Nano-products in the European Construction Industry

State of the Art 2009

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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. The report “Nanotechnology in the European Construction Industry, state-of-the-art 2009, Executive Summary” summarizes the findings of this study that are described in detail in the main report below.

For its research and development on new materials and products, the construction 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 construction industry in particular, this ability has enormous implications for the future of construction materials; on its quality and functionalities but also on its environmental and health performance. This report deals with the application of nanotechnological innovations in the construction industry. It describes the workings and potentials of nano-materials, its current state of development in construction engineering and, on the flip side, its possible hazards for environmental and human health.

The Internet houses a lot of information on nanotechnology in construction. The majority of available information however deals with future potentials and research activities. Information on commercialized ‘nano-products’ and companies working with nanotechnology is by far more scarce and to complicate things further, companies may advertise with “nano” just for sales reasons in products that do not contain any nano-constituent at all. Companies make use of nanotechnology for the development of better products (i.e. in the case of cement where nanotechnology among others is used to study and better understand the cement hydration behavior) or by adding small amounts of nano-sized or nano-shaped ingredients to their products to give them new or improved properties (i.e. in the case of paints, coatings or insulating material).

However, despite the fact that nanotechnology is believed to bring many technical and economic advantages to the sector in the future, 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”.
Consequently, nano-products are still niche market products. Just to give you an impression, ultra high performance concrete (UHPC) containing a maximum concentration of about 4% silica fume (nano-sized silica; see chapter 0), which is likely to be the most widely used nano-product in construction, makes up for less than 5% of the total concrete market, and is applied only when regulation specifically requests so. All other products like coatings or insulation materials are significantly less abundant at the market.

Despite this fact that the use of nano-products at the construction site is no common practice yet, it is of importance to note their growing abundance. Nano-construction products are unique in their characteristics but they might pose new health or safety risks to the construction worker on-site, which, due to the novelty of nano-materials and products in general, are presently only starting to be understood.

This, and the high expectations concerning the near future market potential of nano-products in construction (see for example [www.hessen-nanotech.de](http://www.hessen-nanotech.de)) 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 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.

### 1.1 Two Definitions

Speaking about nanotechnology appears to be difficult and a lot of misunderstanding between people arises because they think of different things when they say ‘nano-product’ or ‘nano-material’. Just to give an example: The term nano-product is used for products containing nano-particles like nano-TiO₂, which are prepared as nanoparticles (particles with a size range between 1-100nm in two (nano-rods 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 definitely applicable. For the second however, this term is much more questionable and rejected by some. As a consequence, it remains a challenge speaking the same language when talking about nano-particles (even among scientists).

What is considered in this document to be a ‘nano-product’ or ‘nano-material’? 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. 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. Chapter 0 does address this issue in more detail.
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.

Despite this lack of agreed definitions, there is still another reason why talking about nano-materials and products in the construction sector (and similarly in all other sectors) is complicated. It is the coupling between the new nano-concept and the still poorly understood health and safety risks involved, which will discussed later in chapter 4, and the fact that nano-materials and products have always been around before we knew they contained nano-ingredients (nano-particles or nano-materials). Examples of these are the color pigments in stained glass or carbon black that is used in i.e. various types of rubber. To give a material or product the prefix nano does differentiate it from its non-nano form. There are two reasons for wanting to do this. First is you want to emphasize its very special (technical) characteristics that become apparent in the nano-form but are absent in the other, and second, you want to address the health and safety issues that can be unique for the nano-form and very different from the non-nano one.
2. Nanotechnology in the Construction Sector

The present report strives to present a comprehensive overview of the current presence 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 nano-products and to signal, and put into perspective, occupational health and safety issues arising from the nano-product used.

To achieve these, three routes were followed. An extensive (scientific) literature and web-search provided the basis for the insight presented 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. Care was taken to exclude all products advertised with only high expectations for the future and include only those products for which prove for real use was found.

In parallel, the FIEC and the EFBWW set out a survey among their members in 24 European countries to probe the general awareness of employers and employees on applications of nano-products in the sector (see also Annex 1 for the questionnaire distributed). Each asked their members/affiliates to distribute the survey in their own country with an individual target of 3 replies. The 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. The survey also aimed at basic information transfer. To this extent, the EFBWW and the FIEC additionally organized a workshop prior to running the survey to inform their members about the very first basic of the “nano-concept”, construction products and occupational health and safety issues. For most attending this workshop it was the very first time they heard about nanotechnology and its uses for the construction sector.

In addition to these, in-depth interviews with construction workers and 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.

Table 0-1 Overview of the typical background (function profile) of the respondents to the 2009-survey

<table>
<thead>
<tr>
<th>Number of respondents</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Employer</td>
</tr>
<tr>
<td>4</td>
<td>Painter (worker, worker representative)</td>
</tr>
<tr>
<td>4</td>
<td>Safety Adviser (worker, worker representative)</td>
</tr>
<tr>
<td>3</td>
<td>Various (worker, worker representative)</td>
</tr>
<tr>
<td>11</td>
<td>Not specified (worker, worker representative)</td>
</tr>
</tbody>
</table>
The results of these interviews were important to place the results from the 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 and Table 0-2 show 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.

Table 0-2  Overview of the different types of organizations approached for the in-depth interviews

<table>
<thead>
<tr>
<th>In-depth interviews (%)</th>
<th>Type of organization</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Construction Industry</td>
</tr>
<tr>
<td>21</td>
<td>(raw) Product Manufacturers</td>
</tr>
<tr>
<td>9</td>
<td>Branch Organizations</td>
</tr>
<tr>
<td>4</td>
<td>Architects</td>
</tr>
<tr>
<td>42</td>
<td>University R&amp;D</td>
</tr>
</tbody>
</table>

The resulting information is presented in the sections below.

2.1  A Roadmap for Nanotechnology in the Construction Sector

In 2003, Peter Bartos and others shared high expectations about the near future developments of nanoproduces for the construction industry. However, in 2009 one has to admit that only little of these expectations became a real market reality (even though research in these field is in fact ongoing).

At the NIFI2008, Spinverse Capital and Consulting presented the status a.o. of the Finnish construction nanotechnology industry stating that “the economic situation will strongly impact the this industry as there are no established commercial products yet and the core of this industry is strongly hit by the downturn”. With an average time of 3 -5 years from product development to market introduction prospects were “that in 2013 a total of 6 companies will have commercial construction products at the market”. Europe wide, this probably is a very conservative estimation but it will be only a small fraction of the total.

Hereby, it is important to distinguish between the development of different products for industry at large and developments for the construction industry in particular. In fact, for the different product groups indentified as nano-developemental areas by Bartos and others various products are offered for sale by a number of different companies. However, only little of those really make it to the construction site. Various reasons can be appointed. The most important ones will be discussed in the sections below.

2.1.1  Price competition

The very first reason why nanoproduces 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 nanoproduces are still significantly more expensive than their non-nano alternatives because of the technology required to produce them. For consumer products the additional costs do not necessarily have to be the largest
obstacle for market acceptance. For the construction sector it does. Already at the research and development phase of a product, initiatives are stopped when 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 rises in total costs when the total volume is considered. To give an example: industrial flooring nano-coatings could be offered at a maximum price difference of no more than about 1 euro per kg.

As a result, manufacturers of construction material are reluctant to develop nanoproduc ts (especially when the performance of existing non-nanoproducts is believed to be sufficient) and those nano-products that are developed remain niche products that are only applied upon specific request. This in particular holds for the larger volume products like concrete or mortar and for construction coatings. However, developments are also seen in the area of e.g. insulation materials and architectural and glass coatings that have the improvement of the energy performance of the construct as their main objective. These also are niche markets still, and the current focus of society on the improvement of energy management in the context of climate change and the reduction of greenhouse gasses does stimulate their further market introduction.

2.1.2 Technical performance

Probably the second most important reason is the technical performance of the product. The technical performance should thoroughly be proven to meet the technical standards for that material. Especially for a new material with new functionalities, this involves a lot of testing and even when laboratory results show positive one does often ask for pilot projects to also showcase their behavior under real life conditions. Like for any new product, the uncertainty about substitution issues does slow down the market introduction of nano-products in construction. 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 smaller as the safety standards for instance are much lower.

2.1.3 Awareness within the sector

As a good third, awareness is one of the key elements hampering the introduction of nano-products in construction works. Without awareness one simply doesn’t know there is anything new to apply or to explore.

Taking the construction industry at large, this sector does involve product manufacturers and suppliers, construction workers and their employers, project developers and architects. Overall within Europe, knowledge among these stakeholder groups with respect to 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 survey set out by the FIEC and EFBWW to monitor the awareness of construction workers and their employers (hereafter denoted as the 2009-survey) resulted in the figure below, showing that the majority of respondents were not aware whether or not they are working with nano-products.
Since the aim of each affiliate was to return 3 completed questionnaires, the overall response of 28 returns on the target of a 144 (Figure 0-1) therefore doesn’t necessarily imply a response of about 20% but might easily be lower (many members could have been approached), and the results of the survey should therefore only be interpreted to give some indication about the present state of knowledge in the sector with respect to nano-products in the construction industry. More significant information is believed to be obtained from a series of in-depth interviews conducted in parallel to the survey with a number key-players in the field (raw material manufacturers, product manufacturers, construction workers and employers, construction companies, architects and researchers). Response to the questionnaire was obtained from 14 different countries with exceptionally high responses from Bulgaria, Poland and the Netherlands (see Figure 0-2). The high Dutch count is the direct result of a parallel project running in the Netherlands on the state-of-the-art of nanotechnology in the Dutch construction industry. Bulgaria and Poland have probably ‘just’ succeeded better than other countries in approaching their promised target of 3 responses per organization, and it would be misleading to draw conclusions regarding the abundance and awareness about the presence of nano-products in their industries.
Figure 0-2 Response distribution of the 2009-survey over the 24 European countries given in percentage of the total response. Of all European countries approached, 14 out of 24 responded.

Overall, about 75% of all respondents (employees and employers) stated they were not aware if they were working with any nano-products, 25% stated they were. However, this should probably be interpreted as an indication of only little awareness because of positive selection: those who replied the questionnaire were more eager to do so when they were aware they were working with nano-products. The ‘awareness figures’ of Figure 0-1 do therefore most likely overestimate the real percentage of employees and employers working with nano-products at the construction site. This is extracted from the fact that, in addition to filled-in questionnaires, various comments were received 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. I would be happy to receive further information regarding this issue so that I can investigate further (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)”, or “…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 that were conducted in parallel to the 2009-survey with a number of involved key players (i.e. BASF, Heidelberg Cement, Skanska, Caparol) 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 minor niche market in the construction industry of today, including some architects that are in the front line of prescribing certain materials and products. However, the opposite is 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”.

The few nano-products that are typically mentioned are either cement or concrete products, coatings or insulation materials (see Figure 0-3). Other types, including products like road-pavement products, fire retardant materials or textiles, are only sporadically noted. Those who indicate they are working with nano-products anonymously do so because of performance reasons (that don’t allow for an alternative product) and in some cases because of the (additional) specific request by the customer. This is a very interesting difference to the consumer-product sector where nano-products are also seen to be introduced just simply for the novelty of it. Despite these, there was also an example of unintended use by a construction worker stating that when the cement product he normally ordered was not in stock he got an alternative product from his supplier, which appeared to be a nano-cement and is used only once since. The remaining material remains piled up in that companies storehouse.

Figure 0-3  Left: nano-products actually mentioned one is working with, from the results of the 2009-survey, presented in total number of products. Right: the total of respondents being aware, not aware or not aware but suspecting they work with nano-products, presented in percentages.

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 (see the chart on the right of Figure 0-3). 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). How exactly this should be interpreted can be many of things, but it does definitely hint at the more general unawareness about the chemical composition of products worked with and the superior technical performances associated with the prefix nano-, which touches on a communication and marketing issue discussed in sections 2.1.5 and 2.1.6. It could also suggest some common understanding about the nano-products that are out on the market, but the products suspected do also reflect those products that normally make-up for the largest market volumes used.
2.1.3 Awareness in the Dutch construction industry

The average construction worker, occupational health and safety advisor or occupational hygienist active in the construction industry, or architect doesn’t have any awareness related to uses of nano-products in the construction industry, and would not recognise a product as such. Results from the 2009-survey set-out under a total of 38 occupational health and safety advisors and occupational hygienists active in the construction industry in the Netherlands showed a similar ‘awareness profile’ as was observed European broad among workers (representatives) and employers (see Figure 0-4). By far, the majority of all respondents replied they were not aware if they were/are working with any nano-product (about 2/3 of all respondents). Approximately 26% of the respondents did state they were not aware of any actual use, but had their suspicion about potential uses of nano-products in their work once they got confronted with a list of typical product types among which nano-products might be found. Only 5% of all respondents did know about they used nano-products. In this context, nano-silica (silica fume) enhanced concrete was the only product identified by them. Suspected products indicated by the respondents involved mostly Coatings (12x mentioned), Ultra high performance concrete (11x mentioned), Isolation materials (7x mentioned) and Flame retardant materials (7x mentioned).

Branch organisations are not necessarily better informed. The NVTB (the Nederlandse Verbond van Toelevering Bouw) was approached but stated that nano-materials were no focus of their association, that he did not have any information on the current status of the Dutch or European market related to nanotechnologies in the construction industry and that he did not have any idea which other person within the NVTB could provide this type of information. A similar story was obtained from the VMRG representing a part of the alumina branch, the MetaalUnie and from the Centrum voor Hout concerned with wood and wood products. From the Fosag, information was received that there are nano-activities in the field of coatings, but
the VVVF, the Dutch association of paint manufacturers remained quiet about any nano-activities, even though inside knowledge did provide the information that they in fact did launch a nanotechnology knowledge transfer platform. In contrast though, the cement and concrete appeared much better aware of the market developments. The Dutch Cement&BetonCentrum (www.cementenbeton.nl Andre Burger) stated that, although the association itself does not play a major role in the developments, the European cement industries are heavily competing in applying nanotechnologies in their research and development activities. According to the CBC, the application of Silica Fume to improve the properties of concrete is now ‘common practice’. Others, like titanium dioxide as catalyst for self cleaning concrete is still more or less in the experimental stage. Despite these, a number of contacts with smaller companies, in particular is the coating and cement sector, do suggest that construction nano-products started first to appear 1 – 3 years ago and are continuing to appear “as-we-speak” at small scale (Baril Coatings, Struyk, Mebin).

2.1.4 Advantages of nanotechnology for the sector
So, what does nanotechnology do for the construction industry?
On the one hand nanotechnology enables material researchers to better understand the working mechanisms underlying the characteristics of presently used materials and products via high technology scientific measurement techniques, allowing for a more focused approach towards material optimization. On the other hand, nanotechnology brings forward nano-materials that make use of specific properties of substances or materials that have been designed at nano scale such as nanoparticles, nanotubes or –rods or nanosurfaces (see also section 1.1 for the definition of a nano-material). Nano-materials accordingly can be used (most often as additive) to improve or design the novel characteristics of the nano-product. One of the best known examples of such a product is Ultra High Performance Concrete (UHPC), prepared by the addition of silica-fume (nano-silica). In chapter 3, a summary is given of the different product types found to be used in construction today.

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 multinational producers like BASF, AKZO-NOBEL, DuPont, Heidelberg and ItaICementi 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 very 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. However, in the coating sector the situation seems to be changing. Nano-coatings are typically ‘far’ in their development with respect to other 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 and fabricate their own nano-product line.

2.1.5 Communicating nano along the user chain
At the level of the construction worker, detailed knowledge of the chemical nature of the product he or she works with is a luxury and most often not priority number one. This is true for “normal” products and is not different for nano-products. The technical and health and safety information is what is needed. But it are as well the health and safety aspects of nano-products that are not yet thoroughly understood. Nano-materials can be much more reactive than their non-nano forms. It is therefore that the legally required concentration levels for registration and communication of their health and safety risks might be too high to ensure a safe working practice. In fact, these concentration levels for registration and communication should be lower to be protective of the worker. For nano-materials this becomes directly apparent as the majority of these substances are added to a product only as additive in small concentrations, below the registration level. 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)\(^2\) 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 0-5). 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. Annex 3 presents the MSDS and technical information sheets of two different nano-products, of which one does

provide nano-specific information and the other one doesn’t. 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 clearly indicate, suggest, or 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-image (Scanning Electron Microscope) of the nano-particle or the description of the active surface area of the 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. One respondent (an employer of a SME construction company employing ca. 200 workers) did state that some of the nano-products he works with (e.g. cement and insulation material) make his work less labor intensive.

However, it should be mentioned here that 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. It is therefore also that there is a general uncertainty with respect to health and safety risks by nano-products. Consequently, nano-products should be treated and used with a certain precaution, which should in some way or another be part of the communication to the user. In chapter 4, this is addressed in more detail.
Figure 0-5 Specification of product information available to the knowledge of the respondents for those nano-products indicated to be used in the 2009-survey. Numbers are given in number of products.

At present the information supply chain be roughly represented as follows (see also Figure 0-6). The “raw material” producers of nanomaterials 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. Sometimes, this manufacturer does notify its customers anyway, but most often only in a way to promote their product by showing the enhanced 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 0-6 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.

Complicating the insight of “outsiders” in the nature of nano-products further is the fact that over the last 5 – 10 years the prefix nano- has been used on a product for
marketing reasons also if that product shouldn’t be considered as a nano-product given the provisional definition in section 1.1.

2.1.6 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-theme3, 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 (e.g. here called semi-nano-products). 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)

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. 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.

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3 Private Communications with a number of different material producing companies.
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 Committee and the large key stakeholder industries like BASF and Dupont, the production of the fast 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 such as packaging material (large bags) that dissolve in water and which material does not affect the foreseen product characteristics (concrete).

However, this doesn’t mean that occupational safety is fully under control. On the contrary, at this moment in time 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. On top of that, correct information from such exposure measurements can often only be derived when one knows with which nano-material one is working. And if all this information would be available, still the majority of the SME’s will not have the practical space nor the financial means to take the necessary protective actions, at least in some industrial sectors. Especially in the production facilities of the nano-materials and in the R&D divisions of the nano-product manufacturers. The European trade union, the ETUC therefore calls for applying the precautionary principle in case of uncertain risks, which can be summarized as “no data, no exposure” and to allow companies to make their own risk assessment and introduce an early warning system, they call for:

- Notification of the content and type of nanoparticles in products for manufacturers and suppliers.
- Registration at the workplace where nanoparticles are produced, processed or used of the workers that are possibly exposed to nanoparticles, the handling, the frequency, time, type of exposure.
- Transparent communication of the uncertain risks that are introduced by handling of nanoparticles containing products.
- The derivation of health-based recommended occupational exposure limits or nano reference values for substances with dimensions at the nano scale is an essential element.
- Development of an early warning system in the context of health monitoring to identify early signals of possible adverse health effects.
At this moment in time the number of nano-products and their volumes used in construction are still limited and consequently the number of events in which construction workers might get exposed to this type of products is small. Furthermore, as one will see in the following of this document, at the construction site, in a number of work situations risks of exposure to nano-products are likely to be fairly well contained. In the construction industry one often works with prefabricated products that arrive at the site in slurries (in the case of cementitious products), pastes or viscous liquids (paints) or as prefab elements (of concrete, wood, metal etc.). In liquid or solid form, exposure to the nano-materials in the nano-product can be well contained and there is only a minimum risk of inhalation. Nevertheless in the case of spraying (of nano-coatings for example) risks become significant and spraying of nano-products should therefore be prevented as much as possible. However, exposure risks are also expected to be limited because in a number of cases one does already take precautionary measures to prevent inhalation or skin contact simply because the “traditional” construction material in itself is already quite hazardous. This is in principle true for activities like working with cement, wet mortar or coating materials and working on concrete or wood when there is a risk of silica or wood dust exposure.

