

Nano-products in the European Construction Industry

State of the Art 2009 Executive Summary

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Executive Summary
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Summary

This report contains a study on the availability, use and health and safety issues of nano-products in the European construction industry anno 2009. A European survey among employers, workers and worker representatives from the construction sector, in-depth interviews with a number of involved key stakeholders and an extensive literature study led to the insights presented.

The awareness of the different actors in the construction industry about the availability and performance of nano-materials is very limited. This holds for the construction employers and employees as well as for the related professions like architects, construction engineers and customers of the constructions.

Only a limited amount of nano-products make it to the construction site of today, because of this lack of awareness and the fact that nano-sized ingredients are often too expensive to result in competitive products. Main product types identified at the market are nanoparticle improved concrete and cement materials, nano-coatings and insulation material. Though, intensive research and development is ongoing and future expectations are that the market share of nano-products and their diversity will grow because of the unique characteristics they do (and are envisaged to) exhibit.

However, these same products might pose new health and safety risks to the worker on-site, which science are only just starting to understand. Especially when the work involves the generation of nanoparticles or aerosols. Typical activities with possible high risks of exposure to nanoparticles are the application of wet or dusty nano-products, machining dried or prefab nano-products and cleaning or maintaining of materials and the equipment used. Detailed information about the product composition and their possible nano-specific health and safety issues though, is generally lacking and the information available to the raw material manufacturer is seen to get lost while stepping down the user chain.

As a consequence, for the average construction company it will be very difficult to conduct a proper risk assessment and organize a safe workplace for its employees. A possibility of dealing with the unknowns themselves is to follow a precautionary approach. However, the development of a select number of tools to support construction companies in bringing this approach into operation (such as a registration and notification system, nano-reference-values or good practices for a select number of high risk work activities) is advisable to support bridging the knowledge gap.

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1. Introduction

Within the European Social Dialogue, FIEC (European Construction Industry Federation) and the EFBWW (European Federation of Building and Wood Workers) 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 construction market. This executive summary summarizes the results of an extensive study of the state-of-the-art 2009 with respect to the availability, use and health and safety aspects of nano-products in the European construction sector. The main report "Nanotechnology in the European Construction Industry, state-of-the-art 2009" describes the findings of this study in detail.

Due to a constant market push towards more durable, more sustainable and more cheap products, products for the construction industry are opt for continuous research and development. One of the most recent technological developments to apply in this R&D is nanotechnology. Nanotechnology simply means the ability to observe, monitor and influence materials (and their behavior) down to the nanometer (nm) detail (e.g. a size range about 10.000x smaller than the thickness of a human hair). This involves advanced imaging techniques to study and improve material behavior, but also the design and production of very fine powders, liquids or solids containing particles of a size between 1 and 100nm, so called nanoparticles. Companies make use of these nanoparticles to give their products new or improved properties. Examples of these are transparent infrared reflective window coatings to support a better indoor climate management, ultra strong concrete material to allow for more thin and more light constructs and self-cleaning coatings that do also support the reduction of organic air pollution.

Though the internet houses a lot of information on nanotechnology in construction and future expectations are high, reality today is that only a limited amount of nano-products make it to the construction site simply because the techniques and nano-ingredients are too expensive to produce products that can compete with those yet existing. According to some large players in the field: *"in this respect construction industry falls about 10 years behind industry at large, because of the costs involved and because of the technical and safety standards required for the materials used"*.

Despite this, it is of importance to note their growing abundance. Nano-construction products are unique in their characteristics but they might pose new health and safety risks to the worker on-site as well. Due to the novelty of nano-materials and products in general, these health and safety risks are only starting to be understood¹. This and the high expectations concerning the near future market potential of nano-products² add up to the importance to follow the developments in the field of nanotechnology from the start and to be aware of existing uncertainties with respect to health and safety issues of nano-materials

¹ There are various open questions related to the health hazards and exposure kinetics of nano-materials and products. On the other hand, there is a lot of existing knowledge and experience in the field of occupational health and safety assessment and the management of exposure risks. Using what we do know to deal with what we don't know is the challenge faced when working with nano-products.

² see for example www.hessen-nanotech.de

and products in order to take appropriate measures when this is judged necessary. This report attempts to provide some more insight into the nano-products used in construction today and their characteristics as to facilitate a better informed risk assessment.

When speaking about nano-materials and nano-products, it is important to realize that no agreed-on definitions do yet exist and as a consequence any misunderstanding does easily arise. The present report considers:

1. a nano-material to be a particulate material containing nanoparticles or agglomerates or aggregates thereof in solid form or dispersed in a liquid, or internal or external nanostructures or nanosized domains.
2. a nano-product to be any product where one deliberately puts in a nano-material to influence the properties of the product.

Nanoparticles are defined as “engineered” particles (man-made to distinguish them from “natural” nano-sized particles that are formed during i.e. volcano eruptions) at the size of 1-100nm. These can be soluble or non-soluble. At the moment, only non-soluble particles are addressed by the term nanoparticles because the non-soluble persistent ones are those that are of key interest with respect to potential nano-typical health effects. However, discussion is currently developing around the issue of possible nano-typical health effects by soluble nano-sized particles also because of their nano-typical fate in the environment.

2. Nanotechnology in the Construction Sector

To obtain a comprehensive overview of the current availability and use of nano-materials and nano-products at the construction site, to provide some insight into ongoing developments that might lead to near future use of nano-products and to signal, and put into perspective, occupational health and safety issues arising from the nano-product used, three routes were followed:

1. An extensive (scientific) literature and web-search provided the basis for the insight in the nano-materials and nano-products used in the construction sector and the occupational health issues that might play a role in their application.
2. The FIEC and the EFBWW set out a survey among their members in 24 European countries to probe the general awareness of employers (representatives) and employees on applications of nano-products in the sector (hereafter called the 2009-survey). The 2009-survey was aimed to get a first impression of experiences in the field, reasons for changing to a nano-product and health and safety issues communicated by the supplier of the products. By no means was it intended to obtain extensive insight into the details of the current use and working practices with nano-products in the construction industry, as this would require a much more elaborate approach.
3. In-depth interviews with construction workers en employers, architects, product manufacturers and R&D scientists for construction materials and products were organized to obtain more in-depth insight in ongoing activities in the field of nano-products for the construction industry. The results of these interviews were important to place the results from the 2009-survey and the literature and web-searches into perspective and to highlight those nano-developments that can currently be assigned as most significant for the construction sector.

Table 0-1 Overview of the typical background (function profile) of the respondents to the 2009-survey and an overview of the different types of organizations approached for the in-depth interviews

Respondents ³	Function	In-depth interviews (%)	Type of organization
6	Employer	21	Construction Industry
4	Painter (worker, worker representative)	21	(raw) Product Manufacturers
4	Safety Adviser (worker, worker representative)	9	Branch Organizations
3	Various (worker, worker representative)	4	Architects
11	Not specified (worker, worker representative)	42	University R&D
38 ⁴	Occupational health and safety advisors / Occupational hygienists (NL only)		

³ In total 28 responses were received from 14 different European countries, plus 38 occupational health experts from the Netherlands that are dealt with separately.

⁴ The pool of responses from Dutch occupational hygienists and health and safety advisors (38 respondents in total) was unique within the 2009-survey. Therefore, these were separately assessed. The results obtained from this assessment were fully in line with the results of the other responses.

The resulting information is presented in the sections below. Table 0-1 shows an overview of the function profile of those who responded to the 2009-survey and the type of organizations approached to conduct the in-depth interviews.

2.1 Factors Influencing Use of Nano-products in Construction

In 2003, R&D specialists shared high expectations about the near future developments of nano-products for the construction industry. However, only little of the products expected that time really made it to the construction site of today ⁵. Various reasons can be appointed. The most important ones will be discussed in the sections below.

Price competition

The very first reason why nano-products may be successful in society but still do not make it in the construction industry is the costs involved. At the moment, nano-materials and consequently nano-products are still significantly more expensive than their non-nano alternatives because of the technology required to produce them. For the construction sector, this implies that already at the R&D phase of a product, initiatives are stopped when it is foreseen that the nano-product to be produced will never reach competitive pricing. Largely this is due to the fact that construction products almost always come in large volumes and small price differences at the kg level add up to enormous increase in total costs when the total volume of the construct is considered.

