suggesting they may contain nanomaterials, but in the end appear to have none.
2. Products are marketed to contain nanomaterials (and do actually contain them) without mentioning what nanomaterial is used
3. Products are brought at the market for which the nanomaterials used are notified
4. Products make no notice of any nanomaterial ingredient, some of which do contain nanomaterials

From an industrial perspective this is understandable:

- There is a high level of confidentiality surrounding exact recipes and product formulations
- Nanotechnology sells, especially in specific areas
- Nanomaterials are often linked to uncertain health and safety issues and therefore consumer trust, or better the fear of losing consumer trust prevents communication

On the other hand there is the strong need of downstream users (those that use or process the nano-products) to become informed about nanomaterials used in their products. They need this information to be able to make a proper risk assessment. However, downstream users are not always an easy group to inform:

- Down stream users may have limited background knowledge to appreciate the details within the information
- Down stream users may not "pick-up" information on nanomaterials communicated because they are not (yet) sensitive to the importance of this information

15 http://www.nanotechproject.org/inventories/consumer/
16 http://www.nanowerk.com
17 http://www.nanodaten.de
18 www.nano.tænk.dk

- Down stream users do not know what to do with the information and how this information will impact on their own information supply to the next down stream user along the value chain
- Down stream users may not know the right questions to ask to their supplier to become informed

As part of this project, various examples were encountered in direct conversation with European furniture manufacturers and suppliers to the furniture industry:

One example was a furniture manufacturer that hesitated on asking its suppliers for information on their possible use of nanomaterials in the products they delivered. The furniture manufacturer feared that simply asking this question might boomerang back, resulting in a trust-scandal with its customers.

Another furniture manufacturer had no idea what the correct question to their suppliers was to become informed about the possible use of nanomaterials. This same furniture manufacturer stated he had no clue on how to inform his customers when it would turn out that he had used nanomaterials in some of his products.

A third example was of a raw material manufacturer producing a nanomaterial binder for adhesives. The adhesives manufacturer did confirm using this binder in his products, also for the furniture industry, but denied it being a nanomaterial.

A fourth example was of a supplier of easy-to-clean coatings that eventually appeared to be teflon-based. The easy-to-clean effect was obtained by using nanotechnology in the formulation process and was therefore marketed as such, but the coating itself did not contain nanomaterials.

A fourth example was a producer of street furniture that uses Ultra High Performance Concrete to obtain strong, light, high corrosion resistant and easy-to-clean street furniture. UHPC is produced by using nano-silica, but upon asking the company denied using nanomaterials in their product.

A fifth was a product supplier to the furniture industry, explaining how his customers got nervous when he mentioned “nanomaterials” in an early phase of the selling process, and often decided for a traditional product. Even though toxicity testing could prove a safe application and use.

These examples give an impression on the current difficulty for both employers and employees to decide if they are informed about the nano content of the materials: *Why ask about nano if there is no reason to assume that you should worry about the presence of nano in your product?*

A suggestion to tackle this state of confusion, was brought forward by various furniture manufacturers approached in the context of the project was to develop a European code of conduct for communicating on the presence of nanomaterials in furniture. Such a code of conduct should be short and simple and should support the sharing of information on nanomaterials in the furniture industry while creating a level playing field with simple rules for communication through the chain. Such an approach though, would only work if it is embraced by the Furniture industry world-wide. Nevertheless it may be a desirable first step to solve traceability in the furniture sector until The European Union/agrees upon action towards ensuring traceability industry broad.

4 Nanomaterials and nano-products for furniture

Nanotechnology is used for material or product enhancement at the level of the individual material or product. Examples hereof are the production of more durable wood, stronger and more durable concrete, special textiles etc. However, nanotechnology is also used to improve or functionalize coatings, which then can be designed accordingly to allow for their application on almost any material. Because of this reason this chapter has been subdivided in two sections. The first section does focus on the individual materials. The second describes different functional coatings that can be envisaged on any substrate material.

4.1 Nanomaterials and nano-products

4.1.1 Glass

Over the last years, nanotechnology has been applied to develop and produce different types of glass, i.e. non-reflectivity glass, privacy-glass, thermal isolation glass (based on InfraRed light reflection or absorption) and biocidal glass. There are many applications thinkable that could make use of these. Think about i.e. glass-cabinets, lamps, tables, office furniture or medical furniture. However, according to large market players like Saint-Gobain and Pilkinton, their market penetration into furniture is low. In those cases where the material is used, the glass parts of the furniture are shaped and processed by the glass-manufacturer. The furniture manufacturer assembles the final furniture product.

4.1.1.1 Non-reflectivity glass

Non-reflectivity glass is traditionally produced as a multi-layered glass construct. Using nanotechnology, it is now possible to obtain an over 98% transparent glass by applying one simple coating on a normal glass surface. The resulting lower production costs open a range of new applications for this type of glass, also for furniture. Claryl by DSM is an example of such a product. Another way in which nanotechnology does facilitate reflection reduction is by nano-etching the glass surface with nano-sized craters. These craters scattering the in-falling light in all directions and thereby prevent for reflection to occur.

4.1.1.2 Privacy-glass

Privacy-glass consists of a double glass sandwich with a liquid crystal inner layer. This liquid crystal is normally opaque but can be made transparent by applying a small electric current to the glass. Examples hereof are SGG Priva-Lite (Saint-Gobain).

4.1.1.3 Thermal isolation glass

Thermal isolation glass can be achieved by coating the glass surface with a (nano) thin layer of metal oxides (FeO, SiO_2…) that absorbs infrared radiation (also known as ‘heat’). The SGG ClimaPlus glass line by Saint-Gobain is an example thereof. One obvious application is in large facades where the glass supports the interior climate control of the building. However, it may also be applied in furniture to prevent for slow heat-up of the construct around a local heat source (for example a light bulb).

4.1.1.4 Biocidal glass

Biocidal glass of i.e. the Bioclean line, also produced by Saint-Gobain, does add easy-to-clean properties to the glass by a thin coating of nano-TiO_2. Induced by UV radiation (or sometimes also by visible light, depending on the exact modification and tuning of the nano-TiO_2), the nano-TiO_2 brakes-down organic pollution and thereby reduces the need for active cleaning. This material may be particularly interesting for outdoor furniture applications like for example garden furniture, but also indoors to lower the service and maintenance required in public spaces, office buildings, swimming pools, saunas or medical care centers like hospitals and dentist clinics.

4.1.1.5 Possible health considerations specific for glass

Most nanomaterial enhancements of the glass are applied during the glass production process. For example, coating the glass and baking this glass in an oven to obtain a nano-thin film. During this baking process, the nanomaterials added to the surface become so to say fused (or melted) with the glass matrix. Nanoparticles exposure is therefore is no longer to be expected when this glass is used by the furniture manufacturer to construct its furniture product. Unless, maybe, exposure to nanoparticles may occur when process generated nanoparticles are produced as part of the glass machining process at the workplace of the furniture manufacturer. A fraction of these nanoparticles may then in fact constitute of the nano-functionalized glass surface. However, as is stated above, this is not likely to occur at large scale as the glass is delivered to the furniture manufacturer as a ready-to-use product.

4.1.2 Composites

At the level of R&D, there is a lot of activity in the field of nanocomposites. Both for “plastic composites” and for wood composites. For wood composites, potential applications have been described that make use of nano wood fibers to optimize the strength and performance of composite materials. First contacts with the composite industry however, do suggest that this application has not reached the market yet. Adding nanofibers to optimize the strength of composite materials is relatively costly and appears not to be as effective as was assumed in earlier research[19]. For many applications at the level of the constructive material, microscopic fibers are similarly effective with an additional cost benefit. At the level of the surface performance however, nanocomposites may have added value.

Direct consultation of the global Society of Plastic Engineers (SPE Polymer nanocomposites) resulted in the following: “I'm afraid I do not know anyone that has applied nanocomposites to furniture, at least not on purpose as a nanomaterial (most pigments and some fillers are actually nanoparticles.)”….” I agree that there are a lot of opportunities to use polymer nanocomposites for furniture: protective coatings, in which the particles enhance the wear resistance; structural materials with improved impact strength; flame retardance supplied by nanotubes or nanoclay; analysis of the release of particles during the end stages of furniture use; and attention to processing to ensure safe handling of nanoparticles”.

One area where developments are ongoing is in the technology bridging of processes and techniques from the paper-industry to other materials sectors. CTP's Process-Pulps&Functional Fibres is an example of a research institute developing and optimizing the extraction of nano-sized cellulose fibers from wood pulp and applying them as reinforcement fiber to coatings and wood composites. In the near future, first pilot projects will run to test these applications in practice. Nano-cellulose can be produced from waste wood or production wastes from the wood industry and is fully made of natural resources. It is expected therefore to become a valuable substitute for the traditional reinforcement materials based on non-renewable materials. It will turn wood waste into a high value renewable material and will contribute to make the final composite material more sustainable.

4.1.3 Wood

The material wood can benefit from innovations made possible by nanotechnology at either the production or the use phase of the wood.

4.1.3.1 Wood forestry phase

Making use of nanotechnology for the improvement of wood occurs at various levels. First is in the production phase of the material, in forestry, where nanotechnology is being applied for the production of more sustainable wood products. Nanotechnology is for example used in the design of biocides to protect the wood against pests or fungi. This may be in the form of co-biocides, in the form of a finer solution allowing for a deeper penetration in the wood, or in the form of a nano-carrier system regulating a gradual emission of the biocide[i]. Nanometals such as nano-silver, copper or zinc have been studied in this context. These nanometals gradually oxidize under environmental conditions releasing biocidal metal ions. The surface area of the nanometal determines the release rate, via which

[19] Direct consultation with R&D institute on composite materials

the dose can be fine-tuned. Nanometals act like a long-term source of gradual biocide release in wood, that may even protect the wood during its functional life time as a wood product.

Alternatively, traditional biocides are being embedded in a nano-sized capsule made of plastic, clay, ceramic or lipid material. Small pores in the capsule or the slow (bio-) degradation of the walls of the capsule then allow for the gradual release of the biocide.

An overview of current developments and market perspectives is given by a report by the Canadian Institute Natural Resources Canada (2009)[20]. This report also includes an overview of novel possibilities with wood itself in the production phase such as the fabrication of nano-cellulose fibers or nano-crystalline cellulose (NCC) to add tensile strength to composite materials. Despite these potentials described though, they are only slowly taken up by society and only limited research does explore their full possibilities for forestry[21]. However, these will be interesting developments that may reach the market in the near future.

4.1.3.2 Using wood in products

When wood is used to make new products, nanotechnology enables researchers to study the wood performance in greater detail. Nano-indentation is a technique that is used in these studies, but also SEM (Scanning Electron Microscopy) or TEM (Transmission Electron Microscopy) are techniques used in these studies that benefit from equipment innovation at the nano-level. These types of studies lead to a better understanding of the wood performance, which is especially interesting for high demanding applications, for example, where strength is a critical factor.

In the production of wood composites like particle board, MDF or OBS, nanotechnology may assist in increasing the durability of the composite material. For example, by improving the glue system. One of the issues related to the long term performance of wood and wood composites is their thickness swelling when they become exposed to water. This may happen due to cleaning activities, but also in kitchens, bathrooms or outside. Various techniques have been developed using nanotechnology that do reduce this swelling. One has been described by Mantanis (2010)[22] that is developed for wood panels. It is a coating technique, SurfaPore™ W by NanoPhos SA that chemically blocks the ability of the wood panel to adsorb water, reducing the possible thickness swelling by at most 13 – 14%. Another technique is by using liquid glass to coat the sides of the panels. This coating technique is described in more detail in section 4.2.1 and 4.2.3. The hydrophobic layer formed at the surface prevents water from penetrating the panel and thereby prevents for swelling by water.

4.1.3.3 Using wood-based products

For wood preservation, nanomaterials may reduce the need for preservation techniques like furfurilation or acetylation. For example, by using nanocoatings for water-protection. However, also the biocide system implanted in the wood during its growth phase may still be active in the application and use phase of the wood product. As the traditional preservation techniques are energy demanding and lead to undesirable emissions of chemicals to the environment, the long lasting effect of nanomaterials used as biocide may contribute to the future enhancement of more durable wood products.