For some products, the nano-material in the raw nano-product will no longer be there as nano-material in the finished nano-product, like is the case for silica fume in UHPC concrete. For other products, the nano-material will be tightly embedded in the nano-product matrix and the risk of inhaling dust at sanding a surface will probably easily outweigh the risk of inhaling the nano-material that is at this surface in very low concentration (but with a potentially high surface reactivity). However, this is no guarantee that the health hazards involved in inhaling dust do also outweigh the hazards due to inhaling the limited amount of nano-material. Despite the low amount, it is possible that their health effects can be severe. In chapter 0 and Annex 5 an indication is given of the possible exposure risks that could reasonably be expected for the nano-products and nano-materials discussed based on the available product information and standard working practices. In chapter 0, a more extensive overview is given on health risks and occupational risk assessment and risk management strategies.
3. Nano-products at the Construction Site

3.1 Introduction
In section 2.1 a roadmap has been presented showing the type of product developments and market introductions of nano-products that were forecasted in 2003. This chapter presents an overview of nano-products that are actually found to be used in the EU construction industry today. It might appear that the list of products presented here looks impressive. Still one should realize that, like is described at various places in the previous sections, the total market share of nano-products in the construction industry is very small and considered to be applied in niche markets. Already now nano-products could in principle be found in nearly every part of an average house or building (see Figure 0-7).

Figure 0-7 Schematic overview of a typical house of today indicating where nano-products could be found.

Despite this current situation, their market share is expected to grow. Moreover, nanotechnologies are expected to play an important future role at the very basis of material design, development and production for the construction industry (i.e. Nanotechnology and Construction 2006; www.hessen-nanotech.de). In this light, it is

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4 Personal communication, BASF
5 Taken from the brochure "Einsatz von Nanotechnologien in Architektur und Bauwesen" published by HA Hessen Agentur 2007, sources: Schrag GmbH VDI TZ
6 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
important to follow the developments in this field from the start and to be aware of existing uncertainties with respect to health and safety issues of nano-materials and products in order to take appropriate measures when this is judged necessary.

As one will see, emphasis is on cement and concrete products, on paints and coatings and on insulation materials as has been found that market activity seems to center around these. Especially the field of paints and coatings is in motion and nano-coatings are being developed (and brought at the market) to be used on practically every type of material. In many cases also, different nano-products are found to be ‘just’ another variation on one specific nano-material theme. TiO₂, to name one, is used in a broad range of product matrices to introduce there its special characteristics. It is therefore that here only the different product types are described whereas in Annex 5 a more detailed overview is given of those nano-materials applied most often in the various types of nano-products. All products identified are summarized in Annex 2 and 4.

3.2 Cement, concrete and wet mortar
Concrete is a special product with specific material properties that are of high value to the construction industry. Required properties for concrete are: the material should be strong, durable, extremely cheap and easily prepared in large quantities. It are these characteristics that made concrete one of the most successful and widely used products in construction. The total volume of concrete marketed in the EU lays around 750 million m³ per year. However, the combination of an already existing good performance that is available at low costs causes that challenges are high for any successful application of nanotechnology (even though technically there are enough reasons to do so) (NICOM3, conference proceedings 2009).

One of the area’s where nanotechnology does prove extremely valuable is the study (and optimization by better understanding) of the material properties of cement, wet mortar and concrete. Cement is the binder material. A substance which sets and hardens independently and can bind other materials together. In wet mortar the mechanism behind this hardening is a chemical process known as hydration: constituents of the cement react with water turning the volume originally contained by the water into a solid. The cement grains bind together and create a stone-like material called concrete. Despite cementitious materials being the most widely used building material in the world, its chemical and physical complexity make that the fundamental mechanisms underlying its behavior are still poorly understood. Development and further optimization of techniques to characterize and study materials at the nano scale, such as Nano indentation analysis, Nuclear Resonant Reaction Analysis (NRRA), X-Ray Diffraction analysis, Attenuated Total Reflection Fourier Transform Infra Red spectroscopy (ATR-FTIR), SEM (Scanning probe Electron force Microscopy), Atomic Force Microscopy (AFM) and TEM (Transmission Electron

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7 Mebin (NL), personal communication
8 Various presentations and private communication with a number of companies and university scientists at the NICOM3, Prague 2009
Microscopy), have provided unique opportunities for studying cement (see Annex 3 for more detail on measurement techniques). Possibly for cement, and definitely at this point in time, these examples of nanotechnology applications (e.g. various high tech measurement devices) might be the most beneficial for its near future developments and will prove most valuable in the production of novel products (see NICOM3 proceedings 2009).

At this same NICOM3 conference, attention was drawn to the opportunity to use concrete to fixate waste materials. Since concrete is such a high volume product, it would be wonderful if one could use it for the fixation of waste streams. However, waste streams are typically non-homogenous and non-constant in quality and therefore difficult to handle for the production of constant quality concrete. With nanotechnology, better insight is gained in the factors that play a key role in this quality control and how to deal with them. R&D focuses i.e. on the development of products that use high concentrations of fly ash, but also limestone or pozzolan. Examples of products currently at the market are i.e. Chronolia™, Agilia™ and Ductal™ by Lafarge and EMACO®Nanocrete by BASF (see later in this section).

Besides advanced scientific equipment, nano-particles and materials do offer interesting possibilities for the optimization of cement based materials. This involves the optimization of strength by a number of methods and optimization of durability by increasing its resistance to i.e. microbial growth or crack progression. As the strength of concrete is based on its nanometer size crystal structure, the usage of nanoparticles as an additive, combined with new insights into crystal structure mechanics, has provided many new ideas for the improvement of cement based materials. Some examples are given below.

![Figure 0-8](left) Block co-polymers in cement to increase flow capacity for excellent boarding adaptation, and (right) paraffin containing polymer nano capsules in concrete for temperature regulation properties.

### 3.2.1 Silica Fume

Silica (SiO₂) is present in conventional concrete as part of the normal mix. The intentional addition of extra nano-silica particles (also known as silica fume) though, does improve the particle packing of the concrete matrix resulting in improved mechanical properties and the construction industry has made use of these characteristics already for many years. Of all nano-materials used in the construction sector, silica fume is among the oldest and most commonly accepted ones (even though the nano-label was only put on it recently). Silica fume particles are about
100x smaller than the average cement particle, which size may range between 1 and 200µm with averages below 50µm. A rough estimate then gives that silica fume particles size below 500nm, with typical surface area’s of 20,000 m²/kg.

Before the use of silica fume, 6,000 psi concrete was considered to be high strength. Today, using silica fume as an additive, concrete with compressive strengths in excess of 15,000 psi can be readily produced. This is an advantage for many applications but can also be seen as a drawback when drilling of holes or insertion of staples and nails is foreseen. Silica fume addition to cement can also control the degradation of the fundamental C-S-H (calcium-silicate-hydrate) reaction of concrete caused by calcium leaching in water as well as block the penetration of water. The addition of silica fume therefore leads to improvements in durability of the material. The reduced permeability for water also holds for chloride ions, which prevents the concrete’s reinforcing steel from corrosion, especially in chloride-rich environments such as those of northern roadways and runways (because of the use of de-icing salts, saltwater bridges and marine constructs in general).

Health and Safety of Silica Fume
Silica Fume is applied in two different physical shapes: an amorphous form that can be characterized by a highly irregular sponge type form and a crystalline form that is highly ordered and structured into small crystals. Due to these morphological differences, amorphous silica, smoothly spherical shaped on the outside (typical diameter 100nm and less), is typically seen to be less toxic than the crystalline form (see Merget et al 2002 for a review on this subject). Amorphous silica fume is normally treated with similar human risk factors related to toxicity as non-nano non-toxic silica dust. It has been observed to cause friibrogenic effects upon occupational exposure and defined exposure safety thresholds for inhalation lay in the range between 4-10 mg/m³. Crystalline silica on the other hand with its needle like structure and sharp edges (typical length of 200nm and less and diameter of about 20nm) is very toxic and is known to cause silicosis upon occupational exposure. Between the two, amorphous silica is most widely used. Applications of crystalline silica fume are found for example as additive in paints or coatings (see also section 3.5). Amorphous silica fume is the form normally used in cement and concrete. Amorphous silica fume does however contain small amounts of crystalline silica (varying between 0.1 and 60% depending on the production process), with the exception of high grade synthetic amorphous silica fume that is for example used in cosmetic or food products. In contrast to amorphous silica fume, for crystalline silica fume much lower threshold limit values (as low as 0.05 mg/m³) have been

It is therefore essential to be informed by the product manufacturer about the potential crystalline silica fume contamination in order to take appropriate safety measures.

Silica fume is incredibly difficult to work with. For one, it does require special mixing equipment because the tiny silica particles are extremely sharp and cause heavy wear to normal cement and concrete apparatus, even in their amorphous form. Health and safety issues of silica fume used to be quite serious in the past when the silica fume was mostly handled as a powder and mixed on site. Examples are there of workers stating that the powder was impossible to handle because it was so dusty it simply remained in the air as a dust cloud upon pouring. This gave rise to high risks of inhalation and many practical difficulties at the workplace. At present though, the word goes that silica fume is no longer deliver as a powder but is premixed in closed systems in the cement factory (using for example a system of dissolvable bags to pack the silica fume to prevent powder exposure) and delivered on site as a slurry. In this way, health and safety risks are significantly reduced.

When silica fume reacts to form the cement or concrete matrix, the nano-particles get hydrated and its nano-character is no longer present. It is therefore not to be expected that any risk of exposure to nanoparticles remains from the eventual construct that is different from a silica fume-free concrete, nor by working on it through drilling, nor through (environmental) wear processes. As the final matrix though, is significantly stronger, the type of dust produced by wear or working on the surface can be expected from simple material physics to be more fine.

**The Market of Silica Fume**
Silica fume is one of the oldest examples of nano-ingredients used in concrete, and definitely at this point in time one of the few successful products that conquered a

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14 Mebin (NL), personal communication
15 Telephonic inquiry with an employee of the Edense Beton Centrale (EBC) in Ede in the Netherlands.
niche nano-market. Its production process and the high demands placed on the 
equipment to handle silica fume cement cause silica fume to be more expensive for 
use than alternative cement types. As a result, silica fume is only applied when the 
customer does ask for it specifically or if regulation does require its use. One 
example are the Nordic countries that prescribe silica fume cement for use in marine 
constructs via regulation.

Of all concrete produced EU wide, rough estimations yield an approximate 
application of less than 5% made of silica fume UHPC (Ultra High Performance 
Concrete). Of this UHPC, silica fume makes up for 4 weight % of the total mixture. 
Overall, these approximate numbers result in a total amount of about 3.6 Mtons of 
silica fume concentrated in few special construction projects.

3.2.2 Ceramic Hematite
In addition to silica fume, ceramic hematite (Fe₂O₃) nanoparticles have shown to 
increase the strength of concrete. Moreover, this additive allows the monitoring of 
stress levels through the measurement of section electrical resistance 
(Nanotechnology and Construction 2006). At present though, ceramic hematite is no 
common additive to improve the strength of concrete and there are no examples 
found of such products used at the market\textsuperscript{16}. Nevertheless, future applications that 
would allow the monitoring of degradation might lead to an actually increased 
lifetime time of concrete constructs if demolition could be based on the material 
quality in each specific situation.

3.2.3 Titanium Dioxide
Titanium dioxide (TiO₂) nano-particles are explored for their ability to enhance the 
durability of concrete and to maintain a concrete like whiteness throughout the 
entire lifetime of the construct (see for example Figure 0-10). The way this works is 
that titanium dioxide assists in the brake down of organic pollutants (but also of NOx 
to NO₃) and micro-organisms that would otherwise speed-up the deterioration of 
the concrete. TiO₂ is a catalyst that requires UV light to work. As a consequence, this 
principle only works out-side (although research is ongoing to shift the active light-
range to visible light wavelengths that would make TiO₂ also active indoors or under 
artificial light), only at the air-concrete boundary layer, and only when the concrete 
is sufficiently clean for the UV rays to get through. Especially this last aspect requires 
regular cleaning of the surface (which can only partly be facilitated by the 
hydrophilic, self cleaning properties also introduced by titanium dioxide, and 
therefore requires regular cleaning depending on the way of application, see later on 
in the text).

\textsuperscript{16} Personal communication
Figure 0-10 The Jubilee Church in Rome, one of the most often quoted successes of photo catalytic concrete by the addition of TiO₂. Material: TX Active (TX Arca) from the Italcementi group.

The actual application of titanium dioxide nano-particles in concrete in the construction industry is minimum and is typically reserved for those concrete systems that can be fabricated as bi-layer systems and for which a relatively high unit price can be asked. Typical examples of products found nowadays at the market are special concrete blocks, bricks, tiles or roof tiles where the titanium dioxide is applied in a top-layer cement coating. The reason behind this is that titanium dioxide nano-particles are expensive in relation to concrete, especially in the large volumes that are normally used to build a concrete construct. Therefore, the presence of TiO₂ in cementitious material does not have to imply the presence of nano-TiO₂. Similar concrete characteristics (although less efficient) can be induced by adding TiO₂ in a microcrystalline form (with particle sizes larger than 100nm) that are in the similar size range as the other concrete ingredients (like in TioCem TX Active by Heidelberg Cement). Especially from an economic perspective, adding micro crystalline TiO₂ is preferred over nano crystalline TiO₂. However, also from an environmental perspective, microcrystalline TiO₂ would be preferred. A study on the leaching of TiO₂ from nano-TiO₂ façade paint does show indications that, although TiO₂ doesn’t seem to leach from the paint matrix, it does come into the environment when the surface wears and small particles brake off (Kaegi et al. 2008), where it could maintain a similar photo catalytic behavior (see EPA/600/R-09/057 for an overview on this topic). The less reactive micro form is therefore preferred also from an environmental point of view.

Products are just about to appear and actual uses of this type of photo-catalytic cement at the market are still small. TioCem TX Active for example has been set in the market only one year ago cement and knows a marketed volume of 330 ton per year. With Heidelberg Cement as one of the major cement producers in Europe it is to be expected that this amount is probably below the 1 kton per year EU-wide. Based on the same formula Italcementi does produce TX Arca, a photocatalytic cement for the construction of exterior walls, facades and tunnels, and TX Aria, which is produced as binder for a wide scope of coating materials like concrete

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17 Personal communication with various product manufacturers
18 Heidelberg Technology Center Germany
floors, paving blocks, tiles, roof tiles, roadmarking paints, concrete pannels, plaster and cementitious paints (see also Figure 0-10, Figure 0-16 and Figure 0-18). NanoGuardStoneProtect by Nanogate AG is yet another example presented as a coating for nature stone and concrete surfaces.

3.2.4 Carbon Nano Tubes
A further type of nanoparticle that is added to cement is the carbon nanotube (CNT). Research in this field has been ongoing roughly since 2003, but can still be considered to be in its infancy (Makar 2009). Nevertheless, some results are very promising and the addition of small amounts (<1% weight) of CNT’s may drastically improve the mechanical properties of the cement matrix. For example, oxidized multi-walled nanotubes (MWNT’s) have been shown to improve both the compressive strength (25N/mm²) and flexural strength (8N/mm²) of the concrete compared to reference samples without this reinforcement (see also Nanotechnology and Construction 2006). Moreover, even better results are expected for SWNT’s as these match better to the topology of the hydrated cement structure. Still, those studies yet available are inconclusive showing different results or are unable to reproduce the results of others. What is observed is that nucleation around the CNT occurs upon hydration, which results in a very strong interaction between the CNT and the cement. For oxidized MWNT’s it is hypothesized that the high defect site concentration on the surface could lead to a better linkage between the nanostructures and the binder thus improving the mechanical properties of the composite.

The actual application of the CNT in practice remains a challenge as CNT tend to aggregate during mixing and there is little consistency in the results between the different procedures and different research labs involved. Practical barriers that have to be overcome prior to any market application are technical barriers of applying CNT and its health and safety issues.

There are various technical barriers such as the quality of different CNT batches and the methods used to disperse the CNT in the matrix that both seem to result in different concrete characteristic when explored in different laboratories (Makar 2009). Second is the volume of CNT needed and the consequent costs related. The costs of a typical CNT batch can vary enormously depending on de quality, homogeneity and surface modification of the tubes but is approximated at about 400,- euro per kg for potential concrete application. Only when the price – performance ratio decreases, chances are that CNT enforced concrete products might become economically feasible, and when this happens there are still the occupational health and safety issues and environmental issues related to the

19 http://www.italcementigroup.com/ENG/Italcementi+Group/
20 http://www.nanogate.de/en/
21 Personal communication
22 From an in-depth interview with Prof. Makar
23 From several in-depth interviews with university scientists and the cement and concrete industry
24 Personal communication NanoCyl SA.
25 Personal communication with BASF and Bayer
application, use and end of life scenario of CNT containing concrete (see also Annex 5).

**Health and Safety issues of CNT in concrete**

Based on a number of in-depth interviews health and safety issues that might arise when eventually CNT-concrete products will reach market maturity relate to the construction worker on site that pours the material and who will have to deal with novel procedures on how to work with the material and deal with possible spills, but relate also to the service and maintenance workers that work the trucks that deliver the CNT-concrete mixture. Suspended CNT shall have to be added to the pre-mixed cement, either on site or shortly prior to use in ready-mix plants. Especially when mixed on site, this would involve additional health and safety risks for the workers involved in the mixing process. Even though it is probably not to be expected that the CNT will evaporate from the mixture and get airborne (because CNT are typically non-volatile but can be extremely dusty when used as powder), one should be careful for inhaling dust from dried spills. This latter also holds for the handling of the wet CNT-cement and working the dried construct. The dust produced during drilling, sanding or cutting CNT-concrete material can be expected to contain at least the original fraction of CNT in the product and inhalation should therefore be prevented. Prefab CNT-concrete products that (in the future) might going to be produced in a manufacturing plant, might present a lower level of occupational health and safety issues as mixing and pouring CNT-cement does not take place on site.

Environmental health and safety becomes an issue when the material gets spilled, when the construct wears during use and when it is taken down at its end of life. Emissions of CNT through wear processes are yet unknown and will have to be studied carefully. Another challenge will be the recycling of CNT-concrete or alternatively, the proper disposal of CNT-concrete. These type of issues should be clarified before any CNT concrete or cement eventually developed, is going to be applied at large scale.

Given the costs involved and provided that the barriers sketched above will be overcome in the near future, applications of CNT-concrete will first be found in high value projects such as large bridges, dams, nuclear power plants and military objects. At present, this is not yet reality.

**3.2.5 First Market Experiences for Cement and Concrete**

Because of the strict quality requirements and the low tolerance of uncertainty related to concrete performance, material developments generally take a long time (typically between 5 and 10 years) before market introduction and acceptance. Partly because of this, material improvements for cement and concrete do focus also on developing specialised coating systems: improve the material properties by adding the appropriate coating to it, as a more easily achievable route to obtain certain material properties (such as for example hydrophobicity or self cleaning properties).
Main players in the field of cement and concrete production and R&D on the use of nanomaterials are Heidelberg Cement and Lafarge. Other large companies active at the European market are CCB S.A., CEMEX Deutschland AG, Dyckerhoff AG and Holcim BV, which are engaged in a strong competition at the nano field. This strong competition is one argument for smaller players such as e.g. Mebin in Den Bosch (NL) not to invest in nano-R&D at this moment\textsuperscript{26}.