As a result, manufacturers of construction materials are reluctant to develop nano-products and those nano-products that are developed are only applied upon specific request. This in particular holds for the larger volume products like concrete or mortar and for construction coatings. However, for e.g. insulation materials and architectural and glass coatings, the current societal focus on the improvement of energy management in the context of climate change and the reduction of greenhouse gasses does stimulate their further market introduction.

Technical performance

The technical performance of the product is a second limiting factor for large scale nano-product introduction. The technical performance should thoroughly be proven to meet the technical standards for that material. Obviously, this does depend on the market sector. For concrete for example this is a major issue. For self cleaning window coatings, this issue is much less important as the safety standards for instance are much lower.

Awareness within the sector

Awareness (or the lack thereof) is another key element hampering the introduction of nano-products in construction works. Without awareness one simply doesn't know there is anything new to apply or explore. Within Europe, knowledge about nanotechnology in construction is very limited and at this moment is still the property of a small number of key players that develop the market. The 2009-survey set out by the FIEC and EFBWW to monitor the awareness of construction workers and their employers resulted in Figure 0-1, showing that the majority of respondents (~75%) was not aware if they do work with nano-products. This result is based on 28 returned questionnaires, where it was aimed at 3 returns

⁵ Bartos PJM 2009, Nanotechnology in Construction 3, Proceedings of the NICOM3. ISBN 978-3-642-00980-8

by each FIEC or EFBWW member from each of the 24 EU countries approached (a total target of 144 returns)⁶.

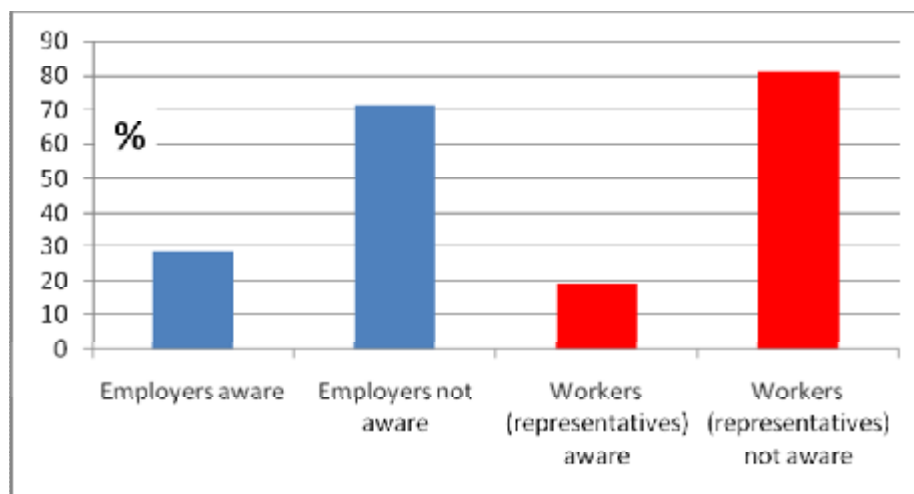


Figure 0-1 2009-survey response of employers and worker (representatives) being aware or not aware of the presence of nano-products at their workplace.

The results of the survey though should only be interpreted to give some indication about the present state of knowledge in the sector with respect to the use of nano-products in the construction industry. In fact, the 25% of respondents being aware likely overestimate the true figures due to positive selection: those that are aware of working with nano-products are more eager to respond. This is extracted from various comments received from construction worker representatives and employers in reaction to the 2009-survey stating i.e.:

- *"...I have spoken to a number of companies regarding this subject and no one is aware of any materials containing these products. I have also spoken to a number of people from the Health and Safety Executive and they are also not aware of the existence of these products... (UK)"*
- *"...we tried to get information from several construction-subsectors, but until today we didn't receive useful indications. The problem (and we are not very surprised) is still unknown (CH)"*
- *"...the subject is simply too abstract and too unfamiliar to respond to the survey at all (NL)"*

These, together with findings from in-depth interviews conducted in parallel to the 2009-survey with a number of involved key players (i.e. BASF, Heidelberg Cement, Skanska) do suggest that nanotechnology did not yet penetrate the construction sector to any significant depth. A series of contacts with different SME's do support this picture of nanotechnology being only a niche market in the construction industry of today. However, opposite signals are also found in a company advising on health and safety in the plumber and electricity industry in Denmark, indicating that they *"...have no information on any nano-product used in these sectors but they are very certain that some of the products they encounter are in fact nano-products"*.

Those respondents to the 2009-survey working with nano-products mostly worked with cement or concrete products, coatings or insulation materials (see Figure 0-2). Other product

⁶ Response to the questionnaire was obtained from 14 different countries with a typical count of 1 or 2 responses per country, except for the Netherlands. The much higher Dutch response is due to a parallel (national) project, dealing with nano-products in the construction industry and related occupational exposure.

types, including road-pavement products, flame retardant materials or textiles, were only indicated by some. All respondents used their nano-products because of performance reasons (excluding an alternative product) and sometimes on (additional) specific request by the customer.

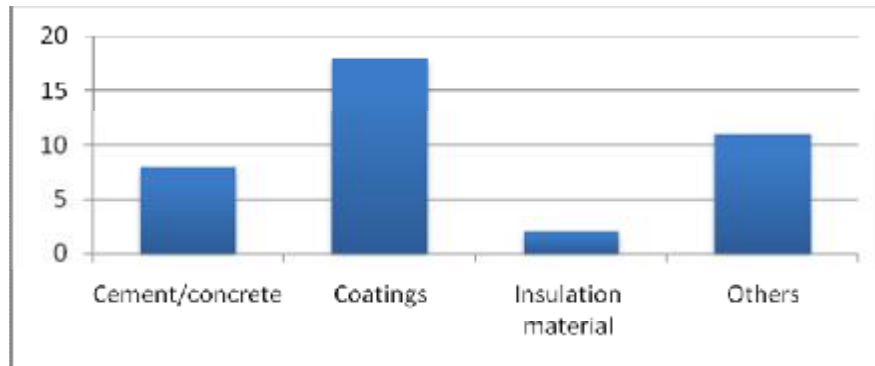


Figure 0-2 Nano-products actually indicated to be used; number of products per product type, from the results of the 2009-survey

Interestingly though is the fact that some of the respondents answering “*No, I’m not aware I work with nano-products*” do indicate they might possibly work with some types of nano-products when they are confronted with a specific list of product types (~18% of all respondents: workers, worker representatives and employers). The product types typically identified by these respondents do overlap with those products mentioned by name by the respondents that are aware of working with nano-products (~21% of all respondents: workers, worker representatives and employers). This does show a more general lack of knowledge about the nature of the products worked with, but could also be interpreted to reflect those product groups where the respondents could expect nano-products first to appear. Alternatively though, the response could be guided by marketing influences associating a superior technical product performance to the prefix *nano-*, suggesting all ‘new’, ‘unique’, or ‘extra strong’ products are suspected nano-products.

Advantages of nanotechnology for the sector

The use of nanotechnology for improved material study and development requires a strong R&D department with the possibility to use expensive equipment worked on by skilled people. However, since the construction industry never has been strongly R&D oriented, R&D activities with respect to nano mainly take place at large multi-national producers like BASF, AKZO-NOBEL, DuPont, Heidelberg and ItalCementi or at specialized Research Institutes (either university based or private). This indirectly implies that SME’s play little to no role in the present pioneering nano activities within the construction sector. Exceptions are SME spin-offs that do have a contract that allows them to use the research facilities of their more large “mother” company, SMEs that were set-up as University spin-offs (and can make use of the university based facilities) focused on specific nano-niche markets like for example the production and design-on-demand of specific nano-materials, and a small amount of SMEs that succeeded in using the successes and break troughs of the more large companies to innovatively develop their own product lines.

At present though, this situation is changing in the coating sector. Nano-coatings are typically ‘far’ in their development with respect to other construction products like concrete

or insulation materials and methods to apply nano-materials are becoming more and more 'common knowledge' among product manufacturers. It is therefore that in the field of paint and coatings SME's are starting to play a role too and fabricate their own nano-product line.