In the area of wood protection and preservation, FCBA and CTP developed a technique called chromatogeny that may be used to “print” fatty acids on the wood surface. This technique was originally developed for the paper industry, but may be equally valuable to make wood surfaces hydrophobic while retaining the natural breathing possibilities of the wood. It is an example of surface modification at nano-level and may become interesting also for furniture applications in the near future.

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[20] McCrank J (2009) Nanotechnology Applications in the Forestry Sector, Canadian Forest Service

[21] Evans P, Matsunaga H and Kiguchi M (2008) Large-scale Application of Nanotechnology for Wood Protection, Nature Nanotechnology, Vol 3, Correspondence

[22] Mantanis GI and Papadopoulos AN (2010) Reducing Thickness Swelling in Wood Based Panels by Applying a Nanotechnology compound, Europ. J. Wood Prod. published on line 29 Feb. 2010

4.1.3.4 Possible occupational exposures specific for wood

Workers in the furniture industry may get exposed to nanomaterials used in forestry when they work the wood that has been treated with them. Especially during machining activities like sawing or polishing where wood dust is generated. Exposure to the nanomaterial may become an issue when it is inhaled as integral part of the wood dust particles. When elaborating a possible risk of exposure, it are the non biodegradable, non soluble nanomaterials that are to be dealt with in a precautionary manner. Those biocides that are simply nano-sized dispersions of the "traditional" biocide will most likely not cause any nano-determined adverse health effects. On the contrary, as these biocides have been designed to allow for a similar effect at lower doses because of a better distribution through the wood, one may expect less adverse effects as a consequence of less biocide usage. However, when biocides are chemically engineered or are encapsulated inside a non biodegradable capsule proper caution should be taken in order to prevent expose when the wood is being worked on.

4.1.4 Metals

Metal improvements using nanotechnology take place at the level of metal-structure modification or at the level of surface modification.

A better control of the metal production process at the nano scale of the material enables the fabrication of stronger, more durable metals. This type of modification takes place at the metal-structure level. This means the organization of the metal structure at the nano-scale and doesn't necessarily involve the addition of nanomaterials. Still this can be the case though, for example in alloys that are being improved by adding small amounts of nanomaterial, allowing for a more homogeneous distribution in the metal structure. With these metals, one can shape more light structures with a similar performance as was achieved before with more heavy alternatives. One example in which this technology is used is in the body of the Audi A6 series, where weight reduction directly pays-off in less fuel consumption. In furniture, no examples could be found to date.

Surface modification of metals focuses on coloring, preservation against oxidation and corrosion and on improving scratch resistance. One way of doing this is via an electroplating process using metal salts. Nano-sizing these salts leads to an optimum surface coverage, which results in a much stronger preservative layer that is better resistant to external factors like corrosion, oxidation and scratching. This technique, being slightly more expensive than the lower quality electroplating, will preferably be used for the more expensive, high quality furniture or for furniture with specific demands. Examples hereof are furniture for outdoor marine environments or boats. Nano-sizing pigments like TiO_2 can be used to change collour depending on the exact size of the particles. Electroplating can accordingly be used to obtain nicely collored metals in shades from yellow to blue to magenta.

Another method of surface modification is by applying protective coatings. This is described in more detail in section 4.2.1 and 4.2.3.

4.1.5 Textiles

In 2007, the EMPA published an overview on the use of nanotextiles in Switzerland[23]. Many different potential applications were described and found in various products. However, only one application, i.e. stain repellent furniture textile, was actually found for furniture. Their overview focuses on Switzerland but the general picture may very well be similar for the European Furniture industry. Anno 2012, this picture still seems valid: only for easy-to-clean and antimicrobial textiles market penetration is observed that is growing in the furniture sector. Other nano-innovations in textile could not be traced. For example, one of the areas where some development might be expected is in the field of alternative fire retardants. Nano-clay is a nanomaterial that is being described as new fire retardant agent. This material is typically considered to involve only little health hazards and may be a preferred substitute for current toxic or biologically persistent flame retardant additives.

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[23] B. Siegfried and C. Som (2007) NanoTextiles: Functions, nanoparticles amd commercial applications, EMPA Materials Sciences & Technology

4.1.5.1 Easy-to-clean textiles

Stain repellent furniture textile can be achieved by applying a liquid-glass coating, by using a UV-active nano-titanium dioxide coating or by using fluorocarbon polymer coating (Teflon type of polymers). They all function by reducing surface tension such that water or oily substances simply pearl off. However, one other side effect is that bacteria cannot "dock" that easily and will be washed-off more effectively upon cleaning compared to a non-treated textile. Especially when one uses a nano-TiO_2 coating that actively degrades organic material (and thus bacteria and microbes). Scotchguard™ by 3M is one of the products that is marketed and named by furniture companies to be used. Two companies that are active in the field of nano-SiO_2 liquid glass coatings are Nanopool GmbH and NanoCare Deutschland AG. NanoServices is a company that is active in the field of nano-TiO_2 coatings for textile.

As nanomaterials are an "expensive extra" in relation to furniture textiles, the added value should be there in order to decide to use it. In home and garden textiles, hydrophobic and oleophobic treatment of the textile might be desired by the customer, but is still considered a luxury product. As a consequence, only a limited number of furniture products seems to be sold "as such", and many do-it-yourself products are found at the consumer market. In office furniture, furniture for public spaces, automotive furniture or in hospitals or other medical care centers, the added value of treated textiles is much more obvious. The resulting reduced service, maintenance and cleaning of the furniture directly do pay back by a reduction in service, maintenance and cleaning costs and time that used to be involved.

4.1.5.2 Biocidal textiles

Various textile companies have developed a technique to attach small amounts of nano-silver to the yarn. Silver is a well known bactericide and nano-silver is even more effective. In the presence of a little amount of water, silver ionizes to yield a positive silver ion (Ag^+) which destroys or damages bacteria or viruses that come into contact with this ion. This way of action is similar to the more "course" form of silver but since nano-silver is smaller, its solubility is increased leading to higher ionization. This treated yarn can accordingly be used to weave anti-bacterial textiles, which can in turn be used for example in hospital furniture where contamination of patients with bacteria or viruses should be minimized at all times, but also in public spaces like trains, busses or airplanes that have become main facilitators for a world-wide spreading of viruses and bacteria because of the enormous amount of people that are traveling the world each day. Trevira GmbH is one of the companies producing this type of yarn. Silver can be brought onto the textile surface as a "lose coating", the textile fibers can be individually impregnated or the nano-silver can be chemically connected to the textile fiber. These three different types of textile treatment do largely affect the quality of the textile and the durability of its performance. When chemically connected, the biocide effect is long lasting, also after multiple cleaning rounds. When the fibers are impregnated, the quality is less than optimum but the biocide effect remains visible after various cleaning rounds. However, when the textile is simply coated with nano-silver, this nano-silver most easily washes of, resulting in a low quality performance.

4.1.5.3 Textile from nano-cellulose

Lyocel is a yarn that is being produced by spinning nano-sized fibers of hemi-cellulose. These cellulose fibers can be extracted from wood-pulp and together they make a highly moisture (or water) absorbing yarn that is more and more used in bed linen, pillows and mattresses, but has also been described in chairs (for example to cover the foam interior) in which it may be used for its excellent moisture regulating properties. Lenzing AG is an Austrian company producing the textile Tyocell that is based on these fibers. An additional property of this fiber is that it has an extremely smooth surface in comparison to e.g. cotton. This has the additional benefit that micro-organisms tend to grow much more slowly on such a type of textile, resulting in a higher hygiene and less odor evolution.

4.1.6 Concretes

Concrete is no common material for indoor furniture but is used primarily in outdoor public spaces. Silica fume (nano-silica), used in the production of Ultra High Performance Concrete (UHPC), and nano-TiO_2, used to provide the concrete with a "self-cleaning" surface are two possible applications of nanomaterials that may be of additional value in this sector. Prima-Marina, by Escofet® is one example of a product line of outdoor benches and tables that make use of UHPC, also known as liquid stone. Indoor applications of UHPC concrete can be found for example in kitchen furniture (Ductal by Lafarge) where the high density UHPC structure makes i.e. kitchen tables more water and stain repellant than normal concrete would do.

In the field of fibre-concrete, a large consortium of research institutes and industries, Inno-CNT, is currently studying the potentials of using carbon nanotubes in concrete. Results from this research may be of future interest for the furniture industry also for the production of even slimmer and lighter furniture products made of concrete. Dyckerhoff AG, the second-largest concrete manufacturer in Germany, presented a table and chairs made of high-performance carbon nanotube (CNT)-reinforced concrete only 3 centimeters thick[24].

4.1.7 Adhesives

There is only very limited information available from open literature describing possible applications of nanomaterials for the optimization of adhesives for furniture applications. Nanomaterials that are described are based on silica or silane compounds that act as cross-linking agents within the adhesive polymer structure[25] (i.e. to optimize the performance of the adhesive) or as a stabilizer of water based adhesives to fine tune the viscosity of the product. The additive dispersion Dermocoll®S by Bayer, is an example of the latter and consists of a silica-polyurethane dispersion. However, the market for this type of additive is still small, especially for furniture applications. According to SABA, a leading company in the field of foams and adhesives for the furniture industry, there is not much R&D activity in the field of applying nanomaterials for furniture adhesives. An important determining factor is the balance between material costs, the material performance and the requirements put down by the furniture industry. Existing non-nano adhesives do meet the furniture requirement and do easily compete with the more expensive nano-adhesive additives. From this information, activities in the field of nanotechnological developments for adhesive optimization are most likely to be expected in the area of dispersion optimization, e.g. the design of nano-dispersions to allow for an optimum interaction between reactants during the polymerization of the adhesive.

One nano-innovation, aimed at optimizing the interaction between materials during gluing is developed by NanoFab. A technique called electron plasma-sputtering is used to roughen the surface of the substrate that is to be glued. In principle, this substrate can be any material, for example a textile, a composite or a plastic or rubber. Roughening takes place at nano-level and can be described as an extremely fine abrasion. The result is a highly optimized interaction between the glue and the substrate surface leading to the formation of high strength adhesion and more durable furniture products. Moreover, the fine abrasion facilitates an efficient distribution of the glue over the substrate surface and allows using much less glue than would have been needed without this nano-roughening. Depending on the actual exposure of the workers and the associated health effects, this may (or may not) have a positive impact on worker health and safety (less volatiles emission from glue) and the environment (less glue, less waste). At this moment, this technique is applied at small scale for the production of furniture, and though promising, it is still a long way to large scale market application because of the specific equipment required.

4.2 Nanotechnology enhanced surfaces

As nanomaterials are typically new and expensive and the majority of the furniture sector is a relatively conservative one, main movements in product development are observed in the application of nanocoatings. These nanocoatings typically make use of one nanomaterial to introduce a specific

[24] http://www.inno-cnt.de/en/news_pm_20110211.php

[25] ZS Petrovic et al (2000) Structure and properties of polyurethane–silica nanocomposites, J. Applied Pol. Sci. Vol. 76(2), 133–151

functionality and then change the coating base to allow for the application on a large variety of substrates.

4.2.1 Scratch resistant coatings

An upcoming market of nano-products are high scratch resistant paints or lacquers. This can be for wooden systems like tables, chairs, doors or floors, but may also be used on any other “soft” material used in furniture that is used intensively like plastics or laminated boards. Different types of coating systems are found with this typical character that can be either aqueous or non-aqueous based.

The one that is found mostly in the furniture industry is based on the addition of (amorphous) nano-SiO_2 to an acrylic binder material in the case of a clear-coat. During drying of the paint or lacquer, the SiO_2 reacts chemically with the acrylic binder forming a highly branched and very strong network of silane polymers, which is then the basis of a high scratch resistance performance introduced. Examples of additives described in this context are Bindzil CC30 (Baril Coatings), Nanobyk 3650 (BYK Additives and Instruments) and Pall-X Nano (Pallmann).

Alternatively, nano-SiO_2 is dispersed in a water or alcohol medium and marketed as a liquid glass product. Companies active in this field in the furniture sector are i.e. Nanopool GmbH, Nanoprotec and NanoCare Deutschland AG. Depending on the concentration of the liquid glass dispersion, the performance of the coating is scratch resistant, anti-graffiti or easy-to-clean like.