However, investing in R&D activities does not necessarily imply these same key players do also have nano-products at the construction market. Moreover, having products called nano in their portfolio doesn’t say that much per se and is merely an indication of nano-involvement somewhere along the line of the products manufacturing process. BASF, for example, is the producer of the brand EMACO\textsuperscript{®}Nanocrete (Figure \textsuperscript{0-9}) which they advertise as a concrete repair mortar with exceptional properties: Improved bond strength and tensile strength, improved density and impermeability and reduced cracking tendency, just to name a few. The material safety data sheet (MSDS) speaks of a modified sand – cement mixture. The term “modified sand” reflects beyond doubt the finer structure of silica nano particles as does the name of the product suggests. However, as it appears from an in-depth interview with BASF the modified sand is indeed “constructed” from a nano-material (aggregated nano-silica) but the resulting material is no longer considered to be nano. According to BASF, EMACO\textsuperscript{®}Nanocrete shouldn’t therefore be classified as nano-product. This example (which doesn’t stand alone, there are various examples of products like this one brought at the market by different companies) shows the difficulty in:

1. where to draw the line between a nano and a non-nano product,
2. how to communicate (or not communicate) information on the production process to downstream users and
3. interpreting marketing and sales information that can easily invite you to unjust assumptions.

3.2.6 Near Future Expectations for Cement and Concrete

Like has been stated in the previous sections, it is probably still a long road to travel before CNT will become an accepted additive for cement and concrete materials. Far more likely it is to expect an increase in the amount of cement products containing significant fractions of ‘waste materials’ like fly ash (made possible by the improved understanding of hydration mechanisms via nanotechnological measurement and monitoring techniques) and an increasing number of high performance cements with improved ductility, strength and compactness. With silica fume for example, one could improve the material strength of concrete containing significant fractions of recycled concrete aggregates (see i.e. NICOM3 conference proceedings).

With respect to nano-material containing cements, titanium dioxide cements can be expected to appear in more and more applications. Nano-fibre containing cements, other than CNT, shall also be developed but are in early R&D stages yet\textsuperscript{27}. Concerning TiO\textsubscript{2} and TiO\textsubscript{2}-containing photo catalytic products, future developments

\textsuperscript{26} Personal communications
\textsuperscript{27} Personal communications
will also focus on preparing different TiO₂ materials that are sensitive also to other light wavelengths (like the visible light range) such that catalytic activity indoors (inside buildings or in tunnels) or at cloudy skies could be improved. Some first steps in this direction are already on their way as Italcementi for example does already market such products for tunnel walls.

Not discussed previously but actually close to real market applications is a technique under development to encapsulate specific additives to prolong the time before these additives start reacting. This technique might have high impact on the market, allowing for example for longer transportation distances of the pre-mixtures and for one large cement distribution plant to supply one large region, instead of many small plants having all their own local distribution areas. Another application of this type is to encapsulate additives in order to gradually release them to optimize for example the process of cement and mortel hardening (NICOM3 Conference Proceedings). This also might open a suite of possible applications, especially when one considers the large complexity of additives influencing each other starting when they get mixed. When one could get a better hand on the order in which these ingredients would react, the process of hardening could be further optimized.

### 3.3 Steel

The Nanoforum report *Nanotechnology and Construction (2006)*\(^{28}\) summarizes the state-of-the-art with respect to applications of nanotechnology to construction steel products. Intensive web- and literature search and personal communication with the sector suggest that the overview presented there seems to be the situation of 2009. One field where one can see some activity is the development of coating systems for metal protection, which will be discussed in more detail in section 3.5.

Like it is the case for concrete, technological advancements with respect to the properties of steel could principally lead to enormous cost benefits when these would result in longer material lifetimes (increased durability) or a reduced material use to build similar constructs. The tradeoff between steel strength and ductility is a significant issue for steel; the forces in modern construction require high strength, whereas safety and stress redistribution require high ductility. The presence of very hard nanometer-sized particles in the steel matrix can lead to a combination of these properties, effectively matching high strength with exceptional formability. However, when the particles become too small, this effect can again be reversed (an example hereof is described by Zhou et al 2008)\(^ {29}\).

Applications found today are:
- Improvement of strength and decrease of wear of stainless steel by manipulating the nano crystallization of the steel matrix\(^ {30}\) (products are found at the market, see later on in this section).


\(^{30}\) (WO/2005/118902) NANO-CRYSTALLINE STEEL SHEET
- Protection against delayed fracturing of joints and bolts in metal structures by adding vanadium and molybdenum nanoparticles, which reduces the embrittlement of grain boundaries in steel by small amounts of hydrogen (R&D stage, uncertain if such high strength joints and bolts are marketed products at this moment).
- Improvement of the toughness of welds by the addition of magnesium and calcium nanoparticles to the steel matrix (R&D stage, uncertain if such high strength joints and bolts are marketed products at this moment).
- Improvement of strength and decrease of wear of stainless steel by surface mechanical attrition treatment (SMAT) to induce nitriding of the steel.

There are several marketed steel products that use the expression nano in their naming but so far this mainly refers to a refinement of their material phases, i.e. reduction of the crystal size into the nano-regime. MMFX2 Steel by MMFX Steel Corp, Sandvic NanoFlex by Sanvik and Super Hard Steel (SHS) by The NanoSteel Company are examples of products in which the metal crystal size structure is reduced to below 75 nm resulting in a very strong steel of which the latter has a Rockwell hardness of 66-69 HRc and an impact resistance of 165 ft-lbs.

CNT have not been found to be applied yet. Main reasons given are the difficult interaction between steel and the CNT and the high temperatures used to work the steel that cause the CNT to degrade.

3.4 Insulation materials
Thermal isolation of buildings is an important issue in construction engineering. Although costs of investment (or disposal as in the case of asbestos) can be high, resulting energy savings can lead to much higher cost savings over the total lifetime of the building. Besides financial benefits, motives concerning the environmental footprint following such an investment may be clear as well.

In contrast to most nano-products, insulation materials do often not contain nanoparticles but rather consist of a matrix of nano-holes or nano-bubbles. Given the definition of a nano-material in Chapter 1, these products can be termed nano-products. When dealing with health and safety issues though, discussions on the uncertainty of nano-specific health hazards due to nano-holes are of a different level than similar discussions relating to nanoparticles.

Nanoporous insulation materials like aerogels and certain polymer nanofoams provide excellent capabilities in this area (Figure 0-11). As an indication, these types of products can be 2 – 8 times more effective than traditional insulation materials.

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32 http://www.mmfx.com/

33 http://www.smt.sandvik.com/nanoflex

34 www.nanosteelco.com/product/8000_twas.html
The aerogels for thermal insulation found today are most often silica or carbon based with approximately 96% of their volume being air. An example is the Insulair® NP nanoporous gel insulation blanket from Insulcon B.V. (Figure 0-12) that are flexible and specifically designed for extreme temperature applications.

![Figure 0-11 a) Improved isolation through aerogel based materials; b) Aerogel: evacuated nanopores in SiO2 matrix](http://www.spaceflightnow.com)

These “blankets” make use of a combination of silica aerogel particles (>100nm in diameter) and reinforcing fibers. It is the size of the pores or bubbles inside the silica aerogel particles that account for the name “nano”. An aerogel is a low-density solid-state material derived from gel in which the liquid component of the gel has been replaced with gas. This results in an extremely low density solid with pore sizes on the order of 20-40 nanometers. Insulair® NP nanoporous gel insulation blankets are available in several product forms for temperature ranges from cryogenic up to high temperature levels.

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

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35 http://en.wikipedia.org/wiki/Aerogel
36 http://www.insulcon.com/page/products/Microporous_and_Nanoporous_products.htm
37 http://www.spaceflightnow.com
39 http://www.aerogel.com/
Yet another way of isolating buildings is by applying special paints and coatings. Especially for large window facades this is a very interesting application of nanotechnology. Developments in this field are discussed in section 3.6.

Health and safety
Health and safety issues of aerogels are generally well understood and due to the fact that their nano-character is not based on the addition of nano-particles but on the formation of nano-holes, chances of unexpected health and safety risks due to this nano-character are not to be expected. At the moment, the market share of aerogels and nanofoams in the construction industry is small, but this is expected to be just a matter of time. In the current era where the sustainability and energy performance of buildings is listed in the top-10 of highest priorities, insulation is one of the big issues. Not only for new buildings, especially also for renovation projects where one is constrained by the building frame provided. In those cases, high effective and thin insulation materials could make a large difference. In the field of insulation materials, the market share of nano-products can therefore be expected to rise in the near future.

3.5 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”. A similar picture is sketched by a recent publication in Chemistry & Industry summarizing the findings of a report on Nanotechnology in the European Coatings Industry by IRL Consultancy. Of these, the 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. Nano-sized dispersions do have improved abilities to interact with the underlying surface, by deeper penetration into the upper surface layer, by improved coverage of irregular surfaces or by an increased coating-surface

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40 In-depth interview with BASF
interaction per surface area. Each of these results in more durable surface coverage.
2. Nano-sized ingredients are transparent allowing for a widened suite of possible applications that require the underlying surface to remain visible prior to coating. Wood and glass are typical examples thereof.
3. The possibility to produce transparent ingredients 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.
4. Improved methodologies (like ultrasonic milling and mixing or polymer dispersing) to homogeneously form and disperse nano-sized ingredients in the coating matrix now do allow for the actual application of these novel additives to obtain truly improved coating products.

These four factors come together in the development of new coating systems for wood, metal, ceramics, natural stone and concrete, which will be addressed in the following subparagraphs. A separate section will be addressed to glass because of its uniqueness and large diversity of nanotechnology applications.

3.5.1 Photo catalytic, anti-bacterial or self-cleaning wall paints
The surfaces of building facades are under the constant corrosive influence of weathering, traffic exhaust fumes or micro-organisms. Nanotechnology offers interesting ways to counteract these unwanted effects: e.g. via self-cleaning coatings. Depending on the specific coating matrix, these can be used on various substrates ranging from natural stone and concrete to ceramics, composite material, metal, plastics or wood. The four different coating-systems that are most observed at the market are based on an active working mechanism, photo catalytic or ionic, or a passive hydrophobic or hydrophobic/lipophobic surface mechanism (or a combination of those). In the following, their nano-characteristics will be discussed.

Self-cleaning coatings that actively degrade organic pollutants or micro-organisms such as fungi, algae or bacteria, thank their characteristics to the addition of small amounts of zinc oxide (ZnO) or titanium dioxide particles (TiO₂) that act via a light induced (photo catalytic) mechanism. The photo catalytic activity of ZnO or TiO₂ per gram of substance increases significantly as their particle size gets smaller and their respective reactive surface area per gram of material increases. Consequently at a similar weight percentage, the self cleaning characteristics of the coating become more effective and moreover, below a particle size of 60 – 100 nm ZnO and TiO₂ can also be used in transparent coatings without significantly affecting this transparency (because the particles size get smaller than the wavelength of visible light), opening a suite of new applications for which the underlying surface should remain visible. One example of such a nano coating is Arctic Snow Professional Interior Paint by Arctic paint LTD. Arctic Snow is a non-toxic, water based, interior wall paint containing nano-TiO₂ with anti fouling properties. An example of a coating containing ZnO nano-particles is Cloucryl by Alfred Clouth Lack-fabrik GmbH&Co.
KG. However, the smaller the particle size, the more elaborate their production process and the more expensive these substances become. As a consequence, when their nano-characteristics are not especially required, self-cleaning coatings do often contain ZnO or TiO₂ additives that are slightly larger than nano size to safe costs. One example hereof is a self-cleaning acrylic coating (Amphisilan) by Caparol that is based on nano-SiO₂ and TiO₂.

In addition to a photo catalytic effect, TiO₂ gives rise to a hydrophobic, water repellent coated surface that supports the coating’s self-cleaning characteristics as (rain) water easily slides down, washing the dirt away. In the specific example of Amphisilan (Caparol), this effect has been obtained by the addition of crystalline nano-Silica (nano-SiO₂). The nano-quarts reacts chemically with the acrylic acid of the coating binder forming a silane type of bond. As such a very strong and dense matrix is formed with an extra smooth and hydrophilic surface allowing for (rain) water to wash-off dirt. Adding SiO₂ however, has yet another advantage. At the interface between the coating and the mineral support (i.e. a basic wall), the SiO₂ binds on one side to the acrylic polymers of the coating and on the other side to the mineral side of the support underlayer, resulting in improved binding. This causes the coating to be more durable than SiO₂-free coatings. Other coatings in this range are TutoPROM by Clariant, a silazane anti-graffiti coating for e.g. concrete surfaces, and Sigma Facade Topcoat NPS (Matt), an acrylic paint by Sigma Coatings for dirt repellent surfaces made for new plaster, concrete, porous concrete, Eternit, tiles and limestone and surfaces previously treated with acrylic paints. The nano-ingredient of this latter product is unclear from the Sigma Coatings information supplied.

Photo-catalytic coatings containing TiO₂ are marketed using different keywords. Often these coatings are advertised as self cleaning or easy-to-clean and water repellent coatings. However, more and more these are commercialized with NOx reducing, air cleaning or air pollution removing character. Induced by (UV) light, TiO₂ does convert NOₓ to “harmless” NO₃, a natural soil fertilizer. Rockidan, the company that markets Amphisilan in Denmark, does sell this product by advertising the superb formaldehyde reducing powers as surplus. Yet another quality of these coatings is their ability to protect the underlying surface from UV-radiation. This is of particular interest on wooden structures and will be discussed in section 3.5.4.

Self-cleaning coatings that actively degrade micro-organisms such as fungi, algae or bacteria can also be based on Ag-compounds that work as a biocide by releasing Ag⁺ ions. However, the actual nano-character of this type of coatings is questionable and their working mechanism is open for critical review. The Ag-compounds consist most often of a carrier substance (like SiO₂) forming a grain on to which a thin

42 http://www.clou.de/frontend_live/start.cfm
43 In-depth interview with Caparol
45 http://www.clasencoatings.nl/nl/werken_met_silica/artikel_nieuwsbrief/gevel/index.cfm?fuseaction=soltec_selfclean&assetmetaAssetmeta_x_nChildID=70401
46 Personal communication with different paint manufacturers
(atomic) layer of silver has been condensed\(^47\). This could result in a nanostructure but, according to experts, is often not so (even though the methodology to produce these materials might be based on nanotechnology). Then, to act as a biocide, Ag\(^+\) ions need to be released which requires water to actually dissolve the ions. Bioni CS GmbH\(^48\) produces Bioni Hygienic (Figure 0-13), a fungi- and bactericidal interior wall paint that is claimed to permanently destroy even the most resistant of hospital germs and bacteria without contaminating the air inside the building. This claim could only hold when it involves a regular water-cleaning process of the hospital walls. If this is not regular practice, this paint is only of little value as the silver ions cannot be released and their biocide effect is not expressed, with the exception of high or extreme humidity rooms where there might be enough water in the air to facilitate the process. The Bioni Roof Dachbeschichtung coating for roof tiles is another Ag-based product by Bioni CS GmbH, which outdoor application is more likely to work\(^49\).

![Figure 0-13 Antimicrobial wall coating containing nano sized silver particles for use in clinics and hospitals](image)

A type of an easy-to-clean coating that is both water and oil repellent, is Fluowet ETC100 by Clariant. This protective coating for ceramics and glass is based on the addition of carbon-fluoride polymers (CF polymer) that give rise to a specific nano-structured surface to which neither water nor oily substances can bind. The CF polymers might be in the typical size range that would qualify them as a nano-material. However, their properties are those of the “traditional” substance, which does actually disqualify them as a nano-material. It is the surface structure these polymers create when the coating hardens that gives the coating it’s nano-character with the polymers standing out of the surface like closely packed tiny (nano-) hairs.

**Health and Safety issues**

In the above paragraph the emphasis was on four types of coatings: ZnO or TiO\(_2\), SiO\(_2\), Ag and CF polymer based coatings. The health and safety issues involved in applying the first two nano-coatings on site will be discussed at the end of this

\(^{47}\) In-depth interview with BASF


\(^{49}\) http://www.nanoproducts.de/index.php?mp=products&file=info&cPath=3_36&products_id=141&OSSID=cab8726442dafa1c91a892ce852e1f70
nanocoatings section as these will similarly apply to various other coatings for i.e. wood or glass surfaces.

As CF polymers are not really nano-materials but actually “traditional chemical polymer structures, their health and safety issues correspond to those of typical CF polymers of comparable length and structure and the methods to determine those hazards are well established. The CF polymer surface structure is relatively fragile and the nano- hairs might break “easily” when there is a force applied\textsuperscript{50}. However, when the nano- hairs break-off exposure will be to (possibly slightly smaller) CF polymers, or clusters of these, and will be in very low concentration. Again, no nano-material exposure is likely to be expected other than would be predicted by a standard risk assessment of such a coating.

The silver based coatings are interesting. Silver is not know as a human toxicant but it is uncertain if Ag-nanoparticles are equally not so. Especially also because silver-nanoparticles aren’t always pure silver but in the context of paints consist of a carrier grain (for example silica based) coated with a nano-layer of silver\textsuperscript{51}. Like macroscopic silver, the Ag\textsuperscript{+} ion is relatively low-toxic for humans. However, it is a very effective biocide and a persistent toxic to the environment (Luoma 2008) and therefore emission to the environment should be prevented. Because of the present uncertainties with respect to the health aspects of nano-Ag occupational exposure has to be dealt with carefully. Handles on how to approach such a risk assessment are described in chapter 4. Exposure might occur when the coating is brought onto the wall (inhalation of aerosols containing nano-Ag could be expected). Once the coating has been applied exposure risks do involve the emission of Ag\textsuperscript{+} but only at a wet surface (see discussion above). Inhalation risks are no longer to be expected at that point and occupational health risks might be an issue for cleaning workers. Occupational exposure risks to Ag\textsuperscript{+} ions though, are well known and their toxicity profile has nothing to do with any nano specific risks. In principle, for construction workers there might be a risk of getting exposed to the Ag-compounds upon sanding of the dried surface. The coating matrix will typically contain between 5-10 weight\% of Ag-nanoparticles (including the silver fraction and the mass of the carrier grain). The hazards introduced by inhaling the coating-binder dust will depend on the actual uptake of silver by the human body. Until more is known about the human toxicity profile of these Ag-nanoparticles it is difficult to quantify this effect any further and a precautionary approach towards exposure prevention is recommended (see also chapter 4).

3.5.2 Fire resistant coatings
A lot of research is ongoing into the use of nano-particles in the development of improved fire resistant coatings. Types of nano-materials explored in this context are CNT, titanium dioxide, silica dioxide and nano-clays. The resulting coatings are planned for use on metal constructs, wood, textile, concrete, composites and plastics. At present though, market applications are difficult to find (even though

\textsuperscript{50} personal communication with various coating manufacturers

\textsuperscript{51} personal communication BASF
websites do advertise for these products\textsuperscript{52}). Some R&D, specific for metal coatings is summarized in section 3.5.3, for glass coatings in section 3.6.

\textbf{NANORESIST\textsuperscript{53}} is one example of a market product applicable to concrete, metal, wood and insulation-material surfaces. Upon extreme heating, the surface coating, which composition is uncertain but might be based on a thin layer of nano-SiO\textsubscript{2}, turns into a ceramic (predominantly glass phase) layer that is able to withstand high temperatures\textsuperscript{54}.

\subsection*{3.5.3 Nanocoatings for metals}

Metal products in the construction industry know two key area’s that are the focus of coating R&D. One is the fire resistance, the second is corrosion protection.