Communicating *nano* along the user chain

For the average construction worker, detailed knowledge on the chemical nature of the product he or she works with is not priority number one. The technical and health and safety information is what is needed. This is true for "normal" products and is not any different for nano-products. However, the use of standardized methods to determine occupational health hazards resulting from any exposure to nano-products is topic of this-moments debate and there are a number of open questions related to the applicability of these methods. Consequently, there is a general uncertainty with respect to health and safety risks by nano-products, which should be treated and used with a certain precaution

Nano-materials can be much more reactive (per gram of material) than their non-nano forms and could behave quite differently. They might therefore also induce different health effects that might be more severe. The safety limits set, beyond which registration and communication of health and safety risks are required, are therefore possibly too high to ensure a safe workplace and should be lowered. Within Europe, lobby of the ETUI and ETUC therefore presses to change this situation via an amendment in REACH that will require the obligatory notification of all nano-materials added intentionally to a product.

At present, the situation is such that there are only limited ways to learn about the chemical details of any nano-product. Not many product manufacturers using nano sized ingredients or nano-materials notify their customers about this fact because the Regulation on the Classification, Labeling and Packaging of Substances and Mixtures (CLP)⁷ does not oblige them to. From the 2009-survey, only for 7 of the 41 nano-products indicated to be used, the respondents do indicate they are informed about the product characteristics via a Material Safety Data Sheet (MSDS) and of these, only in 4 cases did the MSDS prescribe protective measures for the nano-product that differed from the measures prescribed for the (non-nano) products used before by the same construction company (see Figure 0-3). The response obtained does suggest that for the majority of the products the health and safety aspects of the product are poorly communicated in the user chain (for 34 of the products there is no MSDS for the product available to the knowledge of the respondent, which can be either a construction worker or an employer). For those products for which an MSDS is supplied it depends on the manufacturer or the supplier whether or not in that MSDS health and safety information is communicated that is specific for the nano-ingredient. For those products indicated by the respondents in the survey-2009, most MSDS show no indication of any nano-ingredient whereas the technical data sheet does some times clearly indicate, sometimes suggest and sometimes seems to suggest (for example from the product name), that the product does in fact contain at least one nano-material. Nano specific information provided on the technical data sheet does vary from quite detailed: an indicated size-range and SEM-image⁸ of the nano-particle or the description of the active surface area of the

⁷ http://ec.europa.eu/environment/chemicals/dansub/home_en.htm ;English version of the regulation Regulation (EC) No 1272/2008: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:353:0001:1355:EN:PDF>

⁸ Scanning Electron Microscopy

nano-material per gram, to a “simple” note that the product does contain for example nano-quartz (without further specification what this quartz looks like).

In all cases in which more information on the nano-product was provided, the product manufacturers do claim their product is non-hazardous when used as is prescribed, and in no cases (nano-) specific skills or training was required in order to use the nano-product correctly. Moreover, for the majority of the nano-products mentioned in the 2009-survey, the prescribed protective measures were described as ‘*no different from before*’ when non-nano products were used and the work practice was indicated not being influenced by their use. Only for two products more protective measures were prescribed in comparison to the non-nano products used for a similar application. For the 2009-survey products this latter applied to two cementageous products containing nano-silica. However, there were also signs that nano-products can make the work easier.

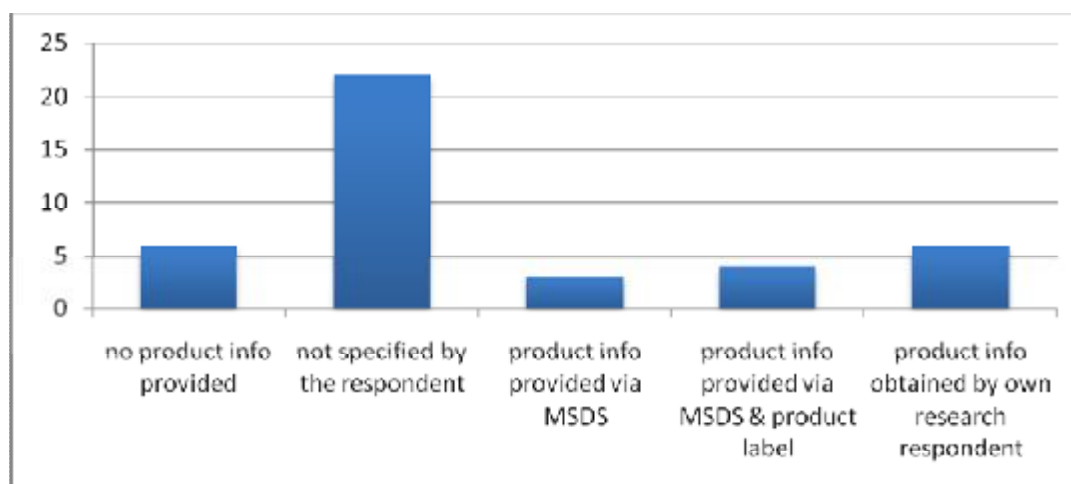


Figure 0-3 Specification of product information for the nano-products indicated to be used in the 2009-survey (given in numbers)

At present the information supply chain is roughly represented as follows (see also Figure 0-4). The “raw material” producers of nano-materials do provide details on the material properties (like reactivity, specific behavioral characteristics, size, shape, crystal structure, mass and density) and specifications on their health and safety and environmental issues (as far as these are known) to the next user down the chain (most often the product manufacturer). Depending on their business relation, these details might be just the minimum legally required or more extensive when there is mutual trust between them. However, at that point of the chain the nano-specific information supply normally stops. The product manufacturers most often only use the nano-material as an additive below the required registration and communication concentration. Only some of these manufacturers do notify their customers anyway. However, sometimes only by using characteristics mentioning “*achieved with nanotechnology*” without going into further detail. For the customer it is then still guessing what is actually in this nano-product.

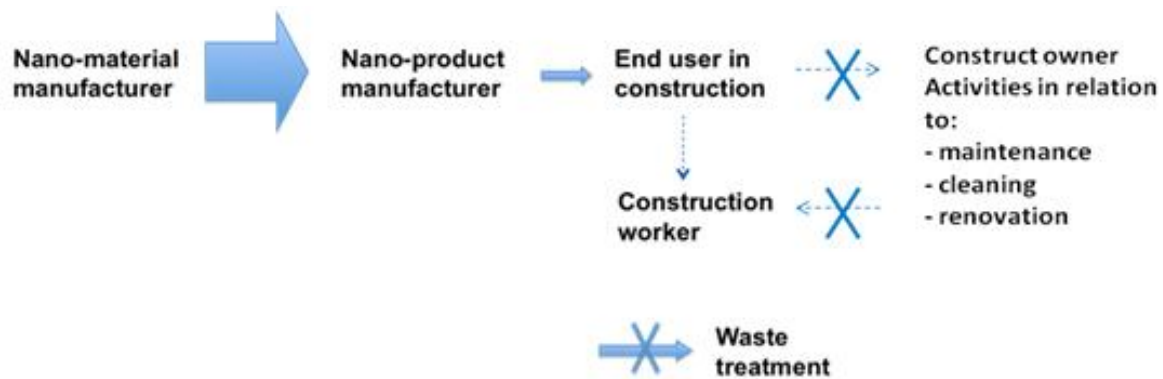


Figure 0-4 Intensity of nano-specific information supply down the user chain from the raw material supplier to those who have to deal with the waste material. The thickness of the arrow represents roughly the amount of nano-specific information supplied to the next user down the chain.

Nano sells

Nanotechnology and the products that this technology brings forward are envisaged to cure many of today's high priority issues like the depletion of mineral resources, environmental pollution, energy consumption and the emission of greenhouse gasses, and even safety issues like terrorist attacks and world peace. These large expectations led to *nano-* being set equal to key words like *success*, *high performance* and *sustainable development*. As a consequence, companies, but also researchers, started to sell their work as *nano-* in order to attract customers or get financed. This trend started roughly about 10 – 15 years ago and even now, as this trend is on its return because of health and safety concerns involved but also because of pressure from branch organizations to prevent confusion around the nano-theme⁹, *nano-* is still used to emphasize a products high technical performance or subtle, clever design.

And not only on products that do contain nano-materials. Also quite standard products containing enzymes (that have typical sizes in the nano-regime) or oily dispersions (containing small oil-droplets of nano-size diameter) have been typed *nano-*. Or products that can be seen as borderline cases, which precursor materials are produced using nano-materials or nano-production processes, but which actual ingredients are no nano-materials anymore. The resulting situation may be a confusing one in which products, manufactured with "nano", but not containing "nano" any more in the end product, are sold as nano-products, while products not manufactured with any "nano" may as well be sold as nano-products.