Another line of scratch resistant paints and lacquers is based on the addition of nano sized Al_2O_3 particles. The actual use of this type of lacquer could not be traced in furniture products. The mechanism by which the lacquer works is not fully clear but seems related to an improvement of the elasticity of the coating matrix. Various additives of this type are produced by BYK Additives and Instruments.

4.2.2 Anti graffiti coatings

Anti graffiti coatings are described for their outdoor applications like street furniture. However, the actual use of this type of coating material is still small and estimated to be used at less than 1% of all street furniture. Nano-SiO_2 liquid glass, described previously in the context of scratch resistant coatings, are frequently used also to add an anti graffiti layer to all kind of surfaces like concrete, brick-walls, ceramics or nature stone. However also, substrates like plastic, composite material, wood and metal can be treated with this type of coating. Effectively the coating forms a nano-thin porous layer of glass on the surface of the substrate that prevents penetration of graffiti paint or markers when applied at the surface. The similar companies active in the field of scratch protection are also marketing anti graffiti products i.e. Nanopool GmbH, Naprotec and NanoCare Deutschland AG (a non exclusive list).

However, there are also other ways to reach anti graffiti performance. An example hereof is Wandflex 2-K PU Blank, by Wandflex. This product makes use of so called “chemical nano” that chemically reacts and organizes at the substrate surface to create a hydrophobic layer. No information was provided on the exact chemical nature of this product. Other examples of anti graffiti coatings may involve the use of cabon fluorides (Teflon kind of structures). However, for these type of coatings question is if these are based on a nanomaterial or rather on large molecular structures.

4.2.3 Easy-to-clean and water repellent coatings

Dirt repellency is one of the applications described in which nanomaterials are used to improve material surfaces for furniture. This technique is often based on the “lotus leaf” principle. The lotus leaf consists of tiny hairs that reduce the surface tension and prevent oil and water to adsorb. As a consequence “dirt” pearls off easily. When this principle in applied to a furniture material, this material surface becomes “easy-to-clean”. This implies for example that fewer detergents are needed for cleaning activities, also when this involves textiles.

One way of achieving this performance is similar to the anti graffiti one by using fluorocarbon polymers (Teflon type if polymers). This same technique can be applied on almost every surface like wood, metal, concrete or ceramics.

Alternatively a nano-SiO_2 liquid-glass coating can be applied to reach the easy-to-clean effect. With a thin layer of nano-SiO_2 water and oil repellency is achieved. The performance of this coating is similar to that of the anti graffiti coatings described before. However, as an easy-to-clean coating, its performance is less demanding in a sense that vandalism or scratching is typically outside de scope of normal use. Consequently, the thickness of the coating brought onto the surface is allowed to be thinner and therefore the liquid glass dispersion is less concentrated than is required for anti graffiti or scratch resistant performance.

4.2.4 UV-protective coatings

Furniture used outside is constantly being under exposure to all sorts of weathering conditions among which one is UV radiation. UV radiation enhances the deterioration of materials and coatings and one way of delaying this process is by the addition of UV absorbing agents.

Especially for wooden surfaces the benefits of nano-additives to facilitate this absorption have been described. UV protection of wood surfaces can be achieved by adding various metal oxides and organic chemicals that work by selectively filtering, i.e. blocking, UV radiation but leaving the visible light spectrum intact as much as possible (to maintain the natural wood appearance). Especially in the case of wood protection where the surface has to keep its *natural* looks. However, UV absorbing additives are also used to enhance the lifetime and color-fastness of paints or coatings that deteriorate as a consequence of UV exposure. Metal oxides are ZnO, CeO_2 and TiO_2, of which the first two are most preferred because of their sudden cut-off of absorption between 350 and 375 nm wavelength (just at the border between UV and Visible light wavelengths) and a high transmission at longer wavelengths. This, in contrast to TiO_2 that does show a cut-off around similar wavelengths but remains less transparent to visible light. One other disadvantage of using TiO_2 is its UV induced reactivity that will act in a destructive way on the paint matrix and on the underlying surface.

ZnO and CeO_2 are therefore the two nanomaterials used most often in the size range between 60-20 nm (depending on the type of coating material, the color or transparency required and the layer thickness needed) and in additive concentrations between 1-6 w/w% (depending on the size of the particle and the protection required). BYK Additives and Instruments [26] is one example of a company advertising with a broad range of different such nano-products.

However, non-nano alternatives are available and are well appreciated by the furniture industry. Examples are organic UV absorbers like hydroxyphenylbenzotriazoles, hydroxybenzophenones, hydroxyphenyl-S-thiazines or oxalic anilides. Their main disadvantage with respect to the nanomaterials CeO_2 and ZnO is their lower long term stability. The nanometal oxides are typically more stable over longer periods of time than their organic substitutes. This may prove an advantage in some products, but in the case of furniture where typical product lifetimes vary between 5 – 10 years, this is less so. Until recently, the cost disadvantage of nano-TiO_2 and nano-ZnO with respect to non-nano alternatives prevented for their large scale use in furniture products. However, as a consequence of increasing yearly production volumes of nanomaterials and a resulting decreased unit price, nano-TiO_2 and nano-ZnO are becoming more and more interesting substitutes, also for furniture application. According to the FCBA, one can therefore expect an increasing contribution by these type of UV-protective coatings at the furniture market in the near future.

4.2.5 Self cleaning coatings

In addition to easy-to-clean surfaces, self cleaning surfaces go one step further in the sense that these are not only easy-to-clean because of a reduced surface tension but that these also actively clean

[26] http://www.byk.com

themselves. This self cleaning effect is facilitated by the same nanomaterials that provide for UV blocking coatings or lacquers. However, instead of absorbing or reflecting the UV radiation, the nanomaterials are modified slightly so that they are able to use the UV to brake down any organic pollution that sits at the surface. In most products this nanomaterial is TiO_2 or ZnO.

The efficacy of these coatings though is limited. Examples of exterior facade coatings do show that these type of coatings do support a longer lasting “whiteness” of a wall that is exposed to traffic exhaust. However, these coatings are presumably much less effective in removing thicker layers of dirt. Consequently, these may be interesting to explore for kitchen furniture where one finds a daily deposit very thin layers of baking oils and baking fumes. These coatings might be less interesting to keep strong polluted surfaces clean.

4.2.6 Bactericidal coatings

Self cleaning coatings do show a large functional overlap with bactericidal coatings. As self cleaning coatings are designed to break down organic pollution, these coatings will as easily brake down bacteria or other micro-organisms such as algae or fungi that will try to live on that coated surface. This can be an important functionality for furniture in large public spaces like the metro system, trains, offices, day-care, hospitals or the bio-industry, where the coating can support a reduced risk of infection from one person or one animal to the other and thereby the development of plagues.

Another example of so-called active biocide coatings are based on nano-silver. Nano-silver is brought onto the surface as a thin layer coating that, depending on the quality, can be chemically linked to the substrate (most durable type) or simply “lying lose” (low quality performance type). In contact with water or microorganisms, small amounts of silver ions dissolve from the nano-silver material. Ionic silver is a well known biocide that has been used in medical treatment as antibiotic against multi resistant bacterial strains. The silver ions react with the microorganism and kill it. In contrast to nano-TiO_2 or nano-ZnO that function as catalyst, nano-silver does slowly disappear upon reaction.

Easy-to-clean coatings are currently marketed as passive anti-bacterial coatings. Instead of actively degrading bacteria and other microorganisms, these coatings form a highly flat surface that prevents these organisms to multiply easily, because of a lack of nutrients and because of more efficient cleaning compared to a non-treated surface.

5 Health and Safety considerations

5.1 Introduction

Nano-materials may behave more hazardous to humans than their micro-scale equivalents:

- Because they are smaller and may penetrate the human tissue more easily;
- Because they are smaller their powders may behave like gases;
- Because they are smaller they may be transported via the nerve system[27], cross the placenta[28], or penetrate the skin;
- Because their shape may induce specific toxicity responses;
- Because they have a larger surface to volume (or surface to mass) ratio;
- Because they may show different chemical properties;
- Because they may show different physical properties.

Even though current knowledge is still insufficient to predict toxicity based on the nanomaterials' composition and morphology, one can expect that the toxicity profile is at least partly related to the unique chemical and physical behavior that makes them interesting for product innovation in the first place.

The health effects of nanomaterials observed most frequently are induced via inflammation or via oxidative stress. At a sufficient dose, these then may lead to cell death, scar-tissue forming (for example in the lungs) or the formation of mutations that again may lead to deformations or cancer. Another effect observed for some nanomaterials is that they can serve as carrier for other toxins. A comprehensive review on the available knowledge on health and safety issues of nanomaterials is provided by Aschberger et al. (2011)[29]. They summarize that toxicity following oral exposure seems low and was only observed at high doses (for nano-TiO_2 and nano-Ag). Toxicity following dermal exposure by nano-Ag from wound-dressings or unpurified carbon nanotubes was found inconclusive as some studies observed these nanomaterials to cause inflammation of the skin and some didn't. Toxicity following inhalation exposure is considered the major portal for nanoparticle entry in the human body. For various nanomaterials, preliminary studies hint that the effect on the lungs (inflammation, scar-tissue forming) shows a concentration threshold, suggesting that a INEL (Indicative No Effect Level) might be derived. However, based on current knowledge non-threshold effects can not be ruled out. With respect to genotoxicity and carcinogenic effect of nanomaterials was observed that different test methods do yield different results. Since there is no agreed-on standard to study this effect the available data remain inconclusive. Even though there are clear signs that specific nanomaterials do interact with cellular proteins or DNA and by doing so affect the cells metabolism and multiplication. A similar situation exists for reproduction toxicity: it is questioned whether the tests are representative for human exposure, even though in Zebra-fish (standard testing animal), reproduction toxicity is in fact observed. To conclude Aschberger et al. state that due to the limited available data for performing a risk assessment and due to the uncertainties in relation to the suitability of the available test methods and risk assessment methodology it is currently difficult to draw any firm conclusions for engineered nanomaterials based on the open literature, and that even on a case-by-case basis this is a tedious operation.

In the wealth of nanomaterials available on the market, only a limited number seems to be used in furniture products to date (see the table below). Among these, most examples of nano-products have been found for nano-SiO_2, nano-TiO_2 and nano-Ag. Section 5.1.1 - 5.1.3 does provide a summary on

[27] Oberdorster G et al. 2004, Translocation of inhaled ultrafine particles to the brain. *Inhalation Toxicology* 16 (6-7): 437-445

[28] Hagens WI et al. 2007, What do we (need to) know about the kinetic properties of nanoparticles in the body? *Regulatory Toxicologie and Pharmacology* 49: 217-229

[29] Aschberger A, Micheletti C, Sokull-KluttgenB and Christensen FM (2011) Analysis of currently available data for characterizing the risks of engineered nanomaterials to the environment and human health – Lessons learned from four case studies, *Environment International, 37, 1143 – 1156*

the health and safety profiles of these three nanomaterials. Section 5.1.4 considers tubular nanomaterials and the current concerns for human health. Even though no applications could be found in 2012, intensive research is studying possible applications that are not specific for furniture but may enter the furniture industry eventually.

Table 1 Nanomaterials dominating the nano-products currently used in the furniture industry

Nanomaterial	Scratch resistance	Easy-to-clean	Anti-graffiti	UV/light stability	Self-cleaning properties	Anti-microbial
SiO_2	X	X	X			
TiO_2 /ZnO				X	X	X
CeO_2				X		
Ag						X
CuO						X

However, regardless their intrinsic hazards, key to any health risk posed by nano-materials or products is the chance of exposure. As long as no exposure can be guaranteed there will be no health risk. Section 5.2 therefore addresses the potential exposure routes inhalation, dermal contact and ingestion. Section 5.3 looks into more detail into possible exposure scenarios found for the furniture industry. The health and safety aspects of three nanomaterials mostly encountered in the furniture industry are highlighted in some more detail in Section 5.4.