Fire resistance of steel structures is often provided by a coating produced by a spray-on cementitious process. Current cement based coatings are not popular because they need to be thick, tend to be brittle and polymer additions are needed to improve adhesion to the steel construct. However, research into nano-cement (made with nano-sized particles) has the potential to create a new paradigm in this field of applications because the resulting material can be used as a tough, durable, high temperature coating. Mixing CNT with the cementitious material is one way of achieving such a matrix, making use of the excellent strength and binding properties of CNT. Nevertheless, suspected health and safety issues of CNT and the current high material costs prevent for the use of this potential. A potentially interesting alternative might be Polypropylene fibers and research in this direction is ongoing\textsuperscript{55}. However, as a coating system for metal protection no such products have been found to be at the market.

Many different paints and coatings are used for corrosion protection of metals, simply by shielding the material from corrodning agents like oxygen, water and salts. An example of a nano-product currently at the market is the anti corrosion layer for metals by the name of Bonderite NT-1\textsuperscript{56}. Henkel GmbH is its German mother company and it is put on the Dutch market by Mavom Chemical Solutions. It is a conversion coating that uses a leading edge nanoceramic, iron-, zinc- and manganese phosphate layer to increase the adhesion of paint and to improve the corrosion resistance of the underlying metal surface. The actual morphology of this coating and the form of the different metals (are they present as nanoparticle in the coating?) is uncertain. Bonderite NT-1 can be used on steel, zinc and aluminium surfaces. Various other products for the corrosion protection of i.e. steel and aluminium are produced by the Spanish company Nanocer (NTC Nanotechnologia)\textsuperscript{57}.

\textsuperscript{52} http://www.advancedepoxycoatings.com/
\textsuperscript{53} http://www.nanoresist.es/
\textsuperscript{54} http://www.qtelamerica.com/nanores.htm
\textsuperscript{55} Kutzing L, Fire Resistance of High Performance Concrete with Fibre Cocktails, Dipl.-Ing., Ingenieurba – Consult Mainz & Erfurt formerly with the Institut für Massivbau und Baustofftechnologie, Universität Leipzig
\textsuperscript{56} http://www.henkelauto.com.cn/automotive/News/2005/Bonderite+NT-1.htm
\textsuperscript{57} This same company Nanocer does advertise for a broad range of anti-corrosion, self-cleaning, fire-protective, anti-graffiti, scratch resistance and easy-to-clean products for concrete, plastics, glass, fibre
that does combine corrosion protection with passive and active photo catalytic self-
cleaning properties. Clearcoat U-Sil and Basecoat U-Sil are examples of these.
Nanocor developed by Incoat\textsuperscript{58} for corrosion and wear protection is another
product, which can be brought onto the metal surface by a nano-particle sized
plasma process. In this case, the applied coating does no longer contain any
nanoparticles as the plasma process “melts” the nanoparticles to form one layer. A
similar situation does exist for the use of nano-particle hybrid coatings for corrosion
protection that are applied by Electrophoretic deposition (EPD). As these protective
coatings are typically applied at the production facility of the metal product,
exposure risks at the construction site are not an issue. Welding activities and
exposure to welding fumes though, remains a source of nanoparticle exposure. It is
unclear to what extent nano-coatings will influence this.

3.5.4 Nanocoatings for Wood Surfaces
Wood products are used in construction for their many advantages but this use is
also bound to limitations. For example, because of its weathering properties by i.e.
rain and UV light, its ‘living’ nature and its relative material softness. Moreover,
because of esthetic reasons wood protection used to be only possible up to a certain
extent. With nanotechnology, coatings to protect and preserve wood surfaces are
now being developed for walls and facades (exterior), but also for parquet flooring
systems and furniture (interior). Most of these coatings 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 sceptisism regarding the durability of these
coating systems. Not so much for the scratch protecting coatings but especially with
respect to coatings protecting exterior walls and facades against water and UV
radiation. The word goes that these coating systems are extremely labor intensive
and need regular repainting (because this has been said to be the case for a great
deal of the first generation products such as some water repellent ones based on the
lotus-leaf effect)\textsuperscript{59}. As a consequence, these coatings have a hard time proving
themselves (even though the current critics might be unjust) and examples of true
applications at the construction site are scarce.

External influences, scratch protection
What does look like an upcoming market are high scratch resistant lacquers for
wooden flooring systems, e.g. parquet floors. Different types of coating systems are
found with this typical character. One is based on the addition of (amorphous) nano-
SiO\textsubscript{2} to an acrylic binder material, similar to the amphisilan (Caparol) described in
section 3.5. During drying of the lacquer, the SiO\textsubscript{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
products using this mechanism, listed in Table 0-3, are Bindzil CC30 (Baril Coatings),
Nanobyk 3650 (BYK Additives and Instruments) and Pall-X Nano (Pallmann).

\textsuperscript{58}\url{http://www.incoat.ch/beta/metal.html} and \url{www.nanopinturas.com}
\textsuperscript{59} Personal communication with various coating manufacturers and people from the wood sector

glass, ceramics, textile, mineral, wood and metal surfaces. 2K Clearcoat Et-Sil 110, Clean Glass and
NANOgraffiti-protector + are examples of products of their Construction portfolio;

Another high scratch resistant lacquer is based on the addition of nano sized Al₂O₃ particles, which mechanism is not fully clear but seems related to an improvement of the elasticity of the coating matrix. Various products of this type by BYK Additives and Instruments are listed in Table 0-3. BYK describes the principle of operation of their nano-coatings. In contrast to micron sized ones, nano particles show a stronger elastic efficiency because of the higher amount of particles per surface area and the decreased inter-particle distance that can be achieved at a similar mass percentage, which together results in a better elasticity of the coating matrix. The result is less deep and less rough edged scratches upon similar scratching activities. Already at 3 w/w% 25 nm Al₂O₃ particles good results are obtained, where it should be noted that sometimes better performance can be obtained with similar amounts of smaller particles (i.e. 40 nm versus 25 nm). Acrylic-water, Acrylic Urethane-water and polyurethane dispersion matrices are effectively improved by adding about 1 w/w% of 40-25 nm Al₂O₃. In a polyurethane coating, but also in other types of aqueous and non-aqueous coatings, nano-silicone can be sometimes added to improve the Al₂O₃ performance, showing its effect already at about 0.1 w/w%.

Table 0-3 Some coating nano-products developed for wood surfaces to improve scratch resistance

<table>
<thead>
<tr>
<th>Product</th>
<th>Producer</th>
<th>Active ingredient</th>
<th>Size (nm)</th>
<th>Function Scratch resistance in:</th>
</tr>
</thead>
<tbody>
<tr>
<td>NANOBKY 3600</td>
<td>BYK additives and instruments</td>
<td>Al₂O₃</td>
<td>40</td>
<td>Aqueous coating</td>
</tr>
<tr>
<td>NANOBKY 3601</td>
<td>BYK additives and instruments</td>
<td>Al₂O₃</td>
<td>40</td>
<td>Non-Aqueous coating UV</td>
</tr>
<tr>
<td>NANOBKY 3602</td>
<td>BYK additives and instruments</td>
<td>Al₂O₃</td>
<td>40</td>
<td>Non-Aqueous coating UV</td>
</tr>
<tr>
<td>NANOBKY 3610</td>
<td>BYK additives and instruments</td>
<td>Al₂O₃</td>
<td>20</td>
<td>Non-Aqueous coating</td>
</tr>
<tr>
<td>NANOBKY 3650</td>
<td>BYK additives and instruments</td>
<td>Silica</td>
<td>20</td>
<td>Non-Aqueous coating</td>
</tr>
<tr>
<td>LP-20693</td>
<td>BYK additives and instruments</td>
<td>Al₂O₃</td>
<td>40</td>
<td>Non-Aqueous coating</td>
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<tr>
<td>LP-20969</td>
<td>BYK additives and instruments</td>
<td>Al₂O₃</td>
<td>20</td>
<td>Non-Aqueous coating</td>
</tr>
<tr>
<td>LP-20637</td>
<td>BYK additives and instruments</td>
<td>ZnO</td>
<td>60</td>
<td>Aqueous coating</td>
</tr>
<tr>
<td>Bindzil CC30</td>
<td>Baril Coatings</td>
<td>SiO₂</td>
<td>7</td>
<td>Aqueous coating</td>
</tr>
<tr>
<td>Pall-X Nano</td>
<td>Pallmann</td>
<td>SiO₂</td>
<td>&lt;100</td>
<td>Aqueous coating</td>
</tr>
</tbody>
</table>

Pallmanns⁶⁰ produced nanoparticles of aluminum have unique spherical and non-agglomerated characteristics that result in very constant properties like transparency, refractive index, ductility and reactivity. Al₂O₃ is stabilized in the resin matrix by a wetting and dispersing mechanism that is based on detergent-like system of a polar head, interacting with the metal oxide, and an apolar tail, sticking into the resin matrix. Using this principle, CNT, ZnO, CeO₂ and Al₂O₃ can be dispersed equally effectively.

In addition to these, various types of coatings are being developed to protect or treat wood surfaces. One of the main issues in this context is to preserve the initial (fresh) wood esthetics: wood changes appearance as it gets older under the influence of e.g. UV irradiation, moist or rainfall and temperature fluctuations. The

nano-coatings developed protect against or delay these influences such that the wood retains its original appearance for a longer period of time.

**External influences, UV protection**

One of the methods to retard this process is by blocking the wood surface from UV light. 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. Organic UV absorbers are i.e. hydroxyphenylbenzotriazoles, hydroxybenzophenones, hydroxyphenyl-S-thiazines or oxalic anilides. Metal oxides are ZnO, CeO₂ and TiO₂, 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 TiO₂, that does show a cut-off around similar wavelengths but remains less transparent to visible light. On other disadvantage of using TiO₂ on wood is its UV induced reactivity that will act in a destructive way on the wood surface.

ZnO and CeO₂ are therefore the two nanomaterials used most often in the size range between 60-20nm (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 ⁶¹ is one example of a company advertising with a broad range of different such nano-products.

**External influences, water and oil protection**

Other coatings for wood mainly focus on the protection against water. Examples of these are 2937 GORI Professional Transparent marketed by Dyrup Denmark ⁶², Percenta Nano Wood & Stone Sealant ⁶³ (protection of wood and stone materials against water and oil, most likely based on nano-carbon fluorides), Pro-Sil 80 by NanoCer ⁶⁴ and Nanowood by Nanoprotect ⁶⁵

However, among these there is also a group of nano-products which nano-character is based on a very fine dispersion of oils in water. These nano-sized micelles are simply small vesicles of fat-molecules and have the advantage that they are very stable in the water (prolonging the expire date for use of the coating) and show improved covering and penetration of the wood surface structure. The result is an optimised coating of the surface that is better and more durable in its protection against water. Despite this, and despite the fact that the technology to produce these micel mixtures does hang on nanotechnology, the products themselves should not be considered to contain nano-materials and any health hazards involved in working with these coating systems have nothing to do with any nano-specific health issues.

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⁶¹ http://www.byk.com
⁶² www.dyrup.com
⁶⁴ http://www.intelcoats.com/nanop%20Indnanocer%20engl.html
⁶⁵ http://www.nanoprotect.co.uk/wood-protection.html
Moreover, as the micel interacts with the wood surface the vesicle will disassemble as the fats bind to the wood. Therefore, sanding or sawing treated wood panels will also not involve any nano-based health risks caused by the coating applied.

**Internal influences, bleeding of wood**

In contrast to external wear factors like UV or scratching, part of the properties of wood, and an integral part of the wood character itself, is the bleeding of complex chemicals like tannins that, in time, decolorize the wood surface. By treating the wood surface with a coating containing the appropriate nanoparticles, this gradual leaking to the surface can be blocked for a significant amount of time. By adding Hydrotalcite (Mg₄Al₂(OH)₁₂CO₃·H₂O; Nuplex) in the form of nanoclay particles, the tannins get trapped and immobilized by an ion-exchange mechanism. The performance of Hydrotalcite is enhanced by the addition of an acrylic dispersion that enlarges the available surface area for tannin-trapping. Already ~2.5 w/w% (between 0.3-4 w/w% depending on the particle size and the material type) of Hydrotalcite is sufficient to block tannins effectively, although a somewhat higher concentration is required at spruce knots. Due to its nano-sized nature, in 6 to 8 hours the Hydrotalcite primer dries as a transparent layer, allowing for many different applications from plain colored to wood-profiled surfaces. Products in this range are produced by BYK.

3.5.5 **Nanocoatings for ceramic products**

Various types of coatings developed for concrete, natural stone or glass products might similarly be used to protect or improve ceramic products. For example to improve further their scratch resistance and make them more easy to clean. The Nanoflex product family by Nano-Care Deutschland AG is an example hereof. Top-Ceram RAK100 for polished stoneware protection against water and oil, or Easyglas PC10 for high scratch resistance of polycarbonate or polymer surfaces are two others by the same company. Peitsman Fournituren B.V. with headquarters in Rotterdam is a wholesale in home furnishing trimmings. Their range consists among many other products of ceramic tiles with typical, “nano-enhanced” surface properties. A tough surface glaze incorporates nylon particles and nano-composite aluminium oxide particles for superior durability and a virtually stain-proof floor. Other products are i.e. roof tiles or tiles for road pavement. Like was discussed in sections, by the addition of TiO₂ or silica fume in the top-layer of these tile-products, this product can be made self-cleaning and the growth of moss can be retarded, and on top of that, the TiO₂ nano-products could assist in the reduction of NOx that is constantly produced by traffic.

3.5.6 **Pigments and dyes**

Even though when thinking about the construction industry thinking about pigments and dyes is not the first that comes to mind, these are essential additives in most paints and coatings and are good examples of materials that have been around since ancient history and which material particle size lays typically in the nano-size range.

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66 www.nanocare-ag.com

67 www.peitsman.nl
In the world of coatings, one of the biggest challenges is to maintain transparency, clarity and gloss while adding color to the coating. The transparency of the coating depends on the grain size of these chemicals just as it depends on the size distribution of other non-soluble additives in the coating (such as those to add characteristics like scratch or UV resistance). A number of water-based ultra-fine dispersed pigments from Clariant are shown in the table below (Table 0-4). Interesting from this table is the fact that most of the pigments are no metal oxides or inorganic materials but organic substances which are brought to nano-size. Within the field of nanotechnology, especially new fields of bio-inks, conductive inkjet inks, intelligent inks and color filters are thought to profit. Architectural and industrial coatings are also mentioned in the range of applications but are not seen as the major growth markets. By ultrasonic milling and dispersing (mixing) of pigment powders in the liquid coating material it recently became possible to improve the homogeneous distribution of the nano-powder, which is essential to guarantee performance and obtain the maximum transparency, clarity and gloss. This technical possibility furthermore allows for the addition of a larger set of organic and inorganic additives that used to be especially difficult to disperse well. Hielscher, Clariant, BYK Chemie, NETZSCH and IQ Chem Inc. are a few examples of companies that are clearly active in this field.

Table 0-4 Some examples of well known pigments (concentrated additive) offered at the market by Clariant which size distribution ranges between 50 and 120 nm

<table>
<thead>
<tr>
<th>Ultra-Fine Dispersions</th>
<th>Colour Index</th>
<th>Chemical class</th>
<th>Pigment content</th>
<th>Light fastness</th>
<th>Particle size distribution (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow GR</td>
<td>P.Y. 13</td>
<td>Diarylide</td>
<td>40</td>
<td>6</td>
<td>89</td>
</tr>
<tr>
<td>Yellow HR</td>
<td>P.Y. 83</td>
<td>Diarylide</td>
<td>35</td>
<td>7</td>
<td>57</td>
</tr>
<tr>
<td>Red HF3S</td>
<td>P.R. 188</td>
<td>Naphtol AS</td>
<td>40</td>
<td>7</td>
<td>92</td>
</tr>
<tr>
<td>Red FGR</td>
<td>P.R. 112</td>
<td>Monoazo</td>
<td>45</td>
<td>7</td>
<td>90</td>
</tr>
<tr>
<td>Red D3G</td>
<td>P.R. 254</td>
<td>Diketo-Pyrrolo-Pyrrol</td>
<td>35</td>
<td>7</td>
<td>118</td>
</tr>
<tr>
<td>Red F5R</td>
<td>P.R. 170</td>
<td>Naphtol AS</td>
<td>35</td>
<td>6</td>
<td>84</td>
</tr>
<tr>
<td>Red P2GL</td>
<td>P.R. 179</td>
<td>Parylene</td>
<td>25</td>
<td>8</td>
<td>70</td>
</tr>
<tr>
<td>Rubine F6B</td>
<td>P.R. 184</td>
<td>Naphtol AS</td>
<td>40</td>
<td>5</td>
<td>73</td>
</tr>
<tr>
<td>Magenta E</td>
<td>P.R. 122</td>
<td>Quinacridone</td>
<td>20</td>
<td>7-8</td>
<td>68</td>
</tr>
<tr>
<td>Violet RL</td>
<td>P.V. 23</td>
<td>Dioxazine</td>
<td>40</td>
<td>7-8</td>
<td>64</td>
</tr>
<tr>
<td>Blue B2G</td>
<td>P.B. 153</td>
<td>Phthaloxyanine</td>
<td>30</td>
<td>8</td>
<td>73</td>
</tr>
<tr>
<td>Green GN</td>
<td>P.G. 7</td>
<td>Phthaloxyanine</td>
<td>40</td>
<td>8</td>
<td>62</td>
</tr>
<tr>
<td>Brown HFR</td>
<td>P.Bk 25</td>
<td>Benzimidazolone</td>
<td>25</td>
<td>8</td>
<td>81</td>
</tr>
<tr>
<td>Black T 30</td>
<td>P.Blk 7</td>
<td>Carbon black</td>
<td>30</td>
<td>8</td>
<td>57</td>
</tr>
<tr>
<td>Black TS 30</td>
<td>P.Blk 7</td>
<td>Carbon black</td>
<td>33</td>
<td>8</td>
<td>57</td>
</tr>
</tbody>
</table>

If nano-sized pigment preparations should be characterized as nano-materials or not remains disputed. By simply following the lines set out by the definition of nano-materials applied in this report (section 1.1) one has to decide they should. Here one stumbles across one of difficulties in the discussion about nano-materials and products, (precautionary) health and safety measures and regulation.
3.5.7 Health and Safety

Occupational exposure to a nano-coating could occur when the coating is prepared (in case of a two component system), when the coating is applied (by rolling, brush or spray application) or when a coated surface is cut, sanded, or otherwise worked. This also involves activities like cleaning and maintenance of the equipment and cleaning up spills.

When a coating is prepared or applied, 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. Consequently also, occupational exposure risks are likely to be larger when working indoors than for outdoor work.

Once the nano-coating is applied and has dried, exposure risks to nano-materials added to surface coatings should be addressed on the basis of the actual interaction of the nano-material with the coating binder. In short, a nano-material can be:

1. inert to the binder but able to physically interact. This results in a coating matrix in which the nano-material is embedded in the binder but did not chemically react with the binder. This way the nano-material remains “loose” and could principally leach out.

2. chemically reactive to the binder. This results in a chemical bond between the nano-material and the binder, making it highly unlikely for the nano-material to leach out.

In the first scenario, there is a chance of occupational exposure of construction workers working a coated surface (for example due to sanding). Three different scientific studies were found to study the exposure potential.

The work of Kaegi et al. (2008) suggests this exposure might be in the form of a similar type of dust that would have been produced in a similar activity on non-nano-coatings. However, in this case the dust does contain the nano-additive with its respective implications to human health. Kaegi et al. (2008) shows the emission of TiO₂ nanoparticles from exterior facades from TiO₂ containing coatings. They observe that these particles become exposed at the surface as the coating wears and run off with the rain water. Interestingly though, they observe that the particles do not run off as plain nano-particles but take with them part of the matrix in which they were embedded. This latter observation hints at a mechanical wear process rather than a leaching (or evaporation) of TiO₂ from the coating and does suggest that the TiO₂ does bind to the coating matrix with forces that lay in the same order of magnitude as the inter-matrix-forces themselves.