2.2 Activities to secure occupational safety

Despite the above, more and more, nano-product manufacturers have become aware of the potential and largely unknown health and safety issues involved in the use and handling of nanoparticles. At the construction site, one could deal with exposure to nanoparticles from:

1. primary use of a nano-product: working with a nano-product (a ready-for-use product or multi-component product that is mixed on site)
2. secondary use of a nano-product: machining a nano-product (for example by drilling, sanding or cleaning activities)

⁹ Private Communications with a number of different material producing companies.

Especially when these activities involve the handling of dusty or liquid materials or the generation of dust or aerosols, a careful risk assessment is required. Typical examples: spraying of a nano-coating, adding silica fume to wet mortar, sandblasting a photo active concrete façade, or cleaning an anti-bacterial (silver containing) wall. On the other hand, exposure risks to nanoparticles by handling solid (prefab) nano-products like nano-enhanced ceramics, glass, steel, plastics, composites, insulation materials, concrete or wood without machining these in any way, are expected to be small (if any) because the nanoparticles are expected to remain contained in the solid matrix. Exposure though, could occur in time when the material wears, when the construct gets renovated or when demolition takes place.

In a first attempt to arrange a safe workplace, following a precautionary approach is advised by various types of organizations such as important material manufacturers and the European commission. As a result of the constant emphasis on following a precautionary approach advocated through the different code of conducts and supported by the European Commission and the more large key stakeholder industries like BASF and Dupont, the production of the vast majority of nano-particles and nano-materials takes place in liquid form (suspension or solution), in 'under-pressure' conditions or under sealed conditions as to maximize particle control and minimize exposure risks. Because of these reasons and in contrast to some years ago, nano-sized additives are most often delivered in suspension or solution, ready for use by the product manufacturer. When this is not possible, for example in the case of silica fume for UHPC concrete, and the additives have to remain in powder form, other solutions are invented to prevent exposure such as the use of packaging material (large bags) that dissolve in water and which material does not affect the foreseen product characteristics (concrete).

However, still it is very difficult to determine whether or not a specific working practice and the protective measures taken are sufficient to work safely. Measurement devices to determine actual exposures at the work floor are highly expensive, difficult to operate and provide only limited answers with respect to true exposure levels. According to today's understanding, there are various types of personal protection materials at the market that are equipped to protect against nanoparticle exposure. Information on personal protection materials can be found in a study recently published by the OECD, presenting a comprehensive overview of skin protective equipment and respirators to protect workers against possible exposure to manufactured nano-materials¹⁰

¹⁰ OECD Environment, Health and Safety Publications Series on the Safety of Manufactured Nanomaterials No. 12 (2009) ENV/JM/MONO(2009)17

3. Nano-products at the Construction Site

3.1 Introduction

The total market share of nano-products in the construction industry is small and considered to be applied in niche markets¹¹. This share though, is expected to grow in the near future¹² and nanoparticles are expected to play an important role at the very basis of material design, development and production for the construction industry¹³. Already now nano-products could in principle be found in nearly every part of an average house or building (see Figure 0-5).

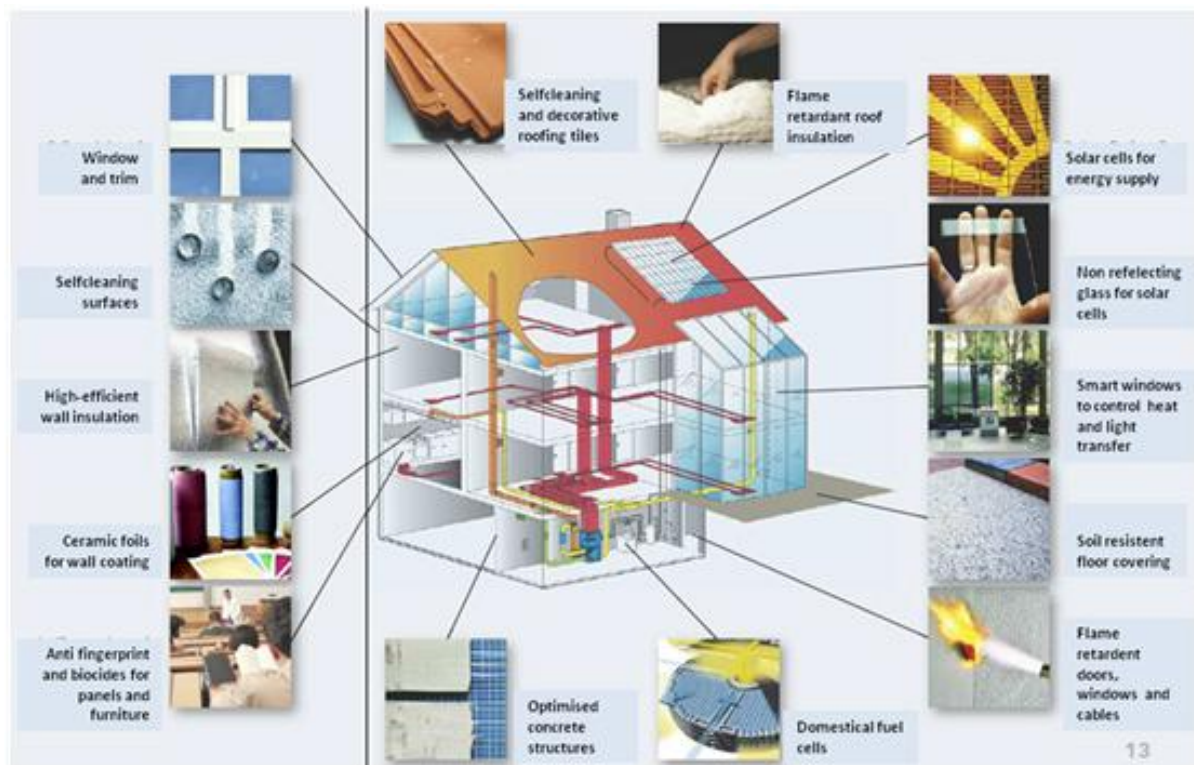


Figure 0-5 Schematic overview of a typical house of today indicating where nano-products could be found¹⁴.

Nano-products indicated in the response to the 2009-survey involved predominantly cement and concrete, coatings and insulation materials. These were found to correspond well to the product types highlighted during the in-depth interviews, sketching that coatings and cement and concrete materials probably make up for the largest market share of nano-products of today's construction industry, followed by insulation materials. This also corresponded well to the findings from an extensive literature search conducted in the

¹¹ Personal communication

¹² From \$20 million (US) in 2007 to ~ \$400 million (US) before the end of 2017; Freedonia Group Inc. *Nanotechnology in Construction* –Pub ID: FG1495107; May 1, 2007

¹³ i.e. Nanotechnology and Construction 2006; www.hessen-nanotech.de

¹⁴ Taken from the brochure "Einsatz von Nanotechnologien in Architektur und Bauwesen" published by HA Hessen Agentur 2007, sources: Schrag GmbH VDI TZ

context of this report. Consequently, cement and concrete, coatings and insulation materials were prioritized to focus on. In this context, the nanoparticles found to be most mentioned are carbon-fluoride (CF-) polymers, titanium dioxide (TiO₂), zinc oxide (ZnO), silica (or silica fume; SiO₂), silver (Ag), and aluminum oxide (Al₂O₃). Interesting to note is also that no evidence was found for the use of carbon nanotubes (CNT) in these products, even though many publications do show evidence of ongoing research and product development in this direction.

Carbon-fluoride polymers (CF-polymers) are Teflon like molecules that are brought onto a surface to make this surface water and oil repellent. Applications are typically found on glass.

Titanium dioxide (TiO₂) absorbs UV light and is used as a protective layer against UV degradation. Some forms of TiO₂ are photo-catalytic and catalyze the degradation of organic pollutants like algae, PAHs, formaldehyde and NO_x under the influence of UV light. Applications are found for practically every surface type that has to be UV-protected, made self cleaning or should assist in the reduction of air pollution.

Zinc oxide (ZnO) knows similar photo-active characteristics to TiO₂ and can be used for similar applications.

Silica fume (amorphous SiO₂) compacts concrete, making it more strong and more durable under alkaline conditions like marine environments. It can also be added to concrete to stabilize fillers like fly-ash, to a coating material resulting in a very strong matrix, or used as fire retardant agent. Typical applications are UHPC (Ultra High Performance Concrete), scratch resistant coatings and fire resistant glass.