5.1.1 Adverse health effects of nano-TiO_2

In 2011, NIOSH (National Institute of Occupational Safety and Health) reviewed all scientific data available on the health and safety profile of nano-TiO_2. NIOSH[30] concluded that there is enough evidence to categorize nano-TiO_2 as a potential occupational carcinogenic substance. However, even more interestingly, NIOSH concludes that the carcinogenic effect observed for nano-TiO_2 is induced via a secondary mechanism, which means that this effect is not "chemical specific" but "particle specific", caused by the fact that nano-TiO_2 is non-soluble and nano-sized. A similar effect may therefore be expected for other non-soluble MNMs. NIOSH furthermore concluded that applying a thin coating around each nano-TiO_2 particle seems to enhance its carcinogenic potency and that the morphology (being amorphous or crystalline) did not seem to have a significant effect on the carcinogenicity. Based on the available literature, NIOSH recommended an airborne exposure limit of 0.3 mg m^{-3} (TWA) for an average working week of 40 hours, 10 hours per day for carcinogenicity and 4 µg m^{-3} (TWA) for inflammation. However, as inflammation is the first step in the development of a possible future cancer, it should be recommended to maintain this lower TWA as the most desirable maximum exposure limit at the workplace.

5.1.2 Adverse health effects of nano-SiO_2

Compared to nano-TiO_2, the toxicity profile of the second nanomaterial, nano-SiO_2, is yet much less well understood. Nano-SiO_2 can be produced in an amorphous or a crystalline form and in a large variety of shapes and morphologies. Depending on the exact structure, their physical and chemical reactivity is different and their toxicity profile may be different as well. Napiersky et al. (2010)[31] reviewed the different forms and synthesis routes, described the available knowledge on the toxicity mechanisms at work. They conclude that the toxicity of nano-SiO_2 seems to be most strongly linked to its crystalline structure. Crystalline nano-SiO_2 is found to cause oxidative stress and consequently, DNA and membrane damage. In contrast, it is the amorphous form of nano-SiO_2 that is most often used by industry to improve product performance. The use in scratch resistant lacquers is an example thereof. The toxicity of amorphous nano-SiO_2 is considered much lower than that of crystalline nano-SiO_2 and consequently only a limited amount of studies did look further into its exact profile. The

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[30] Occupational Exposure to Titanium Dioxide, NIOSH, Current Intelligence Bulletin 63, April 2011

[31] Napiersky D *et al.* (2010) The Nanosilica Hazard:another variable entity, *Particle and Fibre Toxicology*, 7, 39

limited works available do suggest that nano-SiO_2 is not involved in progressive fibrosis in the lungs, but may result in acute pulmonary inflammation at high doses. Still, it might turn out that this picture should be nuanced, depending on the exact design of the amorphous nano-SiO_2. More and more studies become available that point at the strong interaction between nano-SiO_2 and peptides, the large effect of surface area on the reactivity of this nanomaterial and the dependence of toxicity on any surface modification. Interaction with peptides for example may hint an allergic potency (similar to epoxy-products)[32,33,34], and important also, different studies do find different toxicities as a result of the use of different assays.

However, Napiersky et al. (2010) and references therein do suggest that the nano-typical health and safety risks for workers occur primarily when powders of the raw nanomaterial are produced or handled. In suspension or in a solid matrix, they state that nano-SiO_2 is fixed and that exposure through inhalation can be expected to be very low.

No OEL (Occupational Exposure Limit) or TWA has been derived for nano-SiO_2.

Though nano-silica may be hazardous when handled as a pure powder, when this silica fume reacts to form the final lacquer or coating matrix, the nano-particles get hydrated or react with the biner like polyurethane and its nano-character is no longer present. It is therefore not easily to be expected that any risk of exposure to nanoparticles remains from the eventual ready for use product.

5.1.3 Adverse health effects of nano-Ag

The toxicity of silver has been studied intensively in the past, showing that silver is relatively non-toxic for humans but can be extremely toxic for environmental organisms. In contrast to this macroscopic silver, the toxicity profile of nano-Ag is less well understood. In both cases, toxicity is determined by the emission of silver ions (Ag^+). However, in the case of nano-Ag, the nanoparticle itself may cause and increased toxicity as upon exposure it may show a different distribution in the human body (or in the environment) compared to the larger sized silver particles. For example, as a local source of high concentrations of Ag^+, giving rise to an increased hazard, which was found in environmental toxicity studies on nano-Ag. An overview of the public literature on Nano-Ag toxicity has been reviewed by Christensen *et al.* (2010)[35]. In their review, Christensen *et al.* conclude that there is too little information available to be conclusive about possible hazards coused by worker exposure to nano-Ag. However, they do also state that repeated inhalation in the workplace and intensive skin contact may cause adverse effects. For Nano-Ag a Lowest Observed Adverse Effect Level (LOAEL) of 49 µg/m3 derived in a 13-week inhalation study (exposure for 6 hours/day, 5 days/week) with rats was used as a starting point (Sung *et al.*, 2008; 2009)[36]. The main targets of accumulation and toxicity were the lungs and liver. Prolonged exposure to Nano-Ag seemed to cause an inflammatory response within the lung, and induced alterations in lung function. Based on these data, TNO (2011)[37] proposed a chronic $DNEL_{inhalation}$ of 0.33 $\mu g/m^3$ (equivalent to 4000 particles/cm^3 and 7.2 x 106 nm^2/cm^3) for

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[32] Zhen X, Shi-Long W Hong-Wen G (2010) Effects of nano-sized silicon dioxide on the structures and activities of three functional proteins, *Journal of Hazardous Materials*, 180, 375–383

[33] Choi JE *et al. (2011)* A safety assessment of phototoxicity and sensitization of SiO2 nanoparticles, *Mol Cell Toxicol*, 7:171-176

[34] Hirai T *et al.* (2012) Amorphous silica nanoparticles size-dependently aggravate atopic dermatitis-like skin lesions following an intradermal injection, *Particle and Fibre Toxicology*, 9:3

[35] Christensen FM *et al.* (2010) Nano-Silver – feasibility and challenges for human health risk assessment based on open literature. *Nanotoxicology*; 4(3): 284-295

[36] Sung JH *et al.*(2009). Subchronic inhalation toxicity of silver nano particles. Toxicolog Sci 108(2):452–461. / Sung JH *et al* (2008) Lung function changes in Sprague-Dawley rats after prolonged inhalation exposure to silver nano particles. Inhal Toxicol 20:567–574.

[37] van Manen - Vernooij B, le Feber M, van Broekhuizen FA, van Broekhuizen P (2011) Pilot "Kennisdelen Nano in de verfketen", TNO Report V20123 | 1

Nano-Ag, noting that the risk assessment approach used to derive this DNEL is of an exploratory nature and should not be used for regulatory purposes as not all required toxicological end points are thoroughly explored.

However, despite the current lack of a complete toxicity profile for nano-Ag, there are clear signs to be very conservative with the application of nano-Ag in furniture products. One of the most essential applications of nano-Ag is for medical treatment of highly sensitive wounds, bacterial infections or as a disinfectant for bacterial strains that are very persistent and/or have become resistant towards other antibiotics. Misuse though, may contribute to the development of bacterial resistance to silver (see TNO 2011 and references therein), and when this happens this may have an enormous effect on human health.

No OEL or TWA have been derived for nano-Ag.

5.1.4 Adverse health effects of tubular nanomaterials

A group of nanomaterials that deserves special attention with respect to their health and safety performance are the tubular nanomaterials. This can be nanotubes, nanorods or nanofibres, and can be made of carbon (i.e. carbon nanotubes) but may also be made from other materials like metals. Some years ago, carbon nanotubes got world-wide attention because of their mesotheliomal effect. Further study on this subject reveals that the toxicity of carbon nanotubes (and other nanotubes) does strongly depend on the exact shape and functionality of the nanomaterial and shouldn't be generalized as such. Still, these tubular (or rod like) nanomaterials do deserve special care in the evaluation of health and safety of workers, consumers and the environment. Effects observed after inhalation of carbon nanotubes include defect-governed acute pulmonary toxicity, subpleural fibrosis, immune suppression, which are however slightly different from the effects observed for asbestos fibres. The adverse effects observed are found to depend strongly on i.e. the size, shape, agglomeration and the surface chemistry of the tubes. Another factor of influence is the purity of the tubes and the presence of metal catalysts. CNTs were found to cause inflammation of the skin in the presence of residual metals whereas highly purified CNTs did not. A comprehensive review on the current knowledge on carbon nanotube toxicity is provided by Zhao and Liu (2012)[38]. The use of carbon nanotubes has been observed in the furniture industry in relation to a table and chairs made of high-performance carbon nanotube (CNT)-reinforced (see section 4.1.6). Besides this application,no further applications of carbon nanotubes in furniture could be found. However, given their unique electrical properties and their potential to act as reinforcing fiber, alternative flame retardant or algae-growth repellant, their future use could be foreseen.

5.2 Exposure routes

In the furniture industry, workers will be exposed (almost without exception) to nano-products (either in the form in which they are purchased or in forms which are developed due to use or processing) and not to pure nanomaterials, meaning that according the findings of this project exposure involves mainly:

Products in which nanoparticles (or nanomaterials) are embedded (in a solid matrix, in a powder, in a liquid or in a slurry), and the dust or aerosols of these nano-products produced when they are machined, sprayed or otherwise applied at the workplace.

This does have an impact on the actual exposure of the worker to the nanomaterial in the product. Work by Saber et al. (2011a[39],b[40]), does show that there might be a significant difference between

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[38] Zhao X and Liu R (2012) Recent progress and perspectives on the toxicity of carbon nanotubes at organism, organ, cell, and biomacromolecule levels, Environment International, 40, 244–256

[39] Saber AT, Jensen KA, Jacobsen NR, Birkedal R, Mikkelsen L, Moller P, Loft S, Wallin H and Vogel U (2011a) Inflamatory and genotoxic effects of nanoparticles designed for inclusion in paints and lacquers, *Nanotoxicology, Early Online*, 1 – 9

exposure to pure nanomaterials and nanomaterials embedded in a coating. They studied different coatings (acrylic coatings and a UV-cured lacquer) doped with different nanomaterials (nano-TiO_2, nano-SiO_2, nano-Clay and Carbon Black) and found that the pure nanomaterials did show nano-specific inflammatory and DNA-damaging effects whereas, once embedded in the coating or lacquer, the toxicity profile of the sanding dust of these nano-products was similar to the toxicity of the same products without nanomaterials. In other words, first and preliminary scientific work does show that nanomaterials that are embedded in a matrix do not necessarily have to exhibit the nano-specific toxicity profile they present in their pure form. This is a very promising first result that is of high importance to the risk assessment of working with nanomaterials and products in the furniture industry and does encourage further study along these lines to determine if a similar effect is observed with other materials and products.

Generalizing the way in which a nanomaterial can be part of the nano-product is three-fold:

1. A nanomaterial may be chemically inert but able to physically interact. This results in a matrix in which the nanomaterial is embedded but does not chemically react with the matrix of the product. In this way the nano-material remains "loose" and could in principle leach out.
2. A nanomaterial may be chemically reactive. This results in chemical bonding between the nanomaterial and the matrix, making it unlikely for the nanomaterial to leach out.
3. A nanomaterial may be chemically and physically reactive and bonded chemically at the surface of the matrix. In this way the nanomaterial is not likely to leach out but exposure may occur upon direct contact with the surface. Bactericidal surfaces are examples thereof.

In the following three subsections light is shed on the three different ways in which workers in the furniture industry might get exposed to nanomaterials from the products they work with. From the very nature of their daily activities and the products they typically work with, exposure through inhalation of nanomaterial dust (from cutting, sanding, drilling, sewing or machining) or aerosols from paint or glue-spraying are those most likely to dominate any health risks. Skin penetration may play a role as well (although much smaller), for instance with surface reactive substances such as bactericides one might foresee occupational health problems. Exposure through ingestion is also to be expected. Nanomaterials that are cleared from the lungs or nasal area will get ingested with the mucus, and chances are for example of ingesting nanomaterial containing dust or paint at lunch or coffee when hands and faces are not properly washed.

Exposure to nanoparticles by transporting solid furniture parts like nano-enhanced ceramics, glass, steel, plastics, composites, insulation materials, concrete, wood or surfaces treated with hardened coatings is expected to be very small due to the fact that in those cases the nanomaterials are expected to be contained in the solid matrix. It is nevertheless advisable to avoid skin contact also in these situations by wearing gloves in case of uncertainty.