This same study does also suggest that nano-TiO₂ used in coatings for exterior application is more of an environmental problem than an occupational health problem.

Another interesting work by Vorbau et al. (2009), supporting the observations by Kaegi et al. (2008), studies the potential exposure to nanoparticles as a result of domestic abrasion of nano-ZnO containing coatings on either wood or metals surfaces. Three different types of coatings were studied this way: a polyurethane, an
aliphatic urethane acrylic and a styrene acrylate copolymer coating. The abrasion effectiveness of the coating was seen to depend on the type of surface the coating was applied to (the metal surface appeared less susceptible to abrasion than the fiberboard surface) and the type of coating applied. The addition of nano-ZnO particles to a coating matrix had almost no observable effect to the wear of the coating as a result of abrasion. From this study is suggested that nano-particle containing coatings are not expected to result in an increased degradation (wear-off) because of the nano additive. Moreover, this same study could not detect any nanoparticles (smaller than 100nm), nor nano-ZnO released during wear. Instead, nano-ZnO was observed as part of the matrix of the more large wear particles that were formed.

In addition to these two studies, Koponen et al. (2009) studied the release of nanoparticles (TiO₂ and carbon black) upon sanding of various wall paints. The study itself was not conclusive to the question if nano-TiO₂ was released as nano-particle or not. What was observed was that the ultra fine particles detected were dominated by the nanoparticle exhaust emission of the sanding machine. Sanding a painted wall in the presence or absence of nano-TiO₂ did not change the exposure characteristics to any significant extent.

The above cited studies do shed some light on the possibilities of exposure to nanoparticles from painted surfaces containing these particles embedded in the paint matrix. First results in this direction do look promising in a sense that no nanoparticles were observed to be released as such. However, the work done on this topic is still too limited to draw further conclusions regarding exposure risks to nanoparticles from working nano-coatings 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.

In the second scenario, where for example crystalline nano-silica polymerizes in the paint matrix, exposure to nano-silica by leaking, wear or sanding of the paint surface is not readily to be expected. The chemical bond formed between the acrylate and the quarts makes it highly unlikely that exposure to the crystalline nano-SiO2 occurs when the coating is brushed, when the coating wears during use, or when an end-user works on the coating by i.e. drilling holes. However, chances of exposure to the non-reacted nano-SiO2 do remain, though it is yet not possible to quantify this risk.

As is shown by Kaegi (2008), Koponen et al. (2009) and Vorbau (2009) for different nano-coating systems, when the nano-coating wears (naturally by weather conditions or artificially by sanding or abrasion) the nano-particles studied (TiO₂, ZnO and Carbon Black) are likely to be released embedded in the “coarse” dust produced. When this dust gets inhaled, it can be expected that the workers are exposed to the nano-particles at the dust grain surface (and possibly also to those

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68 Personal communication
69 Personal communication
nanoparticles embedded in the dust), which might induce adverse health effects. Protective measures are further described in chapter 0.

3.6 Nanotechnology and glass
Because of the “novelty” of nano-materials to add a specific performance to a product without significantly affecting its transparency a lot of research is being carried out on the application of nanotechnology to glass. Typical products that are at the market do focus on:
1. Indoor climate control, one of the major issues of buildings with large glass facades.
2. Heat or fire protection.
3. Easy-to-clean or pollution reduction.

The principles of operation of a number of these products were already discussed in the context of coatings for concrete and wood and photo catalytic wall paints. Interestingly for glass is that the coatings normally do not have to withstand heavy loads, which allows for somewhat more freedom in their design. However, number one priority is their transparency that should be granted.

Health and safety issues of coatings for glass are assumed similar to the ones described for other nano-coating systems (section 3.5). That is, it is unlikely that construction workers will undergo any significant occupational exposure by working with glass coated with nano-coatings. This is moreover so because in almost all cases the glass is coated (or prepared) at the manufacturer and enters the construction site ready-for-use and ready-for-placement. No cutting, sanding or drilling has to be performed anymore. However also, a significant part of the products has been produced by using nano-materials that were thermally or electrically annealed to form a thin film of the same material of only nanometer thickness.

Figure 0-14 (left) Glass facades for buildings form a large scope for nanotechnological innovations in the construction industry (right) Reversible transformation of a chemical between two forms by the absorption of electromagnetic radiation, where the two forms have different absorption spectra. WO₃ (tungsten oxide) nanoparticles can reversibly change their optical properties with the application of an external voltage.
In the following subsections a number of the most often encountered fields for applications on glass in the construction industry are being discussed.

**Indoor climate control**
Most of the glass in construction is on the exterior of buildings (Figure 0-14). The control of light and heat entering through building glazing is a major sustainability issue and a typical office building (like the one shown in Figure 0-14) requires constant cooling of the indoor environment by active airconditioning systems. R&D activities towards nanotechnological solutions centre around four different strategies to block light and heat coming in through these windows. Firstly, thin film coatings are being developed that selectively filter-out certain ranges of unwanted infrared light that otherwise would cause the interior of the building to heat up. These type of filters work permanently to reduce the heat gain in buildings and are therefore considered a passive solution. An example of these is Econtrol®-Glas GmbH & Co70 in Germany that produce glass sheets with a laminated polymer film containing solar heat adsorbing nanoparticles. Others are various window films by 3M71 and ssg COOL-LITE, ssg PLANITHERM 4S conservatory glass and ssg BIOCLEAN COOL-LITE ST Self-cleaning glass by Saint-Gobain72 of which the latter combines the reflection of infrared radiation (according to their website upto an approx. 50-66% efficiency) with active self-cleaning properties (see the next section) via the superposition of two functional layers.

In addition to this passive one, more active indoor climate control solutions are being studied that make use of thermochromic, photochromic or electrochromic technologies. Like their names already do suggest these systems react on respectively temperature, light intensity or applied voltage by changing their absorption to infrared light in order to keep the building cool. The first two can be considered environmentally regulated as these react on environmental impulses. The third is 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 (WO₃) applied on the glass surface does become more opaque absorbing more infrared light (Figure 0-14). Electrochromic glazing can be reversibly changed from clear WO₃ to dark blue (H₄WO₃) by hydrogen ion insertion. The clear advantage of this manual system is that for example in winter at high light intensity the voltage can be switched off resulting in a less absorbing window to use whatever solar radiation to heat the building. Or in summer, when it is warm but the light intensity is medium, to switch on the voltage to block whatever infrared radiation is out there to prevent the building from heating-up further. An example of this type of system that was however not developed for infrared but for visible light blocking is ssg PRIVA-LITE by Saint Gobain that gives you privacy or transparency at the flick of a switch. The same company does sell electrochrome glass for infrared reflection though oriented at the automobile industry.

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70 http://www.econtrol-glas.de/
71 http://solutions.3m.com/wps/portal/3M/en_US/WF/3MWindowFilms/
72 http://www.saint-gobain.com/en
Figure 0-15 Lotus effect: Self-cleaning effect based on extremely water-repellent behaviour known as super hydrophobia.

Self-cleaning
The same large glass facades that ask for extensive indoor climate control are demanding with respect to regular cleaning to keep the building shiny. Solutions to the problem of constant accretion of pollutants are to prepare surfaces where the pollutant cannot stick to (and will wash off with an average rainfall) or to prepare surfaces that actively degrade any stuck pollutant (and let the degradation products being washed off).

The first is often addressed to as the lotus effect. A schematic of their working mechanism has been shown in Figure 0-15. The principle is based on an effective reduction of the surface area to which any pollutant might stick. This cleaning strategy is observed in nature on lotus plants’ leaves. Their microscopic structure and surface chemistry make sure that the leaves never remain wet and stay clean. Instead, water droplets roll off the leaf’s surface, taking mud, tiny insects, and contaminants with them. Artificially, this same effect can be obtained by treatment of the surface with SiO₂ or silver nanoparticles held in colloidal solutions of water or alcohol (typically). The particles adhere to the surface and self-organize into a thin layer. After evaporation of the carrying solution, a lasting hydrophobic surface is created. Contaminants are simply washed off by rain or when rinsed with water. This type of coating is one of the few that is not necessarily produced at the glass manufacturer but can be manually applied as a spray-on liquid. Examples of products are Nanoprotect®, NewPro®, Nanotol®, and x-view®. However, given the average construction site, it remains questionable if these coatings are actually applied there. It is more conceivable to imagine that for most coatings the glass preparation is done in store of the manufacturer or glass supplier. Under these conditions, one might expect no realistic exposure of the construction worker to any of the colloid systems used to prepare the glass. However, for those nano-coatings that are applied at the construction site, spraying of these coatings will likely introduce a risk of exposure through inhalation by forming aerosols. At this moment,

73 http://www.nanoprotect.co.uk/
74 http://www.g-pro.com/English/150/1.htm
75 http://www.nanotol.de/
not much is known about the actual exposure to nanoparticles as a result of spraying different nano-coatings\(^76\).

The second method to obtain self cleaning glass is by using nano-TiO\(_2\). Like has been
described in section 3.5, TiO\(_2\) is used for its sterilizing and anti-fouling properties.
Under the influence of UV-light, the particles catalyze powerful reactions which
breakdown organic pollutants (including NO\(_x\)), volatile organic compounds and
bacterial membranes. In addition, TiO\(_2\) is hydrophilic and this attraction to water
forms sheets out of rain drops which then wash off the dirt particles broken down in
the previous process. Glass incorporating this self cleaning technology is available on
the market today. BIOCLEAN Self-cleaning glass by Saint Gobain is one of such a
product. Pilkington Active self cleaning glass from the British Pilkington company\(^77\) is
another example currently on the market. However, from their website the active
layer of nano crystalline TiO\(_2\) has erroneously been considered to consist of TiO\(_2\)
nano-particles. In fact a TiO\(_2\) layer is deposited from crystalline TiO\(_2\) nanoparticles by
a high-temperature gas-phase process, which does result in a nano scale crystalline
surface morphology. This structure is the reason for its interesting properties. When
the ultraviolet (UV) component of sunlight interacts with the titanium dioxide the
energy of the UV light is adsorbed; if moisture is present from the atmosphere,
strongly oxidizing free radicals are formed, which clean the glass surface. Glass
cleaned in this way becomes super hydrophilic forming water to spread across the
surface, rather than beading, thereby washing away debris from the surface. It can
be used both for anti-fogging coatings and for self-cleaning windows, but is
sometimes also claimed in the function of an air pollution reducing coatings.

**Heat resistance**

In addition to climate control, fire-protection and heat resistance are essential
elements of materials used in construction. In this line, fire-protective glass is one
application of nanotechnology that is currently under development and various
methodologies are studied to obtain this effect such as thin, transparent (e.g. nano-
sized) metal oxide coatings on glass or thin glass sandwich panels with a clear
intumescent\(^78\) interlayer made of silica fume. The first system simply works by
reflecting heat radiation. SCHOTT PYRAN™ EW by SCHOTT\(^79\) is one type of such a
product based most likely on rutile nano-TiO\(_2\). Pyrodur™, Pyrodur™ Plus,
Pyroshield™ and Pyrostop™ by Pilkington might also be products of this type,
although detailed product information is difficult to extract from the website.
The second system is slightly more advanced in a way that the nano-silica gel reacts to
form a rigid and opaque fire shield when heated. Saint-Gobain, France, is one of the
companies that have these type of products at the market. INTERFLAM™ and
INTERFIRE™ by the Swiss based company INTERVER AG\(^80\) are two other products of

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\(^{76}\) Personal communications

\(^{77}\) http://www.pilkington.com/EUROPE/uk+and+ireland/english/default.htm

\(^{78}\) An intumescent is a substance which swells as a result of heat exposure, thus increasing in volume, and
decreasing in density. Intumescent are typically used in passive fire protection.


\(^{80}\) http://www.interver-special.com/Englisch/index.htm
this type and have been applied in various types of buildings in i.e. the cities of Stockholm, Lund, Ingolstadt, and Heilbronn.

**Antireflection**
XeroCoat® is an antireflective glass using a single layer of nano porous SiO₂. XeroCoat uses simple sol-gel chemistry in combination with conventional spin, dip or spray coating techniques, to produce highly uniform, optically transparent, mechanically robust thin silica films with a controlled refractive index. The refractive index of the porous coating is between that of the glass substrate and air. This reduces the reflectivity and increases the transmission of light at the glass surface. AMIRAN® by SCHOTT is just another example of antireflection glass for architectural applications.

### 3.7 Nanotechnology and Infrastructure
Many R&D work in the field of nanotechnology is looking at new, improved materials and products for infrastructure. Areas of ongoing research do focus on i.e. durability, noise reduction and smart energy collecting systems. In the field of sustainability and environmental pollution control, there has been done a lot of investigation into the possibility to reducing air pollution from trafic exhaust with the help of a TiO₂ activated road. By a similar photo catalytic reaction as was described previously in section 3.5, TiO₂ does degrade organic pollutants (including polyaromatic hydrocarbons) and converts hazardous NOx to NO₃⁻ with a claimed efficiency that could (under optimum environmental conditions) give rise to a reduction up to 60% of the original NOx concentration (Nanotechnology and Construction 2006). However, as a direct mix with asphalt, this material is too expensive and not reactive enough to effectively reduce any pollution (nb. TiO₂ only reacts at the very top-layer to where UV light can penetrate)⁸². In the form of a top-layer coating though, results proved more promising. In 2006 in France, the first self-cleaning road was taken into use that was paved with NOxer® concrete blocks developed by Eurovia and Mitsubishi Materials (see Figure 0-16). These blocks come with a relatively thin layer of nano-TiO₂ containing concrete and can be used as paving stones for roads and sidewalks. However, a similar system could be designed for walls, sound-walls, facades and tunnel-entries (for example), and it shouldn’t be surprising that around that time, various different companies like ItalCementi and Heidelberg Cement started producing comparable materials in the form of bricks, blocks, panels and tiles.

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⁸¹ http://www.xerocoat.com/
⁸² In-depth interview with KWS
Figure 0-16 Left is a side walk in Japan paved with NOxer®, right are TX Aria road pavement blocks by the Italcementi group.

At the website Mitsubishi claims “a 3-kilometer stretch of NOxer® with a 5-meter width will remove about 10% more NOx than 800 ginkgo trees per year”. However, this productivity number depends strongly on the amount of sunny days per year and other weather conditions like wind and rain. Moreover, in order to maintain an optimum reactivity the reactive surface should be cleaned periodically. NOxer® has been utilized in various cities in Japan, as well as at European locations like in Milan (It), London (UK) and Madrid (S) where the material has been used on a street called Martín de los Heros near Moncloa Metro Station. A few years ago, the demand for NOxer® was growing both in Asia and Europe with expected yearly sales between 3,000 to 10,000 square meters of the material (expectation for 2007-2008). The major barrier for large scale market introduction are the costs involved, which unit price around 2007 was about 150% that of plain (no-NOx reducing) paving stones.

Figure 0-17 The preparation of a KonwéClear road (picture from Bouwend Nederland Podium 22, 14 Dec. 2006).

A second type of product with a similar functionality is KonwéClear84. Instead of bricks or blocks this material can be used on “normal” asphalt, which is impregnated on-site with a titanium dioxide containing cement-slurry. The asphalt type used as a best basis is ZOAB (very open asphalt concrete). The KonwéClear is produced on-site

84 http://hbo-kennisbank.uvt.nl/cgi/av/show.cgi?fid=3698
and applied manually or by using a similar machinery that is used to work asphalt concrete. The first Dutch pilot at the initiative of KWS dates from 2005 (at the Groenewoudsedijk, Utrecht\textsuperscript{85}) and in 2008 a pilot at Schiphol (the main Dutch airport\textsuperscript{86}) followed. However, also in other European cities trials have been run (Dinan (F), Antwerp (B) and in Italy). The photo catalytic performance of this system has been proven under laboratory conditions showing a significant conversion rate. However, in practice it is far more difficult to prove a working principle\textsuperscript{82}. Together with the cost issue (like for the NO\textsubscript{xer}\textsuperscript{®} blocks) this prove of principle under real life conditions is currently one of the obstacles for any large scale market introduction. Other limitations are the safety requirements set for different types of roads. For example, highways are potentially the target location for future application. However, for this to happen more pilots tests are required to prove in practice (as well as under standardized laboratory conditions) that road safety can be guaranteed under all applicable weather conditions.

\textbf{Figure 0-18} TX Aria tunnel ceiling coating (left) and sound barrier coating (right) for active pollution reduction by the Italcementi group.

Despite the promising potentials of KonweClear, it has to be said that this system, in the present designs, does interfere with other highly required properties like sound reduction. According to the information from KWS, the sound reducing effect of a ZOAB asphalt layer is being removed when KonweClear fills the pores of the asphalt material. Furthermore, the contact time for photo catalysis and the total surface area of a road are relatively low, which limits the NO\textsubscript{x} and pollution reducing capacity. Ongoing developments therefore focus on introducing similar photo catalytic reactivity to the walls of tunnels and the sound barriers placed near traffic intensive roads (like are shown in Figure 0-18), which, in practice, will have a more large potential to show any significant reduction in exhaust fumes, including a broader range of applications and less demanding service and maintenance.

\textsuperscript{85} http://www.kws.nl/bin/ihp.jsp?ihpDispWhat=zone&ihpPage=S6_FocusPage&ihpZone=S6_KWS_Luchtkwaliteit&ihpDisplay=view&

\textsuperscript{86} http://www.kws.nl/bin/ihp.jsp?ihpDispWhat=object&ihpPage=S6_FocusPage&ihpDispWho=STNI_ITEMS%5El3893&ihpVersion=0&ihpZone=S6_Nieuws&ihpDisplay=view&
3.7.1 Health and Safety
The raw material of KonweClear comes in big bags as a powder mixture containing predominantly portland cement additivated with about 5% of anatase TiO2. Prior to use, this powder is mixed with water to obtain the slurry used to impregnate the asphalt top-layer. Health and safety measures taken to prepare the slurry are as prescribed by de raw material producer and similar to the procedures normally used to prepare cement. This implies a closed mixer-system and normal inhalation protection against cement-dust, but no additional “nano-measures”.

When applying the material slurry, one can expect a minimum exposure risk to any airborne TiO2. Only there where spills dry, cement dust could form that could be a potential source to inhalation. When the material dries, the TiO2 is embedded in the cement-matrix. Although not covalently bound to this matrix, TiO2 is strongly fixed. It is therefore not expected that the nanoparticles leak out. Tests on the nanonature of wear products have not been performed. Based on the study by Kaegi et al. (2008) described previously in this report, it is nevertheless suggested that emission of nano-TiO2 does take place upon wear of the coating film when pieces of the cement material come loose, forming TiO2-containing cement dust as the main wear product. The emission of pure TiO2 nanoparticles is not readily expected because of the high surface forces that are involved.

With respect to the life cycle of this type of asphalt KWS states that a typical top-layer is expected to last between 5 and 20 years depending on the type of traffic and its intensity. This is similar to the normal life time of non-treated asphalt. The addition of fine sand furthermore assures the required surface roughness. At the end of life, the top-layer is taken off separately and can be reused as foundation material. The remaining asphalt can be recycled into new asphalt, which does require no extra processing steps.

3.7.2 Near Future Developments
Further developments in this field are optimization of the production process of the cement and the development of different matrices, for example resin based TiO2 slurries or more fluid water-based cement slurries to allow for a deeper penetration into the asphalt layer and a more broad range of applications. Related to the TiO2, ongoing work aims at the preparation of TiO2 that can get photo activated by more long radiation wavelengths that reach into the visible light spectrum such that a similar photo catalytic activity can be obtained indoors or in tunnels with artificial light only.