Silver (Ag) acts as a bactericide and can be added to all sorts of materials. In construction it is mostly found in coatings. In fact, it is the silver-ion, formed when Ag dissolves in water that is responsible for the anti-bacterial activity.

Aluminum oxide (Al₂O₃) is used in coatings to interact with the binder material and to add high scratch resistance to this coating.

3.2 Cement, concrete and wet mortar

For concrete, the combination of an already existing good performance available at low costs implicates a high challenge for any successful application of nanotechnology¹⁵. One of the area's where nanotechnology does prove extremely valuable now and in the near future is the understanding and optimization of material properties¹⁶.

Nanoparticle use in cementitious and concrete materials does concentrate on TiO₂ and silica fume. Both additives though, are used in small quantities or in a two-layer system and only when specifically required for performance reasons because of the costs involved. Examples of products on a basis of silica fume that are currently at the market are i.e. ChronoliaTM, AgiliaTM and DuctalTM by Lafarge and EMACO®Nanocrete by BASF¹⁷. Examples of photo-catalytic cement are TioCem TX Active (Heidelberg Cement¹⁸), NanoGuardStone-Protect by Nanogate AG¹⁹ and TX Arca and TX Aria (Italcementi), which are produced as binder for a wide scope of coating materials like exterior walls, tunnels, concrete floors,

¹⁵ NICOM3, conference proceedings 2009

¹⁶ Various presentations and private communication with a number of companies and university scientists at the NICOM3, Prague 2009

¹⁷ According to their information, the initial material was in fact a silica fume but agglomerated in the production process to larger particles.

¹⁸ According to their information, the TiO₂ in this product not nano but slightly larger: in the micron-size range

¹⁹ <http://www.nanogate.de/en/>

paving blocks, tiles, roof tiles, road marking paints, concrete panels, plaster and cementitious paints²⁰.



Figure 0-6 Left: "The EMACO® Nanocrete range. Right: The Jubilee Church in Rome, one of the most often quoted successes of photo catalytic concrete by the addition of TiO_2 . Material: TX Active (TX Arca) from the Italcementi group.

No signs were found for the actual use of CNT enforced concrete. Reasons given are the high costs of CNT and the difficulty to disperse them in a matrix. However, studying the possibilities for the application of CNT in concrete is an active field of research.

Because of the strict quality requirements, material developments typically take between 5 and 10 years). Near future developments are expected in the field of silica fume to stabilize concrete containing significant fractions of recycled concrete aggregates¹⁵ and encapsulated additives to optimally tune the hardening process.

3.3 Coatings and paints

Of all nano-products introduced in the construction industry, coatings and paints have up to now been probably most successful in conquering a place at the market: *"Provided that one would find any nano-product at an average construction site at all, the chance of finding nano-paints or coatings is by far the biggest"*^{21, 22}. Decorative coatings are most abundant but also high performance construction coatings like industrial flooring coatings have been found. Nanotechnology finds its way to paints and coatings for the following reasons:

1. nanoparticles do better interact with the underlying surface than their larger forms, by deeper penetration, improved coverage or an increased coating-surface interaction, resulting in a more durable surface coverage.
2. nanoparticles are transparent to visible light.
3. transparency opens the door to novel additives introducing new characteristics to otherwise non-transparent coatings like high scratch or UV resistance, IR absorption or reflection, fire resistance, electric conductivity and anti-bacterial and self-cleaning properties.

These come together in the development of new coating systems for almost every surface thinkable from plastics to steel. Within the product group of nano-coatings, the emphasis is found on anti-bacterial coatings (adding TiO_2 , ZnO or Ag), photo-catalytic "self cleaning" coatings (TiO_2 or ZnO), UV and IR reflecting or absorbing coatings (TiO_2 or ZnO), fire

²⁰ <http://www.italcementigroup.com/ENG/Italcementi+Group/>

²¹ Personal communication

²² <http://www.soci.org/Chemistry-and-Industry/Cnl-Data/2009/16/Nanocoatings-incognito>

retardant coatings (SiO_2) and scratch resistant coatings (SiO_2 or Al_2O_3). These types of functionalities are typically applied on coatings for walls (interior or exterior), wooden facades, glass and different road pavement materials.

Photo catalytic, anti-bacterial and self-cleaning wall paints

The nano wall paints mostly found are marketed for their photo-catalytic, anti-bacterial or self-cleaning properties. Examples of self-cleaning, photo-catalytic coatings are Arctic Snow Professional Interior Paint by Arctic paint LTD (TiO_2), Cloucryl by Alfred Clouth Lack-fabrik GmbH&Co KG²³ (ZnO) and Amphisilan by Caparol²⁴. An example of an anti-bacterial coating based on nano-Ag is Bioni Hygienic by Bioni CS GmbH (see also Figure 0-7)²⁵. An easy-to-clean coating that is both water and oil repellent is Fluowet ETC100 (based on CF-polymers by Clariant).



Figure 0-7 Antimicrobial wall coating containing nano sized silver particles for use in clinics and hospitals

Nanocoatings for Wood Surfaces

Nanocoatings for wood products are developed for walls and facades (exterior), but also for parquet flooring systems and furniture (interior) and do focus on water (and to a lesser extent oil) repulsion, scratch resistance and UV protection. Though there are several products on the market, there is skepticism regarding the durability of especially the water and UV protective coatings because of the quality of some of the first generation products²⁶. As a consequence, the new generation coatings have a hard time proving themselves and examples of true applications at the construction site are scarce.

BYK Additives and Instruments²⁷ is one example of a company advertising new generation UV-protective coatings. These can be based on organic UV absorbers²⁸ or the metal oxides ZnO and CeO_2 . TiO_2 is less used because of transparency and photo-catalytic activity reasons.

Examples of high scratch resistant wood lacquers containing nano- SiO_2 are Bindzil CC30 (Baril Coatings), Nanobyk 3650 (BYK Additives and Instruments) and Pall-X Nano (Pallmann). Nanobyk 3600 (BYK Additives and Instruments) is an example of a high scratch resistant coating based on the addition of nano sized Al_2O_3 particles.

In contrast to external wear factors like UV or scratching, part of the properties of wood is the bleeding of complex chemicals like tannins that, in time, decolorize the wood surface. By treating the wood surface with a nanoclay containing coating (i.e. Hydrotalcite

²³ http://www.clou.de/frontend_live/start.cfm

²⁴ containing micro-scale TiO_2 for cost reasons, but nano- SiO_2 to obtain a high scratch resistance.

²⁵ <http://www.bioni.de/index.php?lang=en>

²⁶ Personal communication with various coating manufacturers and people from the wood sector

²⁷ <http://www.byk.com>

²⁸ i.e. hydroxyphenylbenzotriazoles, hydroxybenzophenones, hydroxyphenyl-S-thiazines or oxalic anilides

$\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot \text{H}_2\text{O}$; Nuplex), this process can be delayed. Products in this range are also produced by BYK.

Nanocoatings that protect wood against water or oil are i.e. 2937 GORI Professional Transparent marketed by Dyrup Denmark²⁹, Percenta Nano Wood & Stone Sealant³⁰ (protection of wood and stone materials against water and oil, most likely based on CF-polymers), Pro-Sil 80 by NanoCer³¹ and Nanowood by Nanoprotect³². However, among these some coatings are based on nano-sized '*micelles*' of fat in water. Though these are produced using nanotechnology, micels shouldn't be considered nanoparticles and consequently the coatings are not to be typed nanocoatings.

Nanocoatings for Glass

Besides self-cleaning, photo-catalytic, heat resistant, anti-reflection and anti-fogging coatings for glass, interesting developments are ongoing in the area of indoor climate control (the blocking of infrared and visible light). Both (re-) active and passive solutions are found. Passive ones are in the form of thin films working permanently³³. Active indoor climate control solutions make use of thermochromic, photochromic or electrochromic technologies, reacting on respectively temperature, light intensity or applied voltage by changing their absorption to infrared light in order to keep the building cool. The latter is the only system that can be manually regulated. By switching on a voltage over the glass by the simple touch of something similar to a light switch a tungsten oxide layer applied on the glass surface does become more opaque absorbing more infrared light (see i.e. Figure 0-8).