5.2.1 Exposure through inhalation and typical health considerations

Exposure to nanomaterials through inhalation may occur when airborne particles are produced at the workplace, either because the processes involved produce dust or aerosols or because nanomaterial powders are handled. In the furniture industry, most nanomaterials enter the workplace embedded in a nano-product like a coating or treated textile. The handling of raw nanomaterials was not observed in the project .

A first approach to assessing exposure through inhalation is by looking at the knowledge available for Fine and Ultra Fine Particles (in particular Fine Particles: PM_{10}, $PM_{2.5}$ and $PM_{<0.1}$). Their behavior and health hazards have been studied intensely over the past years in the context of health effects caused

[40] Saber AT, Koponen IK, Jensen KA, Jacobsen NR, Mikkelsen L, Moller P, Loft S, Vogel U and Wallin H (2011b) Inflamatory and genotoxic effects of sanding dust generated from nanoparticle-containing paints and lacquers, *Nanotoxicology, Early Online*, 1 – 13

by industrial activities and traffic exhaust. Typical health effects observed are (NEAA 2005[41] and references therein):

- Inflammation of the airways;
- Bronchitis;
- Asthma;
- Cardiovascular effects.

Experimental studies on the effect of UFP in test animals did show effects like translocation[42] (and sometimes also accumulation) from the nasal and lung regions to the nervous system, the brain tissue and other organs like the blood, heart and liver and the bone marrow where they cause inflammatory effects leading to a cascade of secondary health effects (Oberdörster et al. 2004 and references therein; and for a more recent review on the topic by Politis et al. 2008[43]). The simple rule of thumb "the smaller the particle, the deeper the lung penetration" was observed to change for the smallest particles. Witschger and Fabriès (2005)[44] and Oberdörster (2005)[45] showed that the particle size has a major impact on the place where deposition in the airways might occur and consequently what health risks are to be expected. For the nasal area this implies an enormous burden on the natural defense mechanism of the human body against particles smaller than 20nm. For the alveolar system, it means that substantial accumulation of nanomaterials may occur for particles between 5 and 50 nm (Kreyling et al., 2002[46]; Oberdörster, 2005b[47]).

Various studies have shown that some nanoparticles can penetrate the lung tissue and reach the bloodstream, via which they can access, other parts of the body (Oberdörster et al., 1992[48], 2000[49]; Kreyling and Scheuch, 2000[50]). Specific for the nasal region has furthermore been shown, that particular nanoparticles (i.e. gold and carbon based) are able to get transported to the brain via the nasal nerve system and cross the blood-brain barrier to accumulate there (Hagen et al. 2007). In addition to this, certain nanoparticles can be transported along the nerves to the central nervous system.

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41 NEAA 2005. Particulate Matter: a Closer Look, www.rivm.nl, Netherlands Environmental Assessment Agency, E. Buijsman, J.P. Beck, L. van Bree, F.R. Cassee, R.B.A. Koelemeijer, J. Matthijsen, R. Thomas and K. Wieringa.

42 Particles, or chemical substances, enter the human body in one place (for example the lungs via inhalation) but, as a result of that, are observed in different places of the body as well (for example in the liver). This change in location (from the lung to the liver) is called translocation.

43 Politis M, Pilinis C, Lekkas TD 2008. Ultra Fine Particles and Health Effects. Dangerous. Like no Other PM? Review and Analysis, *Global NEST Journal.* Vol 10(3), pp.439-452

44 Witschger O, Fabries JF, 2005a. Particules ultrafines et santé au travail: 1- caractéristiques et effets potentiels sur la santé. Hygiène et sécurité du travail. *Cahiers de notes documentaires*, INRS, 199 : 21-35

45 Oberdörster G, 2005b. Inhaled Nano-sized Particles: Potential effects and Mechanisms. Proceedings of the First International Symposium on Occupational Health Implications of Nanomaterials, 12 to 14 october 2004, Buxton, Great-Britain, Edited by the Health and Safety Executive, Great-Britain and the National Institute for Occupational Safety and Health, USA, July 2005, p 65-71

46 Kreyling WG, Semmler M, Erbe F, Mayer P, Takenaka S, Schulz H, Oberdörster G, Ziesenis A, 2002. Translocation of ultrafine insoluble iridium particles from lung epithelium to extrapulmonary organs is size dependent but very low. *J Toxicol Environ Health* 65 (20): 1513-30.

47 Oberdörster G, 2005b. Inhaled Nano-sized Particles: Potential effects and Mechanisms. Proceedings of the First International Symposium on Occupational Health Implications of Nanomaterials, 12 to 14 october 2004, Buxton, Great-Britain, Edited by the Health and Safety Executive, Great-Britain and the National Institute for Occupational Safety and Health, USA, July 2005, p 65-71

48 Oberdörster G, Ferin J, Gelein R, Soderholm SC, Finkelstein G, 1992. Role of the alveolar macrophage in lung injury: studies with ultrafine particles. *Env Health Persp* 97 : 193-199.

49 Oberdörster G, Finkelstein JN, Johnston C, Gelein R, Cox C, Baggs R *et al.,* 2000. HEI Research Report : Acute pulmonary effects of ultrafine particles in rats and mice. HEI Research Report No. 96, August, 2000, Health Effects Institute

50 Kreyling WG, Semmler M, Erbe F, Mayer P, Takenaka S, Schulz H, Oberdörster G, Ziesenis A, 2002. Translocation of ultrafine insoluble iridium particles from lung epithelium to extrapulmonary organs is size dependent but very low. *J Toxicol Environ Health* 65 (20): 1513-30

These two mechanisms could play a major role in the development of certain cardiac or central nervous system diseases.

Physicochemical properties, surface properties and catalytic properties with high potential for generating free radicals are factors that can contribute to a higher toxicity of nanoparticles compared to the larger forms at those places of the body where they end up. Irritation, inflammation, cell death, extraordinary cell growth, DNA damage and hormonal distortion are among the eventual effects that could result from this.

5.2.2 Exposure through the skin and some health considerations

The skin is traditionally considered to be a good barrier against particles. Most studies focusing on micrometer-sized particles have found no penetration of the skin except under conditions of local irritation, abrasion or sensitization of the skin top-layer. Also for most nanoparticles this might be the case. TiO_2 nanoparticles, for example are observed not to penetrate the skin except for those places where the top-layer is disrupted (Lademann et al, 1999[51]). In a 2004 review on health risks, the British Health and Safety Executive (HSE) concluded that systemic toxicity resulting from skin absorption of insoluble nanoparticles should not cause significant problems. However, at present, this statement is questioned by more recent research showing indications that specific nanoparticles do penetrate flexed skin (for example at the wrist) or intact skin tissue depending on their chemical nature, their size, shape and the matrix in which they get in skin contact (Muller-Quernheim, 2003[52], Tinkle et al. 2003[53] and Ryman-Rasmussen et al. 2006[54]). A more recent overview by Lademan (2011)[55] describes the different mechanisms that play a role in the penetration and storage of nanoparticles in the human skin. From the background of pharmaceutical engineering and drug delivery, there is ongoing and intense research and development in the field of using nanomaterials for drug delivery via the skin.

Once a nanoparticle does cross the skin barrier, it should be clear that the underlying skin tissue and the bloodstream are its first two targets, after which the blood might transport it to other organs.

However, the skin itself can also be the target organism of nanomaterials leading to effects of irritation or sensitization. In 2011, Choi et al.[56] published a first safety assessment on the phototoxicity and sensitization of nano-SiO_2. Their results do suggest nano-SiO_2 shows no sensitizing behavior and no phototoxicity when skin contact would occur. For nano-TiO_2, a human health risk assessment performed by Christensen et al. (2011)[57] concluded that the limited number of studies available are not sufficient to obtain more concrete information on the possible adverse dermal effects during occupational exposure. In a similar assessment for nano-Ag, Christensen et al. (2010)[58] concluded that nano silver is most likely not irritating nor sensitizing but that no data are available that explicitly looked into these effects. First data on carbon nanotubes do hint that MCNT and SCNT can be only

[51] Lademann J, Weigmann H, Rickmeyer C, Barthelmes H, Schaefer H, Mueller G, Sterry W, 1999. Penetration of titanium dioxide microparticles in a sunscreen formulation into the horny layer and the follicular orifice. *Skin Pharmacol Appl Skin Physiol* 12 (5): 247-56

[52] Müller-Quernheim J, 2003. Chronic beryllium disease. Orphanet Encyclopedia. September 2003. http://www.orpha.net/data/patho/GB/uk-CBD.pdf

[53] Tinkle SS, Antonini JM, Rich BA *et al.* 2003. Skin as aroute of exposure and sensiization in a chronic berylium disease. *Environ. Health Perspect.* 111:1202-8

[54] Ryman-Rasmussen JP, Riviere JE, Monteiro-Riviere NA 2006. Penetration of intact skin by quantum-dots with diverse physicochemical properties. *Toxicol. Sci.* 91:159-65

[55] Lademann J, Richter H, Schanzer S, Knorr F, Meinke M, Sterry W, Patzelt A (2011) Penetration and storage of particles in human skin: Perspectives and safety aspects, EU J. Phar. BioPhar., 77, 3, 465–468

[56] Choi JA, Park Y-H, Lee EY et al (2011) A safety assessment of phototoxicity and sensitization of SiO2 nanoparticles, Mol Cell Toxicol, 7, 171-176

[57] Christensen et al. (2011) nano-TiO_2; feasibility and challenges for human health risk assessment based on open literature, Nanotoxicol., 5(3), 110-124

[58] Christensen et al. (2010) nano-silver; feasibility and challenges for human health risk assessment based on open literature, Nanotoxicol., 4(3), 284-295

little irritating to the skin and show no sensitizing behavior according to current tests (Ema et al 2011)[59].

5.2.3 Exposure through ingestion

Ingestion doesn't only involve nanomaterials that are directly swallowed (through the mouth), but may concern as well nanoparticles that were inhaled and removed from the lung system with the mucous (called secondary ingestion) and consequently swallowed.

It has been shown that ingested particles smaller than 20 micrometers can be absorbed in the intestine and enter the bloodstream like nutrients normally do (Gatti and Rivasi, 2002[60]; Hillyer and Albrecht, 2001[61]). Besides size, surface characteristics such as polarity and charge are seen to play a significant role, with hydrophobic particles being more efficiently absorbed than hydrophilic particles. In addition to these, the translocation of nanoparticles is likely to be influenced by their ability to bind to proteins and other nutrients that could act as carrier substance to facilitate the uptake of nanomaterials in the intestines.

5.3 Exposure scenarios

Over the last years, more and more research has been published studying the possible exposure of workers to nanomaterials under real life conditions. Main focus of these studies is on the possible exposure during sanding or spraying activities and during working with nanomaterial powders. Preliminary findings do all point in the same direction concluding that exposure to free nanomaterials is only observed when working with nanomaterial powders. Once this nanomaterial is embedded in a matrix, the preliminary findings indicate that exposure is no longer observed. The nanoparticle exposure observed during sanding or spraying activities is typically seen to consist of the product matrix with the nanomaterial remaining part of this matrix. The workplace exposure measurements conducted in the contexts of the present study are in line with these preliminary findings. Their details are described in section 6.3 and in more detail in Annex 1.

Many different exposure scenarios could be formulated for the furniture industry. Central to each scenario though is the *exposure probability*. In a first approach, working with MNMs in furniture could be categorized in three risk "zones":

- **Of highest risk** are those activities in which powders of pure MNMs are handled. First actions to lower exposure should be:

  (1) to investigate if substitution by an alternative product with known less health and safety risks is an option;
  (2) to ask the supplier to supply the MNMs in liquid or paste form;
  (3) to prevent any exposure (by shielding the worker, by ventilation, preferably using a fume hood or by using robotic-arms in a fully closed and automated process, or by personal protection measures).