3.8 Nanotechnology and Other Construction Materials
The product groups discussed in the previous sections do not include all types of products that find their way to the construction industry. Important ones that were not included for various reasons are nanotechnological developments in the field of exterior and interior light-systems, photovoltaic energy systems, nano-sensors, textiles, composites and plastics. Interesting developments are ongoing in these fields also. However, judged from other R&D areas their market share is still very
small and nano-products for the construction industry might only start to appear in the years to come. Partly though, the different coating systems discussed above (or their principles of operation) are relatively easily adapted (and are explored) to be used on these product groups also. Some examples are the use of anti-reflective coatings to improve the efficiency of photovoltaic cells, applying scratch and UV-protective systems to composites and plastics, or the use of nano-silver on textile.

In some sense, what was presented in the above sections could also be read as basic building blocks of nano-materials and products for construction product innovation in general. One striking example hereof is the broad range of applications explored and developed for TiO₂, ranging from concrete to ceramics to wood to glass to asphalt. Essentially, by making use of the appropriate coating system, practically each type of surface could be given a photo catalytic activity. And this is just one example.

Outside the scope of this inventory of the use of nano-materials in products used in the construction industry remain different product groups that are not exclusively characteristic for the construction industry. Concerned product groups are for example:
- Cosmetics (for example the suntan creams containing nano TiO₂ sunscreens. These creams are intensely used by outdoor construction work in summer).
- Fuel (a nano-material is for example the use of CeO₂ as a catalyst in diesel fuel)
- Lubricants (no systemic research has been carried out in this sector, but different nano-applications are described in the scientific literature)
4. Health risks

4.1 Introduction
Evidence is building up that nano-materials could behave more hazardous to humans than their micro scale equivalents. Still, the emphasis should be on the word ‘could’ because at this moment in time (2009) knowledge is too limited to generalize. Like has been addressed in the previous chapters, nano-materials and nano-products might pose unexpected health risks to those exposed because of the same unique chemical and physical behavior that makes them interesting for product innovation in the first place. The two main factors influencing their toxicity are:
1. Size
2. 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 brain (Oberdorster et al. 2004),
- Some nanoparticles might be able to cross the placenta and reach the fetus (Hagen et al. 2007),
- 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 that 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 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. As long as no exposure can be guaranteed there will be no health risk. In the following sections the three potential exposure routes inhalation, dermal contact and ingestion will be shortly addressed. Starting from there a handle will be given for how to perform a precautionary risk assessment from limited information when hazards are not well known and how to take possible appropriate risk management measures. The red line through the whole story is how to use what we do know about working with (hazardous) chemicals to deal with the present unknowns related to the health risks of nano-products.

4.2 Exposure routes
When speaking about exposure to nanoparticles, it should be realized that in the construction industry exposure of workers will be (almost without any exception) to nano-products. With this is meant: products in which nanoparticles (or nano-materials) are embedded (in a solid matrix or in a liquid or slurry). This does impact on the actual exposure of the worker to the nanoparticle in the product. For example, when a worker inhales dust containing nanoparticles, the actual nanoparticle dosis 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.

In the following three subsections light is shed on the three different ways in which construction workers might get exposed to nanoparticles 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 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) under the similar conditions and might (given the often dominant focus on inhalation protection) become an issue in practice when the climate tempts workers to work partly undressed (e.g. road workers). Exposure through ingestion is not expected to be an issue as long as personal hygiene is cared for. However, again in reality chances are of ingesting nano-material containing dust or paint at lunch or coffee when hands and faces are not properly washed. Exposure to nanoparticles by handling solid (prefab) nano-products like nano-enhanced ceramics, glass, steel, plastics, composites, insulation materials, concrete or wood without machining it in any way is expected to be very small (if any) due to the fact that it is expected to be contained in the solid matrix.
4.2.1 Exposure through inhalation
Exposure through inhalation of small airborne particles (in particular Fine Particles: PM2.5 PM10) and consequent health hazards have been studied intensely over the past years in the context of health effects caused by industrial activities and traffic exhaust. Typical health effects observed are (NEAA 2005 and references therein):
- Inflammation of the airways
- Bronchitis
- Asthma
- Cardiovascular effects

For these particles (PM10 and PM2.5) the general rule of thumb has been: the smaller the particles, the more deeply they can penetrate the lungs before they deposit, the more severe their effect on health might be. More recently, focus has been shifted more towards the Ultra Fine Particles (UFP) of PM0.1 (particulate matter smaller than 100nm in diameter, generally called nanoparticles) because some experimental evidence does suggest that it are actually these particles responsible for part of the health effects observed for the more large fine particles (Seaton et al. 1995, Donaldson et al. 2001, Daigle et al 2003). UFP could be considered nothing more than unintentionally produced nanoparticles and it is therefore proposed that these are a reasonable first model to describe the potential behavior of inhaled non-soluble intentionally manufactured nanomaterials (generally called engineered nanoparticles = ENP). Experimental studies on the effect of UFP in test animals did show effects like translocation\(^{87}\) (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 (Oberdorster et al. 2004 and references therein; and for a more recent review on the topic by Politis et al. 2008).

In-depth study on the deposition behaviour of nanoparticles however showed that below a certain particle size, the rule of thumb established for PM10 and PM2.5 does no longer hold (Oberdorster et al. 2003). Figure 0-19 (Oberdorster et al. 2003, taken from the ICRP, 1994) illustrates the deposition probability of spherical particles in the different airway regions depending on their particle diameter. Interesting is that for nanoparticles with a diameter between 5 and 300nm indeed the largest probability is to end up in the deepest parts of the lung (~50%). However for nanoparticles smaller than about 20nm the probability of ending up in the nose and most upper airways starts to increase significantly until it dominates fully for the smallest nanoparticles with a diameter below 5nm.

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\(^{87}\) 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.
Figure 0-19 Modeled total particle deposition probability in the respiratory tract, and deposition probability in the alveolar region (ICRP, 1994). Deposition has been modeled assuming adults breathing through their nose at 25 l/min (light exercise), and exposed to spherical particles with a density of 1000 kg/m³.

The particle size thus has a major impact on the place where deposition in the airways might occur and consequently what health risks are to be expected (Witschger and Fabriès 2005; Oberdörster 2005b). Not only because of the particles themselves, but also because of the local surface area of the specific part of the airways involved that has to deal with these particles. Especially for the nasal area this implies an enormous burden on the natural defense mechanism of the human body against particles smaller than 20nm (Kim and Jaques, 2000; Schiller et al., 1988; Jacques and Kim, 2000; Daigle et al., 2003; Oberdörster, 2005a, 2005b; Zhang et al., 2005b).

Insoluble particles are normally removed from the upper airways together with the mucous to the digestive system, within less than 24 hours (Kreyling et al., 2002). In the deepest regions of the lung, at the alveolar level, macrophages or “killer cells” will take to remove the insoluble particles with a phagocytosis mechanism. They surround the particles, digest them if they can and direct them to be removed with the mucous. This process is relatively slow and it may take up to 100 days to remove about 50% (HSE 2004a, 2004b; Oberdörster, 2005b).

The efficiency of “digestion” depends strongly on the particle’s form and size. Between 1-3 micron this process can be quite efficient (Tabata and Ikada, 1988, Green et al., 1998) but, as other studies have shown, for smaller (for example not-agglomerated) nanoparticles this process can be much more inefficient. This can lead to a substantial accumulation of nanoparticles and a consequent stress and health risk for the lungs through inflammation effects at large enough concentrations (Faux et al., 2003).

Moreover, various studies (i.e. for iridium and carbon black nanoparticles) 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, 2000; Kreyling and Scheuch, 2000). 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 (Oberdörster et al. 2004 and Hagen et al. 2007). In addition to this, certain nanoparticles can be transported along the nerves to the central nervous system. These two mechanisms could play a major role in the development of certain cardiac or central nervous system diseases. Recent findings show the possibility of translocation of larger carbon nanotubes from the alveolar region to the “longvilies” possibly causing mesothelioma-like effects (Donaldsen et al 2009 presentation Helsinki NanOEH conference 2009).

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 (Donaldson et al., 1996; Zang et al., 1998). Irritation, inflammation, cell death, extraordinary cell growth, DNA damage and hormonal distortion are among the eventual effects that could result from this.

4.2.2 Exposure through the skin
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. TiO2 nanoparticles, for example are observed not to penetrate the skin except for those places where the top-layer is disrupted (Lademann et al., 1999). 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, Tinkle et al. 2003 and Ryman-Rasmussen et al. 2006). 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.

4.2.3 Exposure through ingestion
Ingestion doesn’t only involve nano-materials 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). For example, latex, polystyrene and prophylactic polyglycolic acid particles ranging from 20 nm to 50 micron are absorbed in the small intestine (Hillyer and Albrecht, 2001). This absorption is probably related to particle size, with
the smallest particles being the most readily absorbed, and it is therefore to be expected that a number of nanoparticles shall be efficiently absorbed. However, surface characteristics such as polarity and charge are also 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 nano-materials in the intestines.

4.3 Possible approaches for a safe use of nanoproducts

Organising a safe workplace and especially preventing the exposure to hazardous nanoparticles, requires insight in the possible hazardous nature of these nanoparticles and their behaviour when applying products in which they are contained. A proper risk assessment is preferred, including well-considered exposure scenarios. 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 nanoproducts during use, cleaning or maintenance. This means that occupational health policy is still dealing with many uncertainties and therefore it is difficult to perform a reliable risk assessment. Nevertheless, a start in the use of nanoproducts in the construction industry can be observed and in the near future an increase in use is expected, leading to the question how to anticipate on these developments and continue innovation (and not frustrating the developments) while at the same time taking care for the health of construction workers at a safe workplace.

In this respect we can learn from the European debate on nanotechnologies and examine the question what it means to bring a precautionary approach into practice in the construction industry that uses nano-materials. 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. In that respect, the risks do not necessarily outweigh the advantages. 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. Application of this approach is not by 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 working conditions policy. In this way, the principle will be part of the Risk Inventory & Evaluations and the associated action plans, which companies are required to draw up.

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Due to the existing uncertainties and gaps in knowledge, for the construction industry a precautionary approach is preferred that does use as starting point the aim to prevent exposure to nanoparticles: no data → no exposure. However, being aware of actual working situations at construction sites this one-liner may be wishful thinking and it may be more realistic to formulate the aim as follows: where exposure is unavoidable, the employer must ensure that the duration and extent of exposure are as limited as possible. In other words, the emphasis in such situations is on minimizing exposure. Still, it may be quite complex to minimize the exposure if not enough data is available, or if it is not possible to carry out an extensive measuring program. Therefore, for the time being a few practical measures may be considered.

Focus on first priority activities
As a practical aid for companies it is preferred that good practices are being developed for workplaces where nanoproducts are used and where exposure to nanoparticles may occur.
In this regard, when dealing with nanoparticles and – above all – assessing the associated risks a division of the type of nanoparticles into categories according to the manner in which they occur may be helpful. In particular, this involves nanoparticles that do not easily dissolve and which are released into the ambient air in a working situation and can then be inhaled by the employee. This may occur when nanoparticles in the form of dust are being processed or treated but it can also occur when materials or products are being processed that contain nanoparticles. Although account needs to be taken of uncertainties regarding the toxicity of new (insoluble) nanoparticles, this categorization will also determine the seriousness of the measures that are to be taken. The higher the category to which the nanoparticles belong, the greater the risk of those nanoparticles is assumed to be and the more serious the measures that must be taken (category I is taken to be the highest –most risk full- category). A simple three category system may be used as the basis for the categorisation of nanoparticles:

I Fibrous insoluble nanoparticles (length > 5 μm).
II Nanoparticles which are known to be carcinogenic, 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).

This categorisation provides a guideline for ways of reducing exposure. Activities in which dry nano-materials are released merit greater attention and more far-reaching measures than when nano-materials are embedded in solid or liquid matrices. It is known that nanoparticles in the air frequently behave very much like a gas and can penetrate deep into someone’s lungs. Protective measures need to take account of this. For the construction industry, this particularly involves activities like sanding,

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89 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.
drilling, mixing, machining, cutting and spraying of nano-materials and products, as well as cleaning of the workplace and used equipment. These are primary activities to focus the risk assessment when working with nanoproducts. The general recommendation is to avoid exposure through inhalation and/or skin contact at work. The preference is consequently for nanoparticles to be “held”:

1. in a matrix; (without dust formation)
2. suspended in a fluid (without aerosol generation); or
3. in an enclosed area or closed system.

In order to identify measures and prevent exposure, the classic occupational hygiene strategy, applied to dealing with nanoparticles can be assumed:

- preventing the use of dangerous nanoparticles;
- replacing nanoparticles by particles that create less risk;
- enclosing the nanoparticles in a specific area during processing;
- technical protective measures;
- organisational measures;
- personal protection measures.

It can as well be considered that enforcement and information are of major importance when dealing with nanoparticles in the workplace, as are the broadening of knowledge, knowledge generation, and the pooling of knowledge.

**Nano reference values**

Assessment of possible health risks in using nanomaterials may include exposure assessment where exposure is compared with existing occupational exposure limits (OELs), which are limit values that are based on sound hazard data. When these are lacking, which is the case for most nanoparticles, a health based recommended OEL cannot be derived. This is leading to the dilemma that a sound safe working advice cannot be given because safe exposure levels cannot be defined.

A solution for this dilemma is suggested by the introduction *nano reference values* (NRVs). NRVs can be defined as precautionary exposure limit values that are derived by using a precautionary approach making use of safety factors. Connected to the proposed risk ranking system the idea of British Standard Institute may be followed (BSI 2007)\(^{90}\). They call NRVs “benchmark exposure levels”

BSI proposes for category III nanoparticles to use the approach as has been described by NIOSH for the insoluble nano-TiO\(_2\) (NIOSH 2005)\(^{91}\). Based on the increased reactivity of nano-TiO\(_2\), linked to the increase in surface area, NIOSH proposes a 15-fold reduction for a nano-TiO\(_2\) limit value compared to the existing OEL for large-particle TiO\(_2\) (1,5 \(\rightarrow\) 0,1 mg/m\(^3\)). A comparable approach could be used for other insoluble nanoparticles that fall under the definition of category III. For the category II a comparison is made with the carcinogenic, mutagenic,

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\(^{91}\) NIOSH 2005. Draft NIOSH current intelligence bulletin: Evaluation of Health Hazard and Recommendations for Occupational Exposure to Titanium Dioxide, November 22, 2005
reproduction toxic and sensitizing chemical substances that have already an OEL. For
category I an analogy with asbestos fibres is chosen. This may lead to the system in
Table 0-5.

Table 0-5 Insoluble nanoparticle risk ranking and nano reference values

<table>
<thead>
<tr>
<th>Cat</th>
<th>Description</th>
<th>NRV</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Fibrous; a high aspect ratio insoluble nanomateriala</td>
<td>0,01 fibres/ml</td>
<td>Analogues to asbestos fibres</td>
</tr>
<tr>
<td>II</td>
<td>Any nanomaterial which is already classified in its molecular or in its larger particle form as carcinogenic, mutagenic, reproductive toxin or as sensitizing (CMR)</td>
<td>0,1 x existing OEL for molecular form or larger particles</td>
<td>The potentially increased rate of dissolving of these materials in NP form could lead to an increased bioavailability. Therefore a safety factor of 0,1 is introduced.</td>
</tr>
<tr>
<td>III</td>
<td>Insoluble or poorly soluble nanomaterials, and not in the category of fibrous or CMR particles</td>
<td>0,066 x existing OEL for molecular form or larger particles</td>
<td>In analogy with NIOSH 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.</td>
</tr>
</tbody>
</table>

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

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 0-20.
Figure 0-20 An example of a Risk Level matrix of one CB-method as a function of the severity of the possible hazard and the probability to get exposed (from Paik et al. 2008)

Typically, 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.

Two Examples:

1. Applying a wall paint that contains nano-TiO₂

TiO₂ in its macroscopic form is known to be a relatively non-hazardous chemical. Available literature does suggest that nano-sized TiO₂ can be more hazardous (depending on i.e. size, shape, morphology and surface structure). For the sake of this example, it is assumed that the specific characteristics of the nano-TiO₂ in this nano-coating (incl. its concentration) add up to a medium severity. When this nano-coating is regularly used in a spraying application, it is likely that the worker in place gets exposed to aerosols formed during painting. The probability is therefore likely. Applying these to Figure 0-20, one can deduce that this working practice falls into a RL2 (Risk Level 2) implying that under these conditions it is recommended to work with local exhaust ventilation.

However, when, instead of spraying, a brush application is used to apply the coating the probability changes to Less Likely or even to Extremely unlikely. Under these
conditions the work would fall into a RL1, which would suggest that general ventilation would be sufficient for a safe workplace.

2. Placing a prefab product containing CNT
CNT are suspected to be very toxic (especially upon inhalation) and though no generalizing conclusions can be drawn yet, exposure should be prevented at all times. CNT are therefore scaled at a Very High severity. However, embedded in a prefab element (a hypothetic application for which no indication of real use has been found in the present report), the probability of exposure is Extremely Unlikely, placing this work into RL3. Though, when this same nano-material would have been used in wet mortar (a hypothetic application for which no indication of real use has been found in the present report either), the probability of exposure increases and the work would fall into RL4.

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.

Notification for nano-products
From the results of the 2009-survey and the in-depth interviews, it has been concluded that most of the construction employers and employees are not aware of the availability of nano-products, not aware if they might use nano-products themselves. If they are aware that nano-products are used (by them) they are not well-informed about the type of nanoparticles contained in the products and the possible associated risks. The question then rises: how can they make a proper risk assessment?

Information is a first requirement. This is the reason for the growing demand by the market, which can currently be observed, to notify the content of nanoparticles in the products brought at the market. Initiatives to establish a certain way of obligation to notify can be identified in the Netherlands (accepted motion in the Parliament), France (parliament) and Swiss (Code of Conduct of the Swiss retailers organisation).

An idea, elaborated in these proposals, is that a notification obligation should consider the most hazardous and high-risk products containing nanoparticles that may be released into the ambient air during processing or treatment and that may then be inhaled by employees. A notification system should involve importers or producers indicating that their products contain nano-materials, with that information then being passed on along the chain, to inform the user about possible
risks due to nanoparticles exposure. The Material Safety Data Sheets (MSDSs) might be used to transfer this information to the user of the products. Proposals are being made (by the Dutch SER) to involve the imposition of a standard requirement for the particle size of the substance concerned to be specified in MSDSs, together with the possible hazards and the necessary control measures for these nanoparticles. When no information is available regarding certain nanoparticles, this should also be explicitly stated in the relevant MSDS. Such information regarding nanoparticles can help ensure that employers and employees are warned of the risks (including the unknown risks) associated with working with nanoparticles and also that they receive adequate information regarding the measures that are necessary to control those risks.

In this respect an activity of employers and employees in the construction industries 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.

**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. those that fall in the categories I and II. For the construction worker on site, it is difficult to judge if, and under what circumstances, the monitoring of health and safety risks is appropriate and useful. The present state of knowledge simply doesn’t allow for this, even though the various risk levels described for control banding could be interpreted going from RL1 to RL4 as an increasing urgency to keep track of the type of nano-products worked with, the people involved and the exposure, its frequency and duration, just in case some unexpected health effects might evolve. The difficulty for the construction worker is that, except for those cases when dust or aerosol exposure takes place, exposure risks to nano-materials are difficult to quantify. The exposure risks may probably be small.