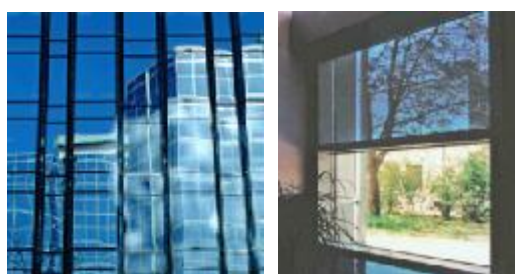


Figure 0-8 (left) Glass facades for buildings form a large scope for nanotechnological innovations in the construction industry (right) Electrochromic glass.

3.4 Nanotechnology and Infrastructure

In the field of sustainability and environmental pollution control, R&D investigates the possibility of reducing air pollution from traffic exhaust with a TiO_2 activated infrastructure. To this extend, products have been developed like NOxer^{®34} concrete road pavement blocks and KonwéClear³⁵, a cementageous asphalt coating (see Figure 0-9). However, various

²⁹ www.dyrup.com

³⁰ <http://en.percenta.com/nanotechnology-wood-stone-sealing.php>

³¹ <http://www.intelcoats.com/nanop%20Indnanocer%20engl.html>

³² <http://www.nanoprotect.co.uk/wood-protection.html>

³³ Examples of companies advertising these are Econtrol[®]-Glas GmbH & Co, 3M and Saint-Gobain

³⁴ <http://www.eurovia.com/en/produit/136.aspx>

³⁵ <http://hbo-kennisbank.uvt.nl/cgi/av/show.cgi?fid=3698>

different companies like ItalCementi and Heidelberg Cement produce materials with this type of activity in the form of bricks, blocks, panels, tiles and sound barriers.



Figure 0-9 From left to right: a side walk in Japan paved with NOxer®, TX Aria road pavement blocks and tunnel coating (Italcementi), a KonwéClear road (Bouwend Nederland Podium 22, 14 Dec. 2006).

3.5 Insulation materials

Among the nano-products used in the construction industry, insulation materials are a bit extra ordinary in a way that these materials often do not contain nanoparticles but are made out of a nano-foam (or aerogel) of nano-bubbles or nano-holes. Especially from an occupational health perspective this difference is a very important one, suggesting there are no *nano-specific* health risks to be expected from working with this material.

Nanoporous insulation materials like aerogels and certain polymer nanofoams can be 2 – 8 times more effective than traditional insulation materials (Figure 0-10). The aerogels for thermal insulation found today are most often silica or carbon based with approximately 96% of their volume being air³⁶. An example is the Insulair® NP nanoporous gel insulation blanket from Insulcon B.V.³⁷ (Figure 0-10) that are flexible and specifically designed for extreme temperature applications.



Figure 0-10 From left to right: improved isolation through aerogel based materials; aerogel: evacuated nanopores in SiO₂ matrix³⁸; Flexible nanoporous insulation blankets by Insulcon B.V. (2x)

Other products in this field are Roof Acryl Nanotech (based on a nano-structured fluor Polyurethane binder in combination with a photo catalytic Iron oxide top layer)³⁹ by BASF and Relius Benelux for hot and cold protection of roofs, PCI Silent by BASF for sound isolation, Spaceloft (specially designed for the construction industry) and Pyrogel XT by Aspen Aerogels⁴⁰ based on a nano-porous silica structure, Pyrogel XTF and Pyrogel 2250 by Aspen Aerogels based on a nano-porous silica structure that is specifically designed for

³⁶ <http://en.wikipedia.org/wiki/Aerogel>

³⁷ http://www.insulcon.com/page/products/Microporous_and_Nanoporous_products.htm

³⁸ <http://www.spaceflightnow.com>

³⁹ <http://www.relius.nl/ViewDocument.asp?DocumentId=419&MenuId=90&MenuLabel=News>

⁴⁰ <http://www.aerogel.com/>

exceptional fire protection, Cryogel Z by Aspen Aerogels based on a nano-porous silica structure that is specifically designed for exceptional cold insulation.

4. Health risks

4.1 Introduction

Evidence is building up that nano-materials could behave more hazardous to humans than their microscale equivalents. Still, the emphasis should be on the word '*could*' because at this moment in time (2009) knowledge is too limited to generalize. A precautionary approach towards working with these materials is therefore advisable. The two main factors influencing the novel toxicity of nano-materials are *size* and *shape*.

Because of the small dimensions of the nanoparticles (either 2-dimensional, nanorods, or 3-dimensional, nanoparticles) their electronic properties behave differently, which is reflected by their chemical reactivity, becoming more aggressive towards the normal functioning of the human body. For example, a number of the nano-materials studied do induce more pronounced inflammatory effects (via a mechanism called oxidative stress), agglomerate or bind more efficiently to specific parts of the human body preventing those to function properly. And moreover, because of their small size, their surface area is relatively much enlarged with respect to their particle-volume (and mass) making them significantly more reactive per mass unit.

The reduction in size and change in electronic properties influences as well their physical behavior. To name a few examples:

- Nanoparticles can be so small that they do behave like gases ,
- Nanoparticles can be so small that they penetrate more deeply into the lungs and are more easily taken-up in the bloodstream,
- unlike most other chemical substances they can be taken-up by the nasal nerve system and "easily" be transported to the human brain⁴¹,
- some nanoparticles might be able to cross the placenta and reach the fetus⁴²,
- because of their size and surface properties they can reach places (cells, organs) in the human body that used to be well protected against such an invasion by larger-sized forms,
- and because of their size and surface characteristics they penetrate the human skin more easily than their larger-sized forms, in particular when the skin is slightly damaged (compromised, dry, sunburned, abraded).

In addition to size, the specific shape of nanoparticles does play a key role in the materials toxic behavior. For example, where particles can be relatively non-toxic, nanorods can behave like true needles perforating human tissue. It is also observed that nanoparticles (because of their shape and surface characteristics) are able to overcome specific human barriers.

Other factors that have been shown to play an important role in determining any nano-typical health hazards are the aggregation and agglomeration state of the material and its

⁴¹ Oberdorster G et al. 2004, Translocation of inhaled ultrafine particles to the brain. *Inhalation Toxicology* 16 (6-7): 437-445

⁴² Hagens WI et al. 2007, What do we (need to) know about the kinetic properties of nanoparticles in the body? *Regulatory Toxicology and Pharmacology* 49: 217-229

morphology (amorphous or crystalline) that do influence the actual chance to get exposed to the nano-sized material and the intensity of any potential hazards of this material, respectively. However, regardless their intrinsic hazards, key to any health risk posed by nano-materials or products is the chance of exposure.

4.2 Exposure routes

When speaking about exposure to nanoparticles, construction workers will in the first place be (almost without any exception) exposed nano-products. This does impact on the actual exposure of the worker to the nanoparticles in the product. For example, when a worker inhales dust containing nanoparticles, the actual nanoparticle doses to which the worker gets exposed depends on the solubility of the dust. If the dust is insoluble, part of the nanoparticles will remain embedded in the matrix and exposure will only be to those nanoparticles exposed at the surface of the dust grain. However, if the dust is soluble, exposure will be to the whole number of nanoparticles contained by the dust grain.

From the very nature of the daily activities of a construction worker and the products they typically work with, exposure through inhalation of nano-material generating dust (from cutting, sanding, drilling or machining) or aerosols from paint-spraying are those most likely to dominate any health risks. Skin penetration may play a role as well (although much smaller) and might become an issue when larger parts of the body are uncovered⁴³. Exposure through primary ingestion is not expected to be an issue as long as personal hygiene is cared for. Exposure due to secondary ingestion (resulting from inhalation of nano-materials due to the natural cleaning mechanisms of the airways) though is a risk when inhalation occurs.

Exposure through inhalation

As a general rule of thumb for inhalation of dust and aerosols: the smaller the particles, the more deeply they can penetrate the lungs before they deposit, the more severe their effect on health might be. Typical health effects observed are (NEAA 2005 and references therein)⁴⁴:

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

However, for nano-particles, this rule of thumb is no longer valid and an important fraction of inhaled nano-particles does deposit in the nose⁴⁵. With respect to any further

⁴³ The skin is traditionally considered to be a good barrier against particles. 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, <http://www.orpha.net/data/patho/GB/uk-CBD.pdf>; Tinkle et al. 2003, *Environ. Health Perspect.* 111:1202-8; and Ryman-Rasmussen et al. 2006 *Toxicol. Sci.* 91:159-65).