- **Of medium risk** are activities performed with MNM-containing materials (liquids or solids) like i.e. paints, lacquers, adhesives, composites or textiles. Spraying, sanding, polishing, cutting or otherwise machining MNM containing materials are examples of activities with a high risk of exposure that may readily occur in the furniture industry. In those cases, exposure to MNM-containing dust or aerosols can be expected and should be avoided. Activities to control any risk of exposure should be:

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[59] Ema M et al (2011) Evaluation of dermal and eye irritation and skin sensitization due to carbon nanotubes, Reg. Toxicol. Pharmacol. 61, 276 - 281

[60] Gatti AM, Rivasi F, 2002. Biocompatibility of micro and nanoparticles. Part I: in liver and kidney. *Biomaterials* 23 (11): 2381-7

[61] Hillyer JF, Albrecht RM, 2001. Gastrointestinal persorption and tissue distribution of differently sized colloidal gold nanoparticles. *J Pharm Sci* 90 (12) 1927-36

(1) to prevent the production of dust or aerosols as much as possible by the application technique,
(2) to apply an effective ventilation system and
(3) to apply personal protection measures against inhalation or skin contact.

- **Of low risk** are activities like the handling of MNM-containing materials, such as transportation of MNM-containing solid or liquids materials without any dust or aerosol production. Carrying a MNM-coated panel board or can of MNM-paint from location A to B is an example of such an activity. The MNM is contained in the matrix and will not easily migrate out upon touch. It is nevertheless advisable to avoid skin contact by wearing gloves, for example when transporting furniture products treated with bactericidal coatings that are surface reactive.

How to deal with these risks in a responsible manner is described in section 6.

5.3.1 Exposure of the end user

Even though the end user of a furniture product will most likely not actively process or machine the product, exposure to nanomaterials may be envisaged as there will often be intense (skin) contact between the end user and the top-layer of the product. For example, in the case of a table coated with a nano paint or nano lacquer, or a chair or couch covered with a nanotextile that causes spilled liquids to pearl off without leaving any stain. When assessing these risks though, one should realize that the reason for enhancing the products with nanomaterials is often to make them stronger or more durable. In other words, the nanomaterials added often function to strengthen e.g. the dried paint matrix or the textile. This suggests that in contrast to e.g. plasticizers, nanomaterials in coatings are often strongly integrated in the matrix and will not readily leach out.

6 Organizing a precautionary safe workplace

Organizing a safe workplace when working with nanomaterials or nano-products requires a proper risk assessment, including well-considered exposure scenarios. However, as has been reflected, the actual knowledge on the toxicological properties of nanoparticles (anno 2012) is still limited. The same holds for the possible release of nanoparticles from nano-products during use, cleaning or maintenance. This means that occupational health policy is still dealing with many uncertainties and a precautionary approach is recommended and advocated by the European Commission and the social partners of the furniture industry. Though, what does that mean for the furniture industry? The sections below summarize the basic ideas underlying the precautionary approach, its building blocks and what tools are available to guide workers and employers in organizing a precautionary safe workplace while working with nanomaterials and nano-products.

6.1 The precautionary approach

A precautionary approach can be explained as to be a strategy for dealing with uncertainties in an alert, careful, reasonable, and transparent manner that is appropriate to the situation. For "nano", it can be applied when information on the nano-content of products is limited and if there is uncertainty about the release of nanoparticles from nano-products. The precautionary principle is therefore a process more than a rule for arriving at a decision. All potential options for action need to be considered in the light of their positive, negative, certain, and uncertain consequences, with the decision then being: *"what is the best option?"*

Over the previous years, the European debate on nanotechnologies[62] did examine extensively what it would mean to bring a precautionary approach into practice. Application of this approach is not per definition the same as prohibiting an activity, although when everything is taken into account that may be the best option in some cases. In general it can be stated that the precautionary approach for dealing with nanoparticles should be implemented within the context of the prevention principles and the working environment policy. In this way, the principle will be part of the workplace risk assessment and the associated action plans, which companies are required to draw up.

Key to the precautionary approach for working with nanomaterials and nano-products in furniture is the first of the five building blocks *"no data → no exposure"* (see table 2). However, since reaching "zero"-exposure is not a realistic goal in almost many working situations, bringing the precautionary approach into operation is complex. The other building blocks involve registration of workers and transparent communication on nano through the value chain of a product.

To support employers and workers in this process, various tools have been developed. One type of tools aims to assist workers and employers in assessing and evaluating the occupational health risk while working with MNM and to help them to install preventive measures to avoid or reduce exposure to a minimum. The *Guidance on Working Safely with Nanomaterials and Nano-products*, developed by the Dutch Social Partners, is an example of such a tool. Stoffenmanager-Nano developed by TNO or the Control banding tool, described in section 6.2, are two others. Other tools focus on the derivation of nanomaterial specific Occupational Exposure Limits (OELs) or Derived No Effect Limits (DNELs) or the development of a more generic approach of preliminary Nano Reference Values (NRV-scheme), described in in more detail in section 6.1.3.

Together, the *Guidance* and the NRV-scheme can be considered a good practice for organizing a precautionary workplace. At EU level, in several EU Member States and in the US, similar initiatives are in progress.

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[62] See especially the Advisory Report of the Dutch Social Economic Council: *"Nanoparticles in the Workplace, health and safety precautions"*, 2009, Sociaal Economische Raad, Den Haag Netherlands. Part of the suggested precautionary approach is based on this advice report.

Table 2 Building blocks for a precautionary approach to working with nanomaterials

Building blocks for a precautionary approach to working with nanomaterials (MNMs) in the furniture industry
1. When there is insufficient data available to determine the health and safety risks of MNMs, exposure of workers in the furniture industry should be prevented. - Avoid exposure to MNM according to the occupational hygiene strategy. 2. Because of the uncertainty on health and safety risks of MNMs, manufacturers and suppliers should notify their down-stream users in the furniture industry about the MNMs in their materials or products. - Declaration of MNM content of and possible release from a product or material through the production chain. - Notification of MNM content of and possible release from a product or material at a central register. 3. Exposure registration for the workplace allows for the early monitoring and retrospective examination of adverse health effects by MNMs on workers in the furniture industry. - Analogue to registration of carcinogens: nano-fibers and carcinogenic, mutagenic, reprotoxic or sensitizing MNMs. - Analogue to registration of reprotoxic substances: all other non-soluble MNMs. 4. Transparent risk communication is essential for workers and employers to organize a safe workplace when working with MNMs in the furniture industry. - Information on MSDS (Material Safety Data Sheet) on known nano-risks, management and knowledge gaps - Information on safe application and use, for example in the form of an instruction manual - Demand a Chemical Safety Report (REACH) for substances >1 ton/year/company 5. Derivation of nano-OELs or use of nano reference values is required for assessing workplace safety. - For nanoparticles that might be released at the workplace.

The following subsections will discuss these building blocks and possible ways to bring them into practice.

6.1.1 The occupational prevention strategy

In similarity to working safely with other chemicals the occupational preventive strategy is the strategy to bring the precautionary approach in to practice in order to identify the needed precautionary measures and prevent exposure. In short, this strategy boils down to the following 6 steps:

1. Prevent the use of nanomaterials or nano-products with uncertain health risks (if possible by using a potentially less hazardous non-nano alternative);
2. Replace (or substitute) the nanomaterials or nano-products by alternatives that induce less risks (for example, by using a paste instead of a powder);
3. Enclose the nanomaterials or nano-products in a specific area during processing (for example by automizing a spraying process by using robotic arms in a closed spraying cabin);
4. Apply technical protective measures (like i.e. local exhaust ventilation);
5. Apply organisational measures (like i.e. limiting the number of workers exposed and reducing the time of exposure);
6. Apply personal protection measures.

Substitution of hazardous substances and replacing them with less hazardous substances is always the first step to take. However, in the case of nanomaterials where the adverse health effects are uncertain, selecting a less hazardous alternative isn't an easy task. For example, if a novel nano flame retardant is the alterative for a known toxic and persistent flame retardant. If substitution isn't an option, one should attempt to minimize exposure to the best of abilities. Using nanomaterials in a pasta or liquid instead of a powder is an effective method to control risks of inhalation. Palletizing the nanomaterial powder is another.

During processing, exposure of workers to nanoparticles can be minimized by working in full containment. Automatic spraying-robot or sanding machines with integrated local exhaust ventilation systems may be effective protecting the workers involved from nanoparticles that may be produced in the process. Important hereby is to use HEPA-filters in the exhaust ventilation system and to prevent recirculation of the exhaust air. However, also when the process isn't fully closed, worker exposure to nanoparticles can be effectively prevented by local exhaust ventilation. Only when technical measures are explored but appear insufficient, personal protection equipment should be applied.

6.1.2 Personal protective equipment

Despite the limited amount of data, the current understanding is that the conventional aerosol control methods like local exhaust ventilation, filtration and respirators are effective methods also to protect against the inhalation of nano-materials (Maynard 2007). Specific studies, looking at the effectiveness of personal protection measures for nano-materials do indicate that P2 and P3 filtration type respirators (marketed as FFP2 ad FFP3) are ~97% and ~99% effective in filtering 30-60nm particles, which lays well within the 94% and 98% efficiency required by the European standards for these types of particle filters (Rengashami et al. 2009). The FP6 European framework project NanoSafe furthermore finds that H12 HEPA filters are typically more effective than electrostatic filter masks, a.o. because of moisture developing from the perspiration formed by wearing these masks, and that the exact efficiency can depend strongly (by one order of magnitude) on the size and chemical nature of the nanoparticles (about 10x more effective against carbon than against TiO_2 at similar particle size).

The NanoSafe project also tested the protective efficiency of different textiles and glove materials. First results indicate that non-woven polyethylene (Tyvek) fabrics are more efficient than non-woven polypropylene fabric or woven cotton and polyester. Each of the fabrics showed similar characteristics against 10nm Pt or TiO_2 particles. With respect to the protective gloves, first results by this project do indicate that nitrile, latex and neoprene gloves are impermeable to TiO_2 (10nm), Pt (10nm) or Carbon (40nm). However, other studies contradict these findings and do show a limited permeability (see overview findings of the technical committee on nanotechnologies TC229 and the RIP oN3 of REACH). These therefore suggest to wear at least two pair of gloves (which can be uncomfortable and should be done with care, especially when gloves are removed again). It should be noted though, that these studies looked at pure nanomaterials in powder, paste or liquid form instead of nanomaterials as part of a larger matrix of the i.e. paint, lacquer, glue or textile in which they are used in furniture.

Further information on personal protection materials can be found in a study recently published by the OECD, presenting a comprehensive overview on the comparison of guidance on selection of skin protective equipment and respirator to protect workers against possible exposure to manufactured nano-materials[63]. However, whether or not personal protective equipment is required depends on the actual exposure level.

6.1.3 Occupational Exposure Limits

To assess workplace safety, occupational exposure limits (OEL) are often used. Current scientific knowledge is too limited to propose health-based OELs for most nanomaterials. Only for a limited number of nanomaterials a health based OEL, recommended exposure limit (REL) or derived no-effect level (DNEL) are proposed by producers for their manufactured nanomaterials or by research organizations[64]. Table 3 summarizes a selection.

[63] OECD Environment, Health and Safety Publications Series on the Safety of Manufactured Nanomaterials No. 12 (2009) ENV/JM/MONO(2009)17

[64] SER Advies 12/01, March 2012, Voorlopige nanoreferentiewaarden voor synthetische nanomaterialen, Annex 1

Table 3 Proposals for OELs, RELs and DNELs for specific nanoparticles

Substance		**OEL or REL mg/m³**	**DNEL mg/m³**	**Reference**
MWCNT (Baytubes) *	8-hr TWA**	0.05		Pauluhn, 2010
MWCNT (Nanocyl)	8-hr TWA	0.0025		Nanocyl 2009
CNT (SWCNT and MWCNT) *	8-hr TWA	0.007		NIOSH 2010
Fullerene		0,8		NEDO-2 2009
Ag (18-19nm)	DNEL		0.098	Stone et al 2009
TiO_2 (10 -100nm) (REL) **	10hr/day, 40hr/week	0,3		NIOSH 2011

* CNT= Carbon Nanotube; SWCNT=single-wall CNT; MWCNT= multi-wall CNT
** REL = Recommended exposure limit; TWA = Time-weighted average

As an alternative until solid health-based nano values are developed, provisional nano-reference values can be used as pragmatic benchmark levels. Different initiatives did look into the possibilities to construct a scheme to derive generic reference values for MNM, like the German IFA (Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung) and the British BSI (British Standard Institute). In the Netherlands, employers' and employees' associations mutually agreed to use such benchmark levels for occupational exposure: the so called provisional nano reference values (NRVs). In March 2012, a NRV scheme was published by the Dutch Economic Council (SER)[64] as an official advice to the Dutch Ministry of Social Affairs and Employment, shown in Table 4.