In the absence of knowledge though, 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 of category III, expected lower hazardous 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 good 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. Still, in the case of construction workers, it might often be the case that activities are so divers that it is a tedious job to pinpoint such an event on one particular activity only for the individual. In time though, when more and more individual cases are described, it might be possible to gain more understanding from correlating those. The first along this line is a study recently published by Song et al (2009), who try 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 construction industry and because of the many knowledge gaps existing today conclusions of this study are controversial and should be questioned, 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.

In summary
The suggested building blocks for a precautionary nano approach are summarized in the following table.

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

Table 0-6 Building blocks for a precautionary approach

These building blocks can be applied as a precautionary approach, when information on the nano-content of products is limited and if there is uncertainty about the release of nanoparticles from nano-products.

Real time exposure measurements
In addition to the above, one could consider performing real time exposure measurements, at least for those working practices where the severity of the possible hazards of the nano-product and the risk of exposure to this product are both expected to be high. Nano-material specific measurement devices that are dedicated (yield material specific information like chemical structure, shape and size), sensitive and portable are under development and no practical, affordable device for the construction site is yet at the market. However, since nano-material exposure of construction work on site 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 nano-material 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. Promising is as well is the recently developed portable NanoTracer, a device that gives the possibility to measure continuously real-time personal monitoring of nano-particles in the size of 10-300nm. Market introduction of this equipment is expected soon.

4.3.1 Protective measures
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 (Tyvec) 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).

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.

4.4 Risk communication from manufacturer to user
The communication of risks, risk assessment and strategies for risk management from the manufacturer of a material to the downstream user is a critical issue for “traditional” chemicals but especially for nanomaterials. Main issues that do limit the extent of information communicated are:
- Confidentiality issues concerning the nanoparticles contained in the products
- The manufacturer’s (or supplier’s) trust that sensitive information will not be misused
- Limited knowledge about the nanomaterial fate in the product
- Limited knowledge on the exact composition of a used nano-ingredient
- Limited knowledge on the hazard of the used nanoparticles
- Limited knowledge on the release of nanoparticles from products, by application, during use and maintenance
The first issue is generally a key issue for most companies. Nanotechnological research and product development can be very delicate and requires highly skilled people and may require large investments (and uncertain revenues). However, when the road is paved and a mature nanoproduct can be brought at the market, the risk of competitors copying the concept must be prevented. Related to this is the possibility that customers could misuse sensitive information provided to them by their supplier. It is therefore that the sharing of information is kept to the absolute minimum level possible, with a consequential limited information exchange on possible health or environmental risks.
However, from contact with various product manufacturers it appears that (even when confidentiality doesn’t play a role) it is not always clear how the nano-material exactly behaves and acts in within the product and what it’s exact composition is (even though the resulting effect is well determined), which is complicating any communication. Partly, this can be due to the characteristics of the nano-material that might react, aggregate or agglomerate during use (which might be difficult to control), but it can also be because the used concentrations nanoparticle are not well measurable in the ready-for-use product and therefore difficult to study. In those situations, the product manufacturer himself has already a limited knowledge on the nano-product and has therefore only limited knowledge to communicate.
The difficulty to measure and quantify nanoparticle behavior (technically (availability of testing methods/equipment), economically (testing is costly) and time wise (testing and gaining knowledge takes time)) is found also in the limited knowledge available on health hazards of nanoparticles and exposure risks throughout the full lifetime of the nanoparticle (production, application, use, service and maintenance and waste treatment.)

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One example is the Amphisilan nano-coating by Caparol described in the previous chapter. This acrylate coating contains crystalline nano-SiO₂ that chemically reacts with the acrylate binder of the coating forming a net-type matrix. What is sure (and communicated) is that crystalline nano-SiO₂ is going in the coating as an additive and that somewhere along the line of the drying process this SiO₂ reacts and “looses” its nano-character. What is uncertain is when this happens (i.e. what is the chemical composition of an aerosol inhaled upon spraying? Does this still contain nano-SiO₂), impacting on the exposure risks during application, and what percentage of nano-SiO₂ remains unreacted in the matrix, impacting on the exposure risks during use, service and maintenance, cleaning of spills and equipment and waste treatment.

Despite the above, there are also many examples for which, according to the Regulation on the Classification, Labeling and Packaging of Substances and Mixtures (CLP)⁹³, a producer is simply not obliged to register a nano ingredient in a specific product when no hazards are known, or not foreseen to exist. In other words, the producer does not have to communicate anything about the nano-material. This is one of the present legislative shortcomings that do allow for a minimal communication along the production-chain. Before any decision has been made related to any obligation to notify nano-ingredients or additives in products, this will be a recurring issue and will not be easily tackled.

5. Concluding Issues and Possibilities for Further Activities to Support a Safe Workplace

Nanotechnology is believed to bring many technical, economic and environmental advantages to the construction industry in the future. The in-depth interviews conducted with product manufacturers, scientists and construction companies in the context of the present study anonymously underline the potential of applying nanotechnology to the development of (novel) products for the construction industry. However, reality today is that only a very 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 and because the long term performance of these novel products is uncertain, which makes architects and project developers reluctant to start using them. Not surprisingly, the 2009-survey, set out under construction workers and their employers, found the awareness about nanotechnology applications and the availability of nano-products to be very limited. A similar situation seems to exist for architects, occupational hygienists and occupational health and safety advisors. With a few exceptions, there is only very limited knowledge about nanotechnology in general and nano-products for the construction industry in particular. Those construction workers and employers that did indicate working with nano-products, anonymously stated this happened on specific request by the project developer or because of the demand for specific technical performance.

However, a limited awareness in the sector is not only caused by a limited availability or use of nano-products. Communication through the user-chain is also an important factor. Because of a current lack of generally accepted definitions there is uncertainty about when to call a product a nano-product and a consequent misunderstanding when talking about the subject. Different situations do exist:
- Products containing nanoparticles that should be indicated as nano-products but are not indicated as such (by their manufacturer or supplier)
- Products that should not be named nano-products are named nano-products (for example because of the production technology involved)
- Products containing nanoparticles that are indicated as nano-products

Moreover, more detailed information about the “nano” aspect of a product is often lacking. For the products specified in the responses to the 2009-survey, the material safety data sheets (MSDS) did not include any nano-specific information on the product. In contrast, some nano-specific information was presented in the technical data sheets of the products with varying detail ranging from a description of the active surface area per gram added nano-material and a SEM\(^{94}\) image of the individual nano crystals to the simple note that the product does contain nano-sized particles. However, an MSDS or technical data sheet was not always supplied with the product, leaving the user without any more detailed product information. When studying the information supply chain in more detail, it was observed from the in-depth interviews and the 2009-survey responses that (with some exceptions) the

\(^{94}\) SEM = Scanning Electron Microscopy
nano-specific information transfer generally stops at the manufacturer of the nano-product. The raw material producer of the nano-particles does supply all information available to the product manufacturer (for which the reality is that this info is limited in most cases due to the technical limitations of the methods to characterize nanoparticles and the costs involved). However, because of the generally low concentration of nanoparticles in a nano-product, the product manufacturer is often not obliged to communicate this information on the product further down the chain to its users. Alternatively, the nanoparticle chemically (or physically) reacts during product manufacturing such that the eventual product doesn’t contain any nanoparticle anymore. Also in these situations, nano-specific information on the product is often lost for the product user.

When working with nano-products, the respondents to the 2009-survey do indicate that no special skills were demanded for this work, neither were there any nano-specific protective measures prescribed, with the exception of some specific applications involving silica fume (nano-SiO₂) containing products. This finding was supported by various in-depth interviews with product manufacturers.

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 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 polymers, TiO₂, ZnO, SiO₂ (or silica fume), Ag, and Al₂O₃. Interesting to note is also that no evidence was found for the use of CNT in these products, even though many publications do show evidence of ongoing research and product development in this direction.

Nanoparticle use in cementageous and concrete materials does concentrate on TiO₂ (added to a thin top-layer to obtain a photo-catalytic surface to degrade organic pollution) and SiO₂ (used in Ultra High Performance Concrete).

Coatings make the most broad product group and are developed for almost every surface thinkable from plastics to steel. Within this group, the emphasis is found on anti-bacterial coatings (adding TiO₂, ZnO or Ag), photo-catalytic “self cleaning” coatings (TiO₂ or ZnO), UV and IR reflecting or absorbing coatings (TiO₂ or ZnO), fire retardant coatings (SiO₂) and scratch resistant coatings (SiO₂ or Al₂O₃). These types of functionalities are typically applied on coatings for walls (interior or exterior), wooden facades, glass and different road pavement materials. Interesting to note here though, is that various functionalities know their limitations. For example TiO₂ and ZnO require light to degrade organic pollutants and act self-cleaning. This implies a certain grade of cleanliness of the surface in order for the light to activate TiO₂ and ZnO. Anti-bacterial Ag coatings on the other hand require water as it is not
the silver itself that acts as a bactericide but its Ag-ion, which only appears ones (part of the) Ag dissolves in water.

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.

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 code 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 of this approach is to prevent exposure to nanoparticles by applying the occupational hygiene strategy. When exposure can be effectively prevented, 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, 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 (unknown to the owner of the construct) and there is a role of the authority and the suppliers of the nano-product improving this situation.

As it will be an elaborate 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. A tool that might assist in the development of these good practices is Control Banding. 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 nano-particle 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 abrasing 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.
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Annex 1  The 2009-Survey (EN)
In survey set out by the EFBWW and the FIEC in 24 European countries has been translated in 10 different languages (English, French, Italian, German, Danish, Hungarian, Dutch, Bulgarian, Polish and Romanian). The English version of the text is given in this annex. All questionnaires were returned to the EFBWW or to the FIEC respectively.

European Federation of Building and Woodworkers

Nanotechnologies in the European Construction Industry
Ref.: Grant agreement No. VS/2008/0500 – SI2.512656

Questionnaire
Nano products have started to being used in the European construction Industry. To identify exactly what products are introduced and on which scale they are currently used (i.e. frequently by the majority of construction workers or only on special request), the European branch organizations EFBWW and FIEC have started a European broad survey among their members and affiliates.

With the questionnaire, we like to identify construction nano-products you work (or worked) with (for example for specific anti-bacterial wall coatings, or in the case of silica fume). However, since nano-products might not be easy to identify you may be less certain if the new products are really based on nanotechnology. Therefore, we would like you to specify as for which products you are sure and for which you are not. In each case, trigger words are new, improved, super-, extra-, anti-dirt, self cleaning etc. and .... the nano products in general have “something clever” in them. For example: you never have to clean your windows anymore (because they are self-cleaning), or concrete walls stay forever white and graffiti can be removed without sweat.

We present to you a questionnaire to identify the type of nano products you work with and to get a better idea about the impact the use of nano products has on your daily life. All the information presented to us will be handled fully confidential within the steering group consisting of the EFBWW, FIEC and IVAM. Nevertheless we are asking you to fill in your contact data. This is to give us the ability to get in contact with you to ask for additional details concerning the use of nano-products. The results of this survey will be made anonymous before publishing.
General Information
Name interviewee: ................................................
Type of work interviewee: ......................................
Contact details: ......................................................
Email: .................................................................
Telephone number: ................................................
Type of company (or organization): ......................
Number of employees: ...........................................(approximately)

The Use of Nano-product Enhanced Materials in Construction Industry

With the introduction of new materials in the construction Industry, often claims are made that these products are more sustainable, consume less raw material and energy, are produced more easily or can be used more easily, last longer, require less service and maintenance or are light-weight while continuing to perform equally well or even better than the traditionally used materials. Nanotechnology is the latest technological innovation that is claimed to significantly contribute to these product innovations. The products this technology brings forward are called “nano-products”.

Products Used

In nano products small nanoparticles may be applied to give those products their new properties. Examples of nanoparticles are nanotubes, silica fume, nano titanium dioxide and nano silver. All these particles have in common that they exhibit very specific and unique properties, which can be used in nano products to give these latter very special and desired qualities. Examples of nano products are some types of cement and ultra strong concrete, antibacterial coatings and enforced steal.

1a. Are you aware whether or not you work with nano products?

<table>
<thead>
<tr>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
</table>

1b. If “yes”, please do select the type of the nano products you work with in the table below. If “no”, please do check the products in the table below and the product examples given to find out if one (or more) of these do fit the description of products you do work with. If so, please do indicate for which products this is the case. If none of the products described in the table below are familiar to you, we highly appreciate your input so far and would like to thank you the time you’ve taken to fill in this questionnaire. You will be notified about the final results of this survey.

<table>
<thead>
<tr>
<th>Yes</th>
<th>Product type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coatings</td>
<td>Examples of nano coatings are outdoor wall paints that create a self cleaning or antibacterial surface. Nano titanium dioxide is one nano particle that is often used in this type of coatings. Other examples are e.g. wood protecting coatings.</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Cement / Concrete</strong></td>
<td>By the addition of silica fume, cement and concrete can be made extra strong such that light constructs can stand high forces. Also, the material durability can be enhanced due to lower water penetration possibilities. In addition to this, Nano products are added to concrete to obtain anti fouling properties and make the material resistant against algae growth. Some new concrete products that are marketed contained nanotubes to improve the flexibility of the concrete.</td>
<td></td>
</tr>
<tr>
<td><strong>Composites</strong></td>
<td>The characteristics of steel and plastics are enhanced by addition of nano products to make the material more strong but flexible, more durable or more light with equally good performance. For example to make ultra light blades for windmills. An example of a type of nano particle that is used for this is the nano tube.</td>
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</tr>
<tr>
<td><strong>Nanosensors</strong></td>
<td>These are small electronic devices (nano sized constructs) that are applied inside a construct to monitor material degradation such as stress, humidity, heat etc.</td>
<td></td>
</tr>
<tr>
<td><strong>Flame retardant material</strong></td>
<td>Nano products such as nano clay are added to construction materials to prolong or optimize their heat resistance and to reduce the flammability.</td>
<td></td>
</tr>
<tr>
<td><strong>Insulation material</strong></td>
<td>With nanotechnology, highly efficient insulation material can be made, consisting of a foam of millions of small bubbles that are far better insulating than the traditional materials.</td>
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</tr>
<tr>
<td><strong>Textile (o.a carpet)</strong></td>
<td>Examples of nano products in this construction material product group may be textile material that is made anti-bacterial or dirt repellant.</td>
<td></td>
</tr>
<tr>
<td><strong>Glass</strong></td>
<td>Glass is given self cleaning, isolating, insulating or heat reflecting characteristics by treating it with a typical nano coatings. Also glass can be &quot;colored&quot; such that the window becomes dark when the sun is shining but remains highly transparent when the sun is away (self-staining glass). New developments are non-reflective glass.</td>
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</tr>
<tr>
<td><strong>Asphalt</strong></td>
<td>Asphalt used for road pavements can be doped with nanoparticles (e.g. titanium dioxide) to stimulate the breakdown of polluting traffic exhaust gasses like NOx. There are also asphaltous products in the market where the addition of nano particles protects the road against moss growth.</td>
<td></td>
</tr>
<tr>
<td><strong>Other, namely:......</strong></td>
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</tbody>
</table>

2. At this moment more and more nano products are introduced in the construction industry and are applied on site. However, their identity is not always clearly communicated with the user. The EFBWW and FIEC like to compile a list of these new
materials and products used today in the European construction industry. Therefore, we ask you to shortly describe the nano-products you identified in question 1.

<table>
<thead>
<tr>
<th>Product number</th>
<th>Product type</th>
<th>Product name</th>
<th>Supplier</th>
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<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3a. Each product, product application and/or product use brings about its own typical risks: for example, the risk of inhaling small paint droplets when spraying a paint or coating, or inhaling dust when sanding a wall. In this respect, nano products are no different. We like to know if you are informed about possible health risks resulting from the exposure to nano particles during the use of the products you listed under question 2. *Please specify for each product individually using the same numbering as in question 2.*

<table>
<thead>
<tr>
<th>Product number</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
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<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3b. If yes, there are a number of ways by which you might be informed about the exposure risks. One way is via the materials safety data sheets or technical information sheets of the products. Other information sources may be for example work instruction sessions or a colleague telling you to be careful when handling the new product. Please indicate for each of the products for which this is relevant how you were informed about the risks. When you are informed via several routes please indicate this also.

<table>
<thead>
<tr>
<th>Product number</th>
<th>Type of information</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2 3 4 5 6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Material Safety Data Sheet</td>
</tr>
<tr>
<td></td>
<td>Work Instruction session</td>
</tr>
<tr>
<td></td>
<td>Product Label</td>
</tr>
<tr>
<td></td>
<td>Website</td>
</tr>
<tr>
<td></td>
<td>Your Supplier</td>
</tr>
<tr>
<td></td>
<td>Your Superior</td>
</tr>
<tr>
<td></td>
<td>A colleague</td>
</tr>
<tr>
<td></td>
<td>Other, namely: _______</td>
</tr>
</tbody>
</table>
4a. Because exposure risks may be different (compared to the traditionally used products) or due to different product characteristics (such as viscosity or dustiness) your work practice might have changed. This can be for the good, but your work might also have become more elaborated. For example, because you have to take more precautionary measures, or because you have to use new equipment with which you are not yet acquainted. Please indicate for each product identified in question 2 if working with this nano product did effect your normal way of working?

<table>
<thead>
<tr>
<th>Product number</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No, it’s the same as before</td>
</tr>
<tr>
<td>2</td>
<td>Yes, the work is more easy / more light with this nano product</td>
</tr>
<tr>
<td>3</td>
<td>Yes, the work is more difficult / more intensive with this nano product</td>
</tr>
<tr>
<td>4</td>
<td>Yes, I have to take more protective measures when working with this nano product</td>
</tr>
<tr>
<td>5</td>
<td>Yes, I have to take less protective measures when working with this nano product</td>
</tr>
<tr>
<td>6</td>
<td>Yes, namely …..</td>
</tr>
</tbody>
</table>

4b. In question 4a. you might have indicated a number of nano products that changed your way of work. This could involve a new work approach and the requirement of different skills or qualifications. If this is the case, could you describe the new skills and qualifications that are asked from you?

<table>
<thead>
<tr>
<th>Product number</th>
<th>Other/new qualifications:</th>
<th>Different skills:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>What?</td>
<td>What?</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4c. However, a new way of work could also involve other protective measures to be taken with respect to the traditional way of work. If this is the case, please describe (if possible) what type of protective measures are prescribed.

<table>
<thead>
<tr>
<th>Product number</th>
<th>Protective measures for nano product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
5. Nano products may be used because of their special performance, like enhanced material strength or improved flexibility, better flame retarding capabilities. They are used because of a very specific reason. Are you aware of the reason why you are using these nano products? *(Please specify for each product individually using the same numbering in question 2.)*

<table>
<thead>
<tr>
<th>Product number</th>
<th>Motive</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I’m not informed about the particular reason for using this nano product.</td>
</tr>
<tr>
<td>2</td>
<td>Because of specific instruction of customer / principal.</td>
</tr>
<tr>
<td>3</td>
<td>Because of desired product performance / characteristics required for the construction</td>
</tr>
<tr>
<td>4</td>
<td>Because of better cost efficiency relative to the traditional material</td>
</tr>
<tr>
<td>5</td>
<td>Because the nano product is less labor intensive for use</td>
</tr>
<tr>
<td>6</td>
<td>Other, namely: ...</td>
</tr>
</tbody>
</table>

We highly appreciate your input to this questionnaire and will process the information fully confidential. All information will be made anonymous before publication.

Please indicate if you would be available for any further questions that may arise from the answers provided by you in this questionnaire.