⁴⁴ NEAA 2005. Particulate Mater: 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.

⁴⁵ ICRP 1995. International Commission on Radiological Protection

transportation in the body, it has been observed that some of these nano-particles do translocate to the nervous system, the brain tissue and to other organs like the blood, heart and liver and the bone marrow where they might cause inflammatory effects leading to a cascade of secondary health effects (Oberdorster et al. 2004 and references therein⁴¹; and for a more recent review on the topic by Politis et al. 2008⁴⁶), like irritation, inflammation, cell death, extraordinary cell growth, DNA damage and hormonal distortion (Donaldson et al., 1996; Zang et al., 1998).

4.3 Health and safety issues of several nanoparticles

Although a lot is still unknown in relation to the toxicity of nanoparticles, research is ongoing and first results are becoming available. CNT, TiO₂, SiO₂ and silver are among the ones best studied to date.

Individual toxicity profiles

CNT got recent media attention due to toxicity studies showing first indications of an asbestos like behaviour in lung tissue⁴⁷. The toxicity though, is observed to depend on the length-diameter ratio, the agglomeration state, the surface characteristics and the presence of small impurities of metal catalysts⁴⁸.

TiO₂ can be applied in the anatase or rutile form for which the first (most often used for photo-catalytic application) is typically found the most toxic form⁴⁹. The International Risk Governance Council concludes that nano-sized TiO₂ exposure to the intact skin probably doesn't affect human health⁵⁰, but penetration through damaged skin might⁵¹. A comprehensive overview of the health effects is given by NIOSH⁵². Nano-TiO₂ might (under certain conditions) show genotoxic potential and does show inflammatory effects upon inhalation. Long term exposure to anatase TiO₂ furthermore shows signs of carcinogenic effects, DNA damage and effects on the development of the central nervous system of the fetus, hinting at the possibility of reprotoxic effects in humans⁵³.

SiO₂ can be amorphous or crystalline. According to the IRGC^{54,55}, synthetically produced amorphous nano-SiO₂ is water soluble, non-toxic, and is normally treated with similar human risk factors related to toxicity as non-nano amorphous silica dust. However, depending on the method of production, amorphous SiO₂ can be contaminated with crystalline SiO₂,

⁴⁶ 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

⁴⁷ for example: Poland CA, et al. 2008, *Nature Nanotechnology*, Vol 3, July 2008, p.223; Pacurari M et al 2008 *Environmental Health Perspectives*, Vol 116, Nr. 9, 1211; Kostaleros K 2008., *Nature Biotechnology*, Vol 26, Nr. 7, 774-776

⁴⁸ Pulskamp K et al 2006 *Toxicology Letters*, 168, 58-74; Wick P et al. 2007 *Toxicology Letters*, 168, 121-131

⁴⁹ Sayes CM et al 2006 *Toxicol. Sciences* 92(1), 174-185

⁵⁰ IRGC 2008. Risk Governance of Nanotechnology Applications in Food and Cosmetics, ISBN 978-2-9700631-4-8

⁵¹ SCCP 2007. Opinion on the Safety of Nanomaterials in Cosmetic Products, adopted 18 December 2007

⁵² NIOSH Draft 2005. Evaluation of Health Hazards and Recommendations for Occupational Exposure to Titanium Dioxide, *Draft Nov. 22, 2005*

⁵³ Simizu M et al. 2009 *Part. Fibre. Toxicol.* Vol 6, 20; Bhattacharya K et al. 2008 *Part. Fibre. Toxicol.* Vol 6, 17

⁵⁴ International Risk Governance Council, 09-2008; ISBN 978-2-9700631-4-8

⁵⁵ Merget R et al. 2002 *Arch. Toxicol.* 75:625

which, depending on the fraction of crystallinity, does affect the toxicity of the total sample. Crystalline silica is very toxic and is known to cause silicosis upon occupational exposure.

Little is known about the toxicity of nano-silver for humans. Wijnhoven *et al.* (2009)⁵⁶ reviewed the knowledge gaps and concludes that, although regular silver is relatively non-toxic, inhaled or swallowed nano-Ag can enter the bloodstream and turn up in the central nervous system where it might have adverse effects that are might be more severe than regular silver. One of the reasons to expect more severe effects is because of the large surface area of the nanoparticles, which will lead to the release of a relatively higher concentration of dissolved (and reactive) silver-ions.

Occupational exposure risks

Only little information is available to assess the occupational exposure risks to nanoparticles of construction workers. Exposure to nano-products through the inhalation of dust or aerosols is to some extent obvious. However, assessing exposure risks for machining or handling a nano-product are much less straight forward. Some first hints can be extracted from the work of Vorbau *et al.* (2009, Koponen *et al.* (2009) and Kaegi *et al.* (2008)⁵⁷. The first study showed that the addition of nanoparticles to a coating doesn't have to lead to increased wear of the resulting coating film. The second study showed that upon sanding, individual nanoparticles are not found to be generated from the coatings studied (though the size of the dust produced is seen to be effected in the micron size regime) and that in contrast ultra fine particles from the sanding machine dominates the emission of particles <50 nm. And the third study does show indications that nano-TiO₂ doesn't leach from a dried coating but does reach the environment when it "breaks off" with the binder material during wear. These first results in this direction do look promising in a sense that no nanoparticles were observed to be released *simply like that*. However, the work done on this topic is still too limited to draw further conclusions regarding exposure risks to nano-particles from working nano-products in general. Neither is there enough knowledge to extrapolate the findings of Koponen, Vorbau and Kaegi to estimate the exposure risks to other types of nanoparticles than the ones studied.

4.4 Possible approaches for a safe use of nanoproducts

Organising a safe workplace requires insight in the possible hazardous nature of the nanoparticles and their behaviour when applying products in which they are contained. However, as has been reflected, the actual knowledge on the toxicological properties of nanoparticles (anno 2009) is rather limited. The same holds for the possible release of nanoparticles from nano-products during use, cleaning or maintenance. This complicates a reliable risk assessment.

Nevertheless, the use of nano-products in the construction industry is a reality and can be expected to grow in the near future. This calls for a responsible approach in which respect we can learn from the European debate on nanotechnologies⁵⁸. The precautionary approach

⁵⁶ Wijnhoven SWP *et al.* 2009 *Nanotoxicology*, 1-30

⁵⁷ Vorbau M *et al.* 2009 *Aerosol Science* 40:209-217; Koponen IK *et al.* 2009 *Journal of Physics Conference Series*, 151, 012048; Kaegi R *et al.* 2008. *Environ. Pollut.* doi:10.1016/j.envpol.2008.08.004

⁵⁸ 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.

discussed there can be explained as a strategy for dealing with uncertainties in an alert, careful, reasonable, and transparent manner that is appropriate to the situation, which should be implemented within the context of working conditions policy (within the Risk Inventory & Evaluation and the associated action plan). In short, this strategy looks the following (see also Table 0-2)

Focus on first priority activities

As a practical aid for companies it is preferred that good practices are being developed for workplaces where exposure to nanoparticles may occur. Categorizing the nanoparticle according to its associated risks may then be helpful to determine on which activities to focus and the seriousness of measures to be taken. A simple system of three categories (with reducing expected hazards going from I to III) may be used as basis⁵⁹:

- I Fibrous insoluble nanoparticles (length > 5 µm).
- II Nanoparticles which are known to be carcinogenetic, mutagenic, asthmagenic, or a reproductive toxin, in their molecular or larger particle form.
- III Insoluble or poorly soluble nanoparticles (not belonging to one of the above categories).

The general recommendation is to avoid exposure through inhalation or skin contact. For the construction industry, priority activities involve sanding, drilling, mixing, machining, cutting

Table 0-2 Building blocks for a precautionary approach

Building blocks for a precautionary nano approach
<ul style="list-style-type: none"> • No data --- no exposure <ul style="list-style-type: none"> - Prevent exposure according to the occupational hygiene strategy (incl. eventual substitution of potentially very hazardous nanoparticles) • Notification nano product composition for manufacturers and suppliers <ul style="list-style-type: none"> - Declaration of nano-content of product through the production chain - Declaration of nano-content of product at a central administration location in the form of some type of database • Exposure registration for the workplace <ul style="list-style-type: none"> - Analogue to carcinogens registration for nano-fibres and CMRS-nano-materials - Analogue to reprotox registration for other non-soluble nano-materials • Transparent risk communication <ul style="list-style-type: none"> - Information on MSDS on known nano-risks, management and knowledge gaps - Demand a Chemical Safety Report (REACH) for substances >1 ton/year/company • Derivation of nano-OELs or nano reference values <ul style="list-style-type: none"> - For nanoparticles that might be released at the construction workplace

and spraying of nano-materials and products, as well as cleaning of the workplace and used equipment. In order to identify measures and prevent exposure, the classic occupational hygiene strategy, applied to dealing with nanoparticles can be assumed.