Table 4 The Dutch scheme of Preliminary Nano Reference Values (NRVs) as advised by the SER in March 2012

Class	Description	Density (kg/m³)	NRV (TWA 8h)	Examples
1	Rigid, biopersistent nanotubes, nanofibers and nanorods for which asbestos like effects are not excluded	-	0.01 fibers/cm³ (= 10,000 fibers/m³)	SWCNT, MWCNT or metal oxide fibers for which asbestos like effects are not excluded by the manufacturer.
2	Biopersistent, granular nanomaterials in the range of 1 to 100 nm	> 6.000	20,000 particles/cm³	Ag, Au, CeO_2, CoO, Fe, Fe_xO_y, La, Pb, Sb_2O_5, SnO_2,
3	Biopersistent, granular nanomaterials in the range of 1 to 100 nm	< 6.000	40,000 particles /cm³	Al_2O_3, SiO_2, TiO_2, ZnO, nanoclay Carbon Black, C_{60}, dendrimers, polystyrene nanotubes, nanofibers and nanorods for which asbestos like effects are explicitly excluded
4	Non-biopersistent, granular nanomaterials in the range of 1 to 100 nm	-	Applicable OEL	e.g. fats, siloxanes, salt (=NaCl)

The derived NRVs are to be used as pragmatic benchmark levels – they do not guarantee that an exposure to nanomaterials below these values is safe. The NRVs may be used as long as the EU or the individual Member States have not tabled health based nano-OELs, or as long as specific Health-Based Recommended Occupational Exposure Limits (HBR-OELs) or Derived-No-Effect-Levels (DNELs) available from the REACH documentation are not available. The NRV is defined as the maximum 8-hour time weighted average amount of nanoparticles (in NP cm^{-3}) allowed in the workplace air that result from specific work activities in which MNMs are used or applied. The NRV scheme should only be applied as long as there is no health based exposure limit value available for the MNM concerned. Since NRVs do not guarantee that exposures below the NRVs are safe, exposure-reducing measurements should also be considered for exposures below the NRVs, according to the ALARA principle (As-Low-As-Reasonably-Achievable).

The collaborative action between the Dutch social partners that resulted in the NRV scheme and its official status as SER advice makes it unique among other approaches. Unique is also the metric defined: number of nanoparticles per cm^3, which expresses the current understanding that the reactivity of nanomaterials is related to surface area instead of mass. Application of the NRV scheme at European level is encouraged by the European Trade Union Confederation (ETUC) and the desirability of its application at the level of the European Union is currently being investigated.

However, when used in a product a nanomaterial isn't necessarily an "unchangeable" particle. In many products the nanomaterial will react with or bind to the product matrix. Examples hereof are nano-silica in scratch resistant lacquers, chemically bonded nano-silver in high quality textiles or a nanomaterial used for electroplating. In other products, the nanomaterial remains more loosely embedded in the product matrix, like nano-titanium dioxide in self-cleaning coatings. The fate of a nanomaterial in a product influences its adverse health effects and the probability of exposure. It is therefore important to realize that its toxicity may change during its various life stages: from potentially hazardous as raw material to a non-toxic consumer product during use to hazardous waste again in the final phase or when spilled in the environment. Central in the health and safety debate on nanomaterials is therefore the question of fate:

What happens to the nanomaterial once it is applied and what happens to its nano-specific character?

6.1.4 Registration of exposure

Given the many uncertainties related to adverse effects of nanomaterials, registration of workers that are working, or did work with nanomaterials is advisable when following a precautionary approach. It is suggested that the exposure register should record who (i.e. which employees) (might) have been exposed to what (i.e. what nanoparticles), as well as when (i.e. during what period of time) and where (i.e. under what circumstances) this exposure has taken place. The system of registration for nanoparticles can be designed in line with the current practice for asbestiform substances and for carcinogenic, and mutagenic substances. For nanoparticles that are soluble or bio-degradable, for which lower hazards are expected as for insoluble or poorly soluble nanoparticles a smoother system of registration could be selected, for example a system comparable to the registration for reproduction-toxic substances. This type of registration may fit in well with the business practices of small companies.

With this record it is possible to trace back those possibly exposed and estimate the extent of their exposure in case in the future a particular nano-material will be proven hazardous, or when a certain health effect is experienced. However, this knowledge will only arrive when the damage is done. A more direct way of monitoring the health status of those workers involved is to conduct a preventive medical screening. Testing the lung function for example is a method to detect early lung damage (even though this damage is then done and might not be reversible). Performing a white blood cell count does furthermore give you more general information on inflammation reactions occurring somewhere in the body. A sudden rise of the level of white blood cells is a clear indication of a sudden increase of inflammation. Even though then it is not directly clear what did cause this effect, one might be in time to allocate most probable sources and take measures if needed. A first study trying to correlate working with nanomaterials to actual health effects was published in 2009 by Song et al (2009), who tried to relate what they call "mysterious" health effects of seven workers in the printing industry to their possible exposure to nanoparticles. This study doesn't directly apply to the furniture industry and because of the many knowledge gaps existing today conclusions of this study are controversial, but this study does indicate the value of detailed exposure monitoring and record tracking if unexpected health hazards do appear in a particular group of workers.

6.1.5 Notification for nano-products

Information is the very first and important requirement for being able as a worker or employer to start the organizing of a precautionary work place. The issue of traceability, regulation and notification of nanomaterials in furniture have been discussed previously in sections 3.1 and 3.2.

6.2 Assessing workplace exposure

To analyse the potential risk of worker exposure to nanoparticles it is important to assess the possible hazards of the nanomaterials involved and the exposure severity (i.e. dose, frequency). This can be done quantitatively by actually measuring the exposure of the worker(s). It can also be done qualitatively by using so-called control banding.Assessing the risks of possible workplace exposure to chemical substances shall be in line with Article 4 of the European Chemical Agents Directive (98/24/EC)

6.2.1 Measurement techniques

Measuring worker exposures to nanoparticles can be a difficult and time consuming activity. This, because typical workplace air contains large numbers of "background" nanoparticles (from i.e. natural origin, wear processes, traffic exhaust) and process generated nanoparticles (i.e. sanding dust, spraying aerosols, engine generated nanoparticles).Nanomaterial specific measurement devices that are dedicated (yield material specific information like chemical structure, shape and size), sensitive and portable are under development. An overview on exposure assessment methodologies is provided by SCENIHR (2006)[65].

However, if nanomaterial exposure in the case of furniture does mainly involve the handling of dusty nano-products or the generation of airborne nano-particles or aerosols a more "simple" and established Ultra Fine Particle (UFP) measurement device might be appropriate to use in order to derive the level of nanomaterial exposure from the information of the product composition. A CPC (Condensation Particle Counter that counts the number of UFP per volume of air) or a Dust Track device that measures the total mass of particles per volume or air (depending on the filter chosen in the range of PM10, PM2.5, PM0.1) are two examples of such instruments. Another is the recently developed portable NanoTracer by Phillips Aerosense, a device that measures real-time air born particle number concentrations of nano-particles in the size range of 10-300nm. This instrument was used to quantify the exposure to nanomaterials at the furniture workplace. Market introduction of this equipment is expected soon. The NanoID NPS 500 and the MiniDiSC are two other small and portable devices that measure amount of particles and particle size.

Information on the chemical composition and structure of the nanoparticles detected in the air can be obtained by various chemical analysis techniques. Most often used are SEM (Scanning Electron Microscopy) or TEM (Transmission Electron Microscopy) that both provide insight on the structural outline of the nanomaterial or the nanoparticles collected. These are off-line techniques that require samples of air are taken during the work activity with the particular nanomaterial of interest. Sampling can be done by using a little filter to collect nanoparticles from the air (i.e. gold, carbon). These techniques are often complemented by a third technique EDX (Energy Difraction X-ray) that provides information on the chemical composition of the nanoparticles collected on the filter. In the exposure cases studied here, SEM/EDX was used to analyse the structure and chemical composition of the nanoparticles detected by in the NanoTracer. SEM/EDX apparatus and expertise was provided by the

[65] ; referring to SCENIHR (2006) The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies,

University of Utrecht (NL), Department of Electron Microscopy and analysis was performed under the assistance of JA Post and JW Geus.

Alternatively, or in preparation of workplace measurements, control banding can be used to assess the probability that one is dealing with a risky work activity, or to prioritize which work activities to monitor first.

6.2.2 Control Banding

One other way of dealing with uncertain hazards in a given work setting and for a specific activity, and estimating the potential risks at hand in a pragmatic and precautionary way, is to use a so-called control banding tool (CB). The use of CB's has been widely promoted by organizations like NIOSH (USA), HSE (UK), BAuA (GE), GTZ (GE), ILO (Int.) and the WHO (Int.). This resulted in a number of different CB-tools and a world-wide use by small and medium enterprises (see Tischer et al. 2009 and references therein). CB assigns an advice to take generalized protective measures based on the relating material hazards, the dustiness and nano-characteristics like size, shape and surface reactivity of the nano-materials and the amount of the material that is used. An example of such a CB method was developed by Paik et al. (2008) is shown in figure below.

In the CB-tool shown in the figure, the severity of the potential hazards involved are estimated based on factors like particle size, shape and solubility, CMR characteristics of the parent nano-material, the toxicity and the dermal toxicity that are all rated (between 0-10 points) according to their severity of the hazard involved. "Unknown" information is treated according to a worst-case approach of "very high severity" for the factor it involves. The probability of exposure is rated (between 0-30 points) according to the number of employees exposed, the exposure duration, its frequency and intensity (amount of material) and the dustiness of the material. Depending on the sum of the total number of scored points, a nano-material is assigned a risk level (RL) and the appropriate risk management measures can be taken. Hereby, it should be made clear that in all cases, except for the RL1 scenario, the first step should be to try and reduce the RL by a source reduction approach.

		Probability			
		Extremely Unlikely (0-25)	Less Likely (26-50)	Likely (51-75)	Probable (76-100)
Severity	Very High (76-100)	RL 3	RL 3	RL 4	RL 4
	High (51-75)	RL 2	RL 2	RL 3	RL 4
	Medium (26-50)	RL 1	RL 1	RL 2	RL 3
	Low (0-25)	RL 1	RL 1	RL 1	RL 2

Control bands:

RL 1: General Ventilation

RL 2: Fume hoods or local exhaust ventilation

RL 3: Containment

RL 4: Seek specialist advice

Figure 1 **An example of a Risk Level matrix of one CB-method as a function of the severity of the possible adverse effects on human health and the probability of exposure to occur**

Evaluation of the predictive strength and safety level of such a CB by Tischer et al. (2009) indicates that at least for conventional chemicals for which OELs (occupational exposure limits) have been established it seems that exposure control measures and actually measured exposures remain below the established OELs. Although this particular evaluation doesn't prove safety for designing the work with nano-materials, the CB Nanotool by Paik et al (2008) has been shown to produce recommendations for control measures that appeared to be consistent with (or even more requiring than) a number of "*good working practices*" with nano-materials, suggesting its usability.

However, most CB-tools require detailed information on the nanomaterial, information that is normally missing in a company that has to rely on the Safety Data Sheet of the material or product only. In 2011, The Dutch Social Partners therefore developed the *Guidance Working Safely with Nanomaterials and Nano-products*. Through control banding, this guidance allows the making of a risk assessment for working with nanomaterials using only the information as it should appear on the SDS. Simplifying the process of control banding strongly increases its practical value at the workplace. In the autumn of 2012, an update of the Guidance is expected, integrating a quantitative evaluation of the workplace exposure using the preliminary nano reference values (NL) in the CB risk assessment. By doing so, the final part of the Guidance, making a plan of action for reducing exposure, becomes more concrete suggesting not only possible exposure control measures but also providing a method to evaluate the effectiveness of the control measures taken.

6.3 Examples of working with nanomaterials in furniture: 4 Cases

In case of high and medium risk activities (see section 5.2) with nanomaterials or nanomaterial-containing materials, it is advisable to monitor the actual nanoparticle exposure of the worker(s) involved.The aim of this monitoring should be to check an make sure that the exposure control measures implemented are in fact effectively preventing the exposure of the workers to nanomaterials

Below, the main findings of the workplace exposure measurements conducted in the context of the present study are described. Workplace measurements were conducted using two time-resolved nanoparticle counters (NanoTracer, Philips Aerasense) that measured the amount of nanoparticles present in the air and their average particle diameter. The composition of the nanoparticles present in the air was analyzed using a Scanning Electron Microscope combined with Energy Dispersive X-ray spectroscopy (SEM/EDX[66]). Different analyzing techniques are available on the market for assessing workplace exposure to nanomaterials. For a thorough assessment it is important at least:

1. to quantify the exposure in amount of nanoparticles resulting from the work activity
2. to determine the chemical composition of these nanoparticles

The following cases are based upon short term observations. They only serve as inspiration for designing the preventive measures to be taken at the specific workplace.

6.3.1 Spaying of paints, lacquers or adhesives

When a nano-product is sprayed the inhalation of aerosols is potentially the most important exposure risk and for that reason spraying and working with dusty materials should be avoided when possible. Risks of exposure are smaller when using a brush or roller than when using a

Figure 1 High pressure spraying in the spray cabin. The air flow of the ventilation system is represented by the arrow: green indicates low number of nanoparticles, red indicates high number of nanoparticles.

[66] SEM/EDX Analyses were performed at the University of Utrecht (NL), Department of Electron Microscopy, under the assistance of JA Post and JW Geus.

spray-pistol. Occupational exposures are also smaller when a spraying process is performed automatically in a closed environment by a robot arm than when the spraying is done manually.

Observation case 1: High pressure spraying of a MNM-containing lacquer on wood panels was done in a spray-cabin shown in fig.1. No (nano) special measures were taken to prevent exposure to MNM, except from the normal measures to prevent exposure to the solvent-based lacquer. A large MNM-exposure gradient was observed, indicated by the arrow in Fig. 1. At the worker, MNM particles' number concentration was very low. Near the vacuum wall, concentrations measured were much higher. This observation suggests that a well designed ventilation system is effective for removing MNMs from the breathing zone of the worker. No health based nano-OEL is established for this MNM to assess the workers' exposure. Comparing this work activity with the NRV as an example of good practice, no further exposure control measures would have been strictly required. Nevertheless it is advised to wear the proper personal protection. Uncertainty still exists regarding long term adverse effects of incidental peak exposures or low doses that motivate avoiding MNM exposure whenever possible.

When there is a risk of exposure to MNM-aerosols or dust, it is important to equip the ventilation system with a HEPA filter, wear a respiratory mask designed with FFP3 filter, and glasses, nitrile gloves (preferably two pairs[67]) and a Tyvek© (or similar non woven) suit for skin protection.

Observation case 2: Low pressure spraying of a MNM-coating was done with a manual pump-spray. The activity is shown in Fig.2. The spray was used to wet a wiping cloth with which the surface of a cushion was treated. The room was not ventilated. Spraying was applied at "hip-height". No MNM exposure was detected. The present case suggests that careful low pressure pump-spraying may result in a low, non-detectable exposure, and that consequently, no additional exposure control measures are required to prevent MNM-inhalation. Skin protection should be applied.

Among other factors, exposure to MNMs depends on the actual organization of the work during the activity with MNMs and the intensity and duration of the work. It is advised always to evaluate the effectiveness of the exposure control measures, preferably by quantitative and qualitative analysis.

6.3.2 Sanding and polishing of paints and lacquers

During sanding, nanoparticles are being produced as a fraction of the total sanding dust produced. Nanoparticles are additionally formed by the engine of the sanding machine. Available data show that low energy sanding

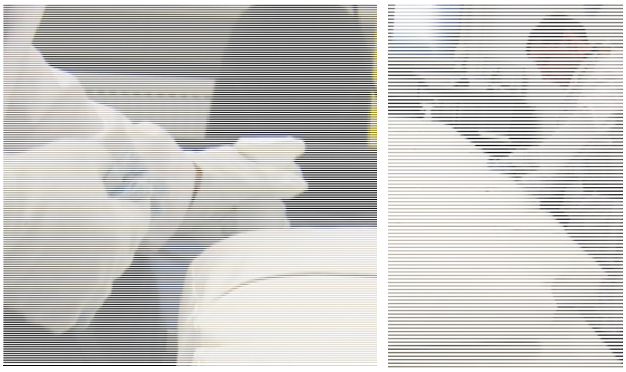

Figure 2 Coating of a dentist chair cushion using a pump-spray and a soft wiping cloth

[67] The reason to advice to wear two pairs of gloves originates from the still unsettled discussion on the actual effectiveness of nitril gloves to protect against nanomaterials exposure. Care should be taken while removing the gloves as electrostatic charge may build-up causing skin-burns when removed too quickly. Because of the remaining discussion, it is advisable to consult always the most recent insights on personal protective equipment and ask the supplier about this.

produces little nanoparticles (Vorbau *et al*, 2009[68]). High energy sanding produces more nanoparticles (Koponen *et al*, 2010[69]). Available data do also suggest a similar emission of nanoparticles from coatings containing and coatings not containing nanomaterial additives (Vorbau et al. 2009; Kaegi et al. 2008[70]), and suggest that nanomaterials are not emitted as such but remain part of the material-matrix. Work by Saber et al. (2011) furthermore suggests that sanding dust from nanomaterial containing paints may be similarly toxic as the sanding dust of the same non-nano paint. Given the current knowledge, no *additional* risk of exposure to the nanoparticles caused by fracturing/abrasion of surfaces treated with nanocoatings may therefore be assumed. However, depending on the matrix and the time that the inhaled ultra fine particles remain in the lungs, the possibility remains that the matrix will dissolve in the lung fluid exposing the nanomaterials that were embedded in this matrix.

When one deals with a solid (non dusty) nano-product, the probability of exposure to the nanomaterial ingredient depends on its interaction with the matrix it is contained in (or at). When the MNM is inert but able to physically interact, this results in a matrix in which the nano-material is embedded but not chemically bonded to the matrix. In this way the MNM remains “loose” and could principally leach out, increasing the risk of exposure upon touch. One could also envisage the MNM to be chemically bound to the surface and reactive, for example a bactericidal surface. Also in this case exposure to the MNM could lead to adverse effects. Only when the MNM is embedded and fixed inside the matrix, exposure is probably unlikely.

Observation case 3: Sanding of wood panels treated with high scratch resistant lacquer.

The sanding of wood panels of observation case 3 took place at a non ventilated work bench. The sanding machine was equipped with local exhaust ventilation. MNM exposure was observed during dry sanding and during polishing. When these activities stopped exposure was quickly reduced. During wet-sanding activities no MNM-exposure could be measured. The present measurement suggests that dry sanding and polishing lead to MNM-exposure that may be higher than advised by the Dutch NRV scheme, especially when sanding takes a full working day. In this case, working in a non-ventilated environment isn’t effective enough to control exposure and further exposure control measures should be installed. Examples of a vacuum ventilated work-table or wall and personal protection measures are shown in fig. 3.

Figure 3. Two examples of exposure control measures to prevent exposure to MNM while sanding or polishing MNM containing materials. Left: a vacuum exhaust ventilation workbench; right: personal protection using nitrile gloves, a Tyvek suit and respirator mask with FFP3 filter.

Also when the work is completed it remains important to avoid skin contact to MNM powders, dust or liquids. For example, when MNM containing dust is still contaminating the sanded panel. Never use pressurized air to clear this dust. When cleaning the workplace, an industrial vacuum cleaner with HEPA filter and wet wiping tissues should be used to prevent nanoparticles from spreading. The use

68 Vorbau M, Hillemann L and Stinz M (2009) Method for the characterisation of abrasion induced nanoparticle release into air from surface coatings. *AerosolScience* 40:209-217

69 Koponen IK, Jensen KA, Schneider T 2009. Sanding dust from nano-particle containing paints: Physical characterisation, *Journal of Physics Conference Series*, 151, 012048

70 Kaegi R, Ulrich A, Sinnet B, Vonbank R, Wichser A, Zuleeg S, Simmler H, Brunner S, Vonmont H, Burkhardt M, and Boller M, 2008. Synthetic TiO_2 nanoparticle emission from exterior facades into the aquatic environment, Environ. Pollut. (2008), doi:10.1016/j.envpol.2008.08.004

of a broom, brush or household vacuum cleaner should be avoided. Spills, empty packaging, or leftovers should be labelled and removed as toxic chemical waste.

6.3.3 Cutting textile

Observation case 4: A nylon textile treated with a water-repellent coating is cut with normal scissors. No nanoparticle exposure could be detected. Special care should be taken to avoid possible exposure to nano-fibers. Even though no exposure to fibers containing MNM was detected, it is advisable to work in front of a vacuum wall or on a vacuum ventilated table when there is a risk of exposure to fibers containing MNMs.

Actual exposures do vary strongly depending on factors like the specific product, the exact environmental conditions and the concrete work situation of the worker(s) involved.

The four examples for the activities in the furniture industry presented here should not be generalized. For each new individual case a risk assessment shall be undertaken to judge the effectiveness of the exposure control measures in place and which preventive measures to install in order to protect the health of the workers. The four observation cases however do suggest that the current exposure control measures prescribed for the furniture industry may be effective to protect workers also against exposure to MNM in the products they work with.

7 Concluding remarks

In depth study of the European furniture industry and interviews with furniture companies and material suppliers shows that the market for nanomaterial use in furniture products in 2012 is still in an early phase of development. Nanotechnology may have huge implications for the future of furniture manufacturing; on furniture quality and functionalities but also on environmental, occupational and public health performances related to the manufacturing and end-products. Bactericidal, water-repellent, high scratch resistant and UV protective coatings are examples hereof. Despite the many potentials for furniture innovation, major barriers are encountered with respect to costs, (long term) quality performance, uncertain health and safety issues and consumer acceptance. However, a number of market applications of nanomaterials were also observed. Examples thereof are liquid-glass based coatings to obtain high scratch resistance, water-repellence, anti-microbial or easy-to-clean effects, UV protective coatings, bactericidal and easy-to-clean textile and ultra high performance concrete.

The study of the European furniture industry furthermore shows a high level of ignorance. Furniture manufacturers are typically not well informed about the nanomaterials they may use and the information that is communicated is often difficult to interpret. This situation deserves serious attention. It is necessary for furniture manufacturers to ask their suppliers whether or not their materials contain nanomaterials and get informed on how to apply them responsibly.

Nanomaterials can be more toxic than their micron-sized equivalents and may show unexpected adverse health effects due to their nano-specific character, including cardiovascular diseases, inflammation of the lungs, effects on the central nerve system, cell death, scar-tissue forming (for example in the lungs), malfunctions in embryos and the development of cancer cells in affected tissue. At the same time, furniture manufacturers have to organize a precautionary safe workplace when they work with nanomaterials. There are various tools available to support employers and workers in making a risk assessment, including a plan for action for working safely with nanomaterials.

Risks of exposure can typically be expected when nanomaterial-containing dust or aerosols are produced. The spraying of paints or adhesives, sanding of coated surfaces and polishing or sawing solid materials are examples of work activities where this could happen. Various exposure control measures available, like specific ventilation systems and personal protection equipment, have shown to be effective also for preventing exposure to nanomaterials. The automation of production processes, using robotic arms in a closed system, is another method to avoid exposure of workers. Preliminary findings furthermore hint that nanomaterials embedded in dust may no longer exhibit their nano-specific toxicity. Low risk of exposure to nanomaterials is expected when workers touch these materials embedded and fixed in a matrix.

When exploring the potentials of MNMs, the furniture manufacturers shall set up precautionary preventive measures protecting the health of the workers – based on information delivered by the supplier of the MNMs, a risk assessment and the general principles for prevention associated with the actual chemical substances.

Annex 1 Exposure cases in the furniture industry

[i] CA Clausen, The International Working Group on Wood Protection (2007) Nanotechnology: Implications for the Wood Preservation Industry, IRG/WP 07-30415