Notification for nanoproducts

From the results of the 2009-survey and the in-depth interviews, it has been concluded that most of the construction workers and employers are not well-aware or well-informed about the nano-products they might work with. So, how can they make a proper risk assessment?

⁵⁹ BSI 2007 (December 31), "Public Document" PD 6694-2:2007, "Nanotechnologies -- Part 2: Guide to safe handling and disposal of manufactured nanomaterials.". In this document a fourth category is included: soluble nanoparticles. However, as the main focus here is non-soluble nanoparticles this category is left out.

Information is a first requirement and a growing demand by the market pushes to establish a certain way of obligation to notify (i.e. in the Netherlands (SER), France and Switzerland). Notification is especially required for the most hazardous and high-risk nano-products. The Material Safety Data Sheets (MSDSs) might be used to transfer this information from the manufacturer to the user of the products. An activity of employers and employees in the construction industry can be to refer to these initiatives and actively demand for explicit information on the nanoparticle content of used products and the precautionary measures that will have to be taken to avoid possible adverse health effects due to the exposure to nanoparticles.

Nano reference values

Under normal conditions, health based occupational exposure limits (OELs) indicate the exposure level below which work can be considered safe. For nanoparticles though, these do not exist. *Nano reference values* (NRVs), defined as precautionary exposure limit values derived by using a precautionary approach, may provide a solution until OELs are established. One example are the "*benchmark exposure levels*" shown in Table 0-3 (based on BSI 2007)⁵⁹.

Table 0-3 Insoluble nanoparticle risk ranking and nano reference values

Cat	Description	NRV	Remark
I	Fibrous; a high aspect ratio insoluble nanomaterial ^a	0,01 fibres/ml	Analogues to asbestos fibres
II	Any nanomaterial which is already classified in its molecular or in its larger particle form as carcinogenic, mutagenic, reproductive toxin or as sensitizing (CMR)	0,1 x existing OEL for molecular form or larger particles	The potentially increased rate of dissolving of these materials in nanoparticle form could lead to an increased bioavailability. Therefore a safety factor of 0.1 is introduced.
III	Insoluble or poorly soluble nanomaterials, and not in the category of fibrous or CMRS particles	0,066 x existing OEL for molecular form or larger particles	In analogy with NIOSH ⁶⁰ a safety factor of 0,066 (=15x lower) is advised. An alternative benchmark level is suggested as: 20.000 particles/ml, discriminated from the ambient environmental particle concentration.

^a A fibre is defined as a particle with an aspect ratio >3:1 and a length greater than 5000nm.

Register of companies and registration of exposure

Another possibility to implement a precautionary approach as raised by the Dutch SER is the set up of a system for registering exposure at companies working with nano-products that contain the most hazardous nanoparticles (i.e. categories I and II). For the construction worker on site, it will be difficult to judge if, and under what circumstances, the monitoring of health and safety risks is appropriate and useful. In the absence of knowledge, it is suggested though 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), in a system that can be

⁶⁰ Based on the approach as has been described by NIOSH for the insoluble nano-TiO₂: NIOSH 2005, Draft NIOSH current intelligence bulletin: Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide, November 22, 2005

designed in line with the current practice for asbestiform and CMR substances. This type of registration may fit in well with the business practices of small companies and 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 a certain health effect is experienced.

Control Banding

One other way of dealing with uncertain hazards in a given work setting and activity, and estimating the potential risks at hand in a pragmatic and precautionary way, is to use a so-called control banding tool (CB). Different CBs do exist and are used by SMEs world-wide (see Tischer et al. 2009 and references therein⁶¹). 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, the amount of the material that is used and the probability of exposure. An example of such a CB method was developed by Paik et al. (2008)⁶².

⁶¹ Tischer M, Bredendiek-Kamper S, Poppek U, Packroff R 2009. How Safe is Control Banding? Integrated Evaluation by Comparing OELs with Measurement Data and Using Monte Carlo Simulation, *Ann Occup. Hyg.* Vol 53(5):449-462

⁶² Paik SY, Zalk DM, Swuste P. 2008. Application of a Pilot Control Banding Tool for Risk Level Assessment and Control of Nanoparticle Exposures. *Ann Occup. Hyg.* Vol 52(6):419-428

5. Options for Further Activities to Support a Safe Workplace

At present, the health risks involved in working with, applying or machining nano-products are uncertain and only starting to be better understood. This involves the health and safety profiles of the nanoparticles themselves as well as the actual risks of exposure to these nanoparticles from working with the product. However, because of an enlarged surface to volume ratio, novel electronic properties, different transport kinetics and biological fate and altered chemical reactivity observed for a number of nanoparticles compared to their macroscopic parent material, the suspicion has raised that nanoparticles might involve yet unpredictable and potentially severe health risks. This complicates a proper risk assessment and risk management, and to this date no codes of conduct or good practices have been developed for the construction industry to help dealing with these unknowns. However, from what is known about working with (hazardous) chemicals, precautionary measures can be designed in order to deal with the present unknowns related to the health risks of nano-products in a responsible manner. This strategy is generally referred to as the precautionary approach. A starting point for this approach is to prevent exposure to nanoparticles by applying the occupational hygiene strategy. When exposure is effectively prevented (in case of insufficient hazard data), this is in line with the REACH principle *no data--- no market*. Within a precautionary approach, the following possible building blocks are proposed to support a safe workplace:

- No data --- no exposure
 - Prevent exposure according to the occupational hygiene strategy (incl. eventual substitution of potentially very hazardous nanoparticles)
- Notification nano product composition for manufacturers and suppliers
 - Declaration of nano-content of product through the production chain
 - Declaration of nano-content of product at a central administration location in the form of some type of database
- Exposure registration for the workplace
 - Analogue to carcinogens registration for nano-fibres and CMRS–nano-materials
 - Analogue to reprotox registration for other non-soluble nano-materials
- Transparent risk communication
 - Information on MSDS on known nano-risks, management and knowledge gaps
 - Demand a Chemical Safety Report (REACH) for substances >1 ton/year/company
- Derivation of nano-OELs or nano reference values
 - For nanoparticles that might be released at the construction workplace

Complicating further a proper risk assessment is that in many cases the nano-specific information that is available to the raw material producer gets lost while stepping through the user chain and only a small fraction of this information actually reaches the construction worker on site. This situation may be even worse for construction workers involved in (for example) a renovation project of a construct containing nano-products (due to ignorance of the owner of the construct). There is a role for the authorities and the suppliers of the nano-materials to improve this situation.

As it will be an elaborative task, especially for the SME's in the construction industry, to operationalize these precautionary measures on an individual basis, it is advisable to support the establishment of good working practices for a select number of high priority activities where exposure can be expected such as working with nano-coatings and nano-

cement/concrete. Examples of these are the spraying of nanocoatings, handling nanoparticles containing wet mortar, machining nano-products (i.e. sanding or drilling) or cleaning or servicing equipment used in these contexts. A tool that might assist in the development of these good practices is Control Banding. This generates a risk ranking based on the knowledge about the nanoparticle, its parent material (macroscopic form), the working practice and the actual working conditions. The severity of the potential hazard and the likeliness of occupational exposure are estimated and coupled to a risk level ranging from 1 to 4. Depending on the risk level, a general risk management strategy is suggested, which can vary from *'apply ventilation'* to *'wear personal protection'* or *'work in a closed environment'*.

Equipment to measure real-time nanoparticle exposure at the workplace does exist but is typically expensive and difficult to work with. Portable and more easy to use apparatus have been developed and less expensive models will be brought at the market within the next years, which will make these devices accessible to a larger public. Personal exposure measurements to nanoparticles in the construction industry are still very limited. First measurements from abrading surfaces painted with nanopaint could not detect exposure to engineered nanoparticles, but are too limited to draw general conclusions for exposure to nanoparticles generated at the construction sites.