<table>
<thead>
<tr>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
</table>

Please return the completed questionnaire to:
Annex 2  Nano-products from the 2009-Survey

In the table below, all products are listed by type, product name and supplier that were mentioned by the respondents of the 2009-Survey to be actually used on site. Most of these products are only mentioned by one respondent each. Emaco NanoCrete (by BASF), Sigma Facade Topcoat (by Sigma Coatings) and Pilkington Active are the only three products that were actually named by two. For what it is worth given the low response rate, this does correspond to the more general impression obtained from the in-depth interviews and the extensive web- and literature search that nano-enforced concrete, photoactive wall paints and photoactive glass are among the applications that are most found to be used in the construction industry.

<table>
<thead>
<tr>
<th>Product type</th>
<th>Product name</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement/concrete</td>
<td>TX active</td>
<td>FYM-Italcementi group</td>
</tr>
<tr>
<td></td>
<td>TX Arca</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TX Millenium</td>
<td></td>
</tr>
<tr>
<td>Concrete</td>
<td>Flocrete</td>
<td>Roadstone/JA wood</td>
</tr>
<tr>
<td>Concrete</td>
<td>SIKACRETE HP (silica fume)</td>
<td>SIKA</td>
</tr>
<tr>
<td>Concrete</td>
<td>Emaco NanoCrete AP (polymer modified cement for active corrosion inhibition)</td>
<td>BASF</td>
</tr>
<tr>
<td>Calcestruzzo</td>
<td>SILCRETE</td>
<td>Calcestruzzi Mo.Ba. s.r.l.</td>
</tr>
<tr>
<td>Coatings</td>
<td>TX Active</td>
<td>FYM-Italcementi group</td>
</tr>
<tr>
<td></td>
<td>Nanograffiti Protection</td>
<td>Nanoresist</td>
</tr>
<tr>
<td></td>
<td>Sigmacare Cleanair</td>
<td>Sigma Coatings (PPG)</td>
</tr>
<tr>
<td></td>
<td>Sigma Facade Topcoat Matt NPS</td>
<td>Sigma Coatings (PPG)</td>
</tr>
<tr>
<td></td>
<td>Sandtex V Nanotec</td>
<td>Nordsjö (Akzo)</td>
</tr>
<tr>
<td></td>
<td>Tcnano Solutions for buildings PRO</td>
<td>Tcnano in close cooperation with Nanogate Technologies</td>
</tr>
<tr>
<td></td>
<td>Amphisilan</td>
<td>Rockidan/Caparol</td>
</tr>
<tr>
<td></td>
<td>AmphiBolin 2000 Universal</td>
<td>Rockidan (Caparol)</td>
</tr>
<tr>
<td></td>
<td>Capasan 1010 Indemaling</td>
<td>Rockidan (Caparol)</td>
</tr>
<tr>
<td></td>
<td>AmphiSilan 1060 Facademaling</td>
<td>Rockidan (Caparol)</td>
</tr>
<tr>
<td>Coatings on Wood</td>
<td>Pro Sil Wood</td>
<td>Nanocer and NTC Spain</td>
</tr>
<tr>
<td></td>
<td>2937 GORI Professional Transparent, GORI Nanoforce™</td>
<td>Dyrup</td>
</tr>
<tr>
<td></td>
<td>Percenta Nano Træ &amp; Sten-Forsegling</td>
<td>percenta</td>
</tr>
<tr>
<td>Product type</td>
<td>Product name</td>
<td>Supplier</td>
</tr>
<tr>
<td>------------------------------------</td>
<td>--------------------------------------------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td>Wood coating</td>
<td>Parla Floor</td>
<td>OR Group</td>
</tr>
<tr>
<td>Wall paint</td>
<td>Sigmacare Cleanair</td>
<td>Sigma Coatings (PPG)</td>
</tr>
<tr>
<td>Facade paint</td>
<td>Sigma Facade Topcoat Matt NPS</td>
<td>Sigma Coatings (PPG)</td>
</tr>
<tr>
<td>Facade paint</td>
<td>Sandtex V Nanotec</td>
<td>Nordsjö (Akzo)</td>
</tr>
<tr>
<td>exterior and interior surface coating</td>
<td>TCnano Solutions for buildings PRO</td>
<td>Tcnano</td>
</tr>
<tr>
<td>Coatings on Glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellicole rivestimento vetro glass and plexiglass coating (hydrophobic, oleofobic and lipophobic)</td>
<td>3M Prestige</td>
<td>3M</td>
</tr>
<tr>
<td>Self-cleaning Glass</td>
<td>Nanotol</td>
<td>CeNano GmbH &amp; CO</td>
</tr>
<tr>
<td></td>
<td>Pilkington Active</td>
<td>Pilkington</td>
</tr>
<tr>
<td>Insulation material</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insulation</td>
<td>Aerogel</td>
<td>Aerogel</td>
</tr>
<tr>
<td></td>
<td>Polyisocyanurate</td>
<td>Kingspan</td>
</tr>
<tr>
<td>Road Pavement</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pavimenti fotocatalitici</td>
<td>BioTi Ecopan</td>
<td>Paver Costruzioni S.p.A.</td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sepiolite</td>
<td></td>
<td>Tolsa</td>
</tr>
<tr>
<td>Flame retardant-silica</td>
<td>Nanogel</td>
<td>Cabot SA</td>
</tr>
<tr>
<td>Nanoadditives:</td>
<td>Nanoaf (antifouling)</td>
<td>Nanocer and NTC Spain</td>
</tr>
<tr>
<td></td>
<td>Clearcoat (Silver nanoparticles)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metalcoat (Metallic nanoparticles)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Basecoat (Carbon nanotubes)</td>
<td></td>
</tr>
<tr>
<td>Nano Composites</td>
<td>Unknown</td>
<td>FYM-Italcementi group</td>
</tr>
<tr>
<td>Ceramic</td>
<td>Ductal</td>
<td>Lafarge</td>
</tr>
<tr>
<td>Flame retardant materials/nanoclays</td>
<td></td>
<td>Hybrid nanoclays S.A</td>
</tr>
<tr>
<td>Textile, fibers and polymers</td>
<td></td>
<td>La seda de Barcelona</td>
</tr>
</tbody>
</table>
Annex 3  Measurement techniques for research

In the context of the project NanoCap, on the capacity building of environmental NGOs and trade unions on the risks, benefits and ethics related to nanotechnologies, an overview was made of the measurement techniques that are currently in use to study and monitor nano-particle, nano-material and nano-product behaviour or study the behaviour and characteristics of materials and products at the nano-size level. The overview given below has been prepared by the University of Essex by Prof. Ian Colbeck.
Measurement Techniques For Nanoparticles

Introduction

There are various techniques for detecting, measuring and characterising nanoparticles. There is not a method that can be selected that is the “best” method but rather a method is chosen to balance the restriction of the type of sample, the information required, time constraints and the cost of the analysis. A straightforward technique may simply detect the presence of nanoparticles, others may give the quantity, the size distribution or the surface area of the nanoparticles. These measurement techniques differ from characterisation techniques for assessing the chemical content of a nanoparticle sample, the reactions on the surface of the nanoparticles or for the interactions with other chemical species present. There is also a divide between techniques that give information on an amount of nanoparticulate material and those that can look at the individual nanoparticle within the sample. Sometimes measurement techniques will be combined to provide more information from one sample.

Different techniques will suit different types of sample. For example some techniques require the sample to be as an aerosol and others will use a suspension or liquid sample. There may be a sample protocol to be followed for collection of the sample for analysis by a certain technique. There are techniques for in situ measurements of samples and others that require treatment of the sample before analysis. Sometimes samples may not be able to withstand the required treatment and decompose or react. The amount of sample required can also vary and restrict choice of technique.

Since different techniques provide different information and accuracy, efforts have and will be made to standardise the way nanoparticles are measured to assess occupational exposure, health risks from products and environment risk. The most common techniques are shown in table 1. Small variations on a technique can generate a different name and abbreviation for a very similar technique. An example of this is in aerosol measurement where differential mobility analysers or electrical mobility analysers can be combined with other instruments or have minor adjustments to generate different measurement techniques.

Some techniques will use other measurements than the one required to apply to a mathematical model to calculate the required measurement. For example an Electrostatic Low Pressure Impactor (ELPI) can be used to calculate the mass concentration of an aerosol sample if the particle charge and density are known.

All the techniques have related costs whether they are provided by an analysis company or if the equipment is purchased. These must also be a restriction on the choice of technique as with some techniques the ongoing costs of calibration and maintenance, essential to maintaining accuracy, can be substantial.

Measurement techniques are continuously evolving as they are stretched and improved by research. For example the Nanomechanical Reasonator which
<table>
<thead>
<tr>
<th>Technique</th>
<th>Measures</th>
<th>Sample</th>
<th>Sensitivity</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission Electron Microscopy</td>
<td>particle size and characteristics</td>
<td>sample must be conductive or amenable to vacuum deposition and be stable under high vacuum</td>
<td>down to 1nm</td>
<td>can provide more information using Transmission Electron Microscopy (TEM), High-Resolution TEM (HRTEM) or in situ measurements using Environmental SEM.</td>
</tr>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>particle size and characteristics</td>
<td>sample must be conductive or amenable to vacuum deposition and be stable under high vacuum</td>
<td>down to 1nm</td>
<td>can be used in situ as Environmental SEM.</td>
</tr>
<tr>
<td>Atomic Force Microscopy (AFM)</td>
<td>particle size and characteristics</td>
<td>samples must adhere to a substrate and be rigid and dispersed on the substrate. Appropriate substrates must be chosen. Air or liquid samples.</td>
<td>1nm - 8nm</td>
<td>a form of Scanning Probe Microscopy (SPM), provides less detail and resolution than SEM and TEM.</td>
</tr>
<tr>
<td>Photon Correlation Spectroscopy (PCS)</td>
<td>average particle size and size distribution</td>
<td>sample must be a very dilute suspension</td>
<td>1nm - 10μm</td>
<td>based on Dynamic Light Scattering, an estimation of the technique is Photon Correlation Spectroscopy (PCS) for high concentration aqueous suspensions giving particle size and stability of nanoparticles.</td>
</tr>
<tr>
<td>Nanoparticle Surface Area Analyzer (NPSA)</td>
<td>area of nanoparticles</td>
<td>aerogel, concentration 0 to 10,000μg/ml cm&lt;sup&gt;2&lt;/sup&gt;, 10-30nm</td>
<td>down to 10nm</td>
<td>similar to an Electrostatic Aerosol Detector (ESAD).</td>
</tr>
<tr>
<td>Conventional Particle Counter (CPC)</td>
<td>number concentrations of particles</td>
<td>aerosol, concentration 0 to 100,000 particles/cm&lt;sup&gt;3&lt;/sup&gt;, can be in a flow, higher than 200°C possible</td>
<td>2.5 to &gt;3,000</td>
<td>can be used for a low, manual model. Available.</td>
</tr>
<tr>
<td>Differential Mobility Analyzer</td>
<td>particle size distribution</td>
<td>aerosol, can be a concentrated sample of 1,000,000 - 9,000,000 particles/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>3 - 1,000mm</td>
<td>can be used with other techniques to confirm S DMA or DMA.</td>
</tr>
<tr>
<td>Scanning Mobility Particle Sizer (SMPS)</td>
<td>particle size distribution</td>
<td>aerosol, can be a concentrated sample of 1,000,000 - 9,000,000 particles/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>3 - 1,000mm</td>
<td>uses an electrostatic classifier and a CPC. Can also add DMA.</td>
</tr>
<tr>
<td>Nanoparticle Tracking Analysis (NTA)</td>
<td>average particle size and size distribution</td>
<td>520k suspension, temp 0 - 10°C, wide range of particles can be used</td>
<td>10 - 1,000nm</td>
<td>use with DLS or PCS.</td>
</tr>
<tr>
<td>X-Ray Diffraction (XRD)</td>
<td>average particle size and size distribution</td>
<td>aerosol, can be a concentrated sample of 1,000,000 - 9,000,000 particles/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>10 - 1,000nm</td>
<td>can identify individual crystals.</td>
</tr>
<tr>
<td>Aerosol Mass Spectrometer</td>
<td>particle size and composition</td>
<td>aerosol, can be a concentrated sample of 1,000,000 - 9,000,000 particles/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>10 - 1,000nm</td>
<td>the efficiency of this method is less for smaller particles.</td>
</tr>
<tr>
<td>Aerosol Particle Mass Analyzer (APMA)</td>
<td>particle mass</td>
<td>aerosol, can be a concentrated sample of 1,000,000 - 9,000,000 particles/cm&lt;sup&gt;3&lt;/sup&gt;</td>
<td>10 - 1,000nm</td>
<td>gives more mass information and is not dependent on particle size or shape.</td>
</tr>
</tbody>
</table>
aims to measure the mass of biological molecules is being researched to measure smaller nanoparticles and single bacterial cells.

There are different measurements of nanoparticles and it is not clear which measurement relates closest to the risk posed by that nanoparticle. The Health and Safety Executive NanoAlert Bulletins from 2007 suggest looking at mass, number and surface area measurements until a decision is made on which is necessary to assess the potential adverse effects. It must also be noted that the accuracy of methods will vary. The accuracy of the methods is not always determined by comparison of results on the same sample by different techniques can provide an indication of accuracy.

The details of techniques given here are a general overview. Instruments will vary in their accuracy, sensitivity and application ability depending on their manufacturer. Details of individual instruments can usually be referred to on a manufacturer’s website.

**Microscopy Methods**

Transmission Electron Microscopy (TEM) uses an electron beam to interact with a sample to form an image on a photographic plate or specialist camera. The sample must therefore be able to withstand the electron beam and also the high vacuum chamber that the sample is put into. The sample preparation can be difficult as a thin sample on a support grid must be prepared. The process can also be time consuming and this, along with the cost, are the main criticisms of TEM. High-Resolution TEM (HRTEM) looks at the interference of the electron beam by the sample rather than the absorbance of the beam as with ordinary TEM. This gives a higher resolution which is beneficial when studying nanoscale samples. However it does require understanding of the sample to allow interpretation of the results, as the phase-contrast resulting information can be difficult to interpret. This can therefore restrict the use of HRTEM. Environmental TEM allows TEM to be carried out in-situ by using the relevant gaseous atmosphere as opposed to the vacuum used for TEM.

Scanning Electron Microscopy also uses a high energy electron beam but the beam is scanned over the surface and the back scattering of the electrons is looked at. The sample must again be under a vacuum and for SEM it must be electrically conductive at the surface. This can be achieved by sputter coating a non-conductive sample. This requirement can be restrictive and again this technique can be time consuming and expensive. Environmental SEM is available where samples can be looked at again in a low pressure gas environment as opposed to a vacuum. Scanning Transmission Electron Microscopy combines the ideas of looking at the surface of the sample and into the sample with an electron beam.

Atomic Force Microscopy is a form of Scanning Probe Microscopy. It uses a mechanical probe to feel the surface of a sample. A cantilever with a nanoscale probe is moved over the surface of a sample and the forces between the probe tip and the sample measured from the deflection of the cantilever. The deflection moves a laser spot that reflects onto an arrangement of photodiodes. This can offer a 3D visualisation. Air samples or liquid dispersions can be looked at and AFM is less costly and time consuming than TEM or SEM. However the sample must adhere to a substrate and be rigid and dispersed on it. The roughness of the substrate must be less than the size of the nanoparticles being measured.

Criticism of the microscopy methods for nanoparticle measurements is mainly due to the difficult sample preparation required. However criticism has also been given of the resolution of crystalline samples and whether individual crystal particles are correctly identified and the need...
for a "representative" sample to be chosen to be studied. A small sample is chosen to be viewed and this may not be an average of the sample as a whole.

Photon Correlation Spectroscopy (PCS)

PCS measures the scattering pattern produced when light is shown through a sample. It combines this with calculations of the diffusion caused by Brownian Motion in the sample in a relationship described in the Stokes-Einstein equation. This will give the radius of a particle and therefore an estimation of the average particle size and distribution of particles through the sample. The sample must be a liquid, solution or suspension. It must also be very dilute or the scattering of light can be unclear. The technique is sensitive to impurities and the viscosity of the sample must be known. The range of particle sizes that can be measured has been quoted between 1nm - 10μm.

An extension of this technique for higher concentration or opaque samples, such as emulsions, is Photon Cross Correlation Spectroscopy (PCCS). This can also be applied to nanoparticles.

Nanoparticle Surface Area Monitor (NSAM)

This technique is aiming towards applications of inhalation of nanoparticles by humans. It is therefore useful for health effects studies, occupational exposure monitoring and research into aerosols and inhalation toxicology. The argument for looking at surface area of the particle over mass of the particles is that the exposure to possible toxicity will come from the amount of alien particle in contact with the human tissue. This is therefore the surface area rather than the mass of the particle. This initial contact may of course be superseded if the particle were to decompose in the lung, which gives an argument for both surface area and mass to be known.

A NSAM uses an electrometer to measure the charge of an aerosol sample that has through a diffusion charging chamber. A calculation based on these measurements is then made to work out the deposited surface area of the sample particles in respect to different regions of the human lung, mainly the trachea bronchial and the alveolar. The accuracy is quoted as + or − 20%.

Techniques working on the same principle but not involving the human lung-deposited surface area of the particles are the Electrical Mobility Analyser, the Electrical Aerosol Detector and the Differential Electrical Mobility Analyser.

Condensation Particle Counter (CPC)

A CPC uses a condensation technique to enlarge small particles, such as nanoparticles, to a size that can be easier detected by an optical detector. The concentration of particles in a sample can therefore be calculated. Portable CPCs are common and hand held devices are available. The technique is suitable for aerosol samples and knowledge of solubility of the sample is required to ensure the particles do not dissolve in the chosen solvent in the condenser. This technique can be used for higher temperature samples, such as exhaust emissions, up to 200°C.

Differential Mobility Analyser (DMA)

A DMA will classify charged particles according to their mobility in an electric field. An aerosol sample is charged and sent in an air flow into a chamber where an electric field can be applied.
The rate at which the particles migrate to the end of the chamber will depend on their electrical mobility. Particles with the same electrical mobility will be the same size. Particles can therefore be sorted into different sizes and the size distribution worked out.

The sorted different particle sizes can then be put into a CPC to find the concentration of each particle size. This combination of techniques is called a Differential Mobility Sizer (DMPS).

Recent developments in the use of DMA for nanoparticle characterisation include the improvement of a Radial DMA. This variation in technique is reported as improving the measurements in the 1 – 13nm range. There have also been efforts to scale up the DMA to use flow rates as high as 90 l min\(^{-1}\), far greater than the few litres per minute of sample currently used. The success of this would have application for use in an industrial situation, where nanomaterial is used, as opposed to the current laboratory based use of DMA.

**Scanning Mobility Particle Sizer (SMPS)**

This technique uses a CPC to establish the size distribution of particles in an aerosol sample. In the SMPS an electrostatic classifier is combined with the CPC. The electrostatic classifier separates the particles by size so that the sample becomes a monodispersed aerosol (with particles of the same size, shape and mass).

SMPS and DMA are useful techniques for applications of aerosol and nanotechnology research as well as for air measurements to establish air pollution or occupational exposure.

**Nanoparticle Tracking Analysis (NTA)**

This technique provides information of particle size, size distribution and a real time view of the nanoparticles in the sample. The sample must be a suspension for which a wide range of solvents can be used. It is placed on an optically opaque background and a laser light used so that the nanoparticles can be directly visualised through an optical microscope. A digital camera is also used to record the observed particles. Software can then produce a frequency size distribution graph.

NTA could be combined with techniques such as PCS to maximize the information obtained about the sample and check accuracy.

**X-Ray Diffraction (XRD)**

XRD can be used to look at single crystal or polycrystalline materials. A beam of x-rays is sent into the sample and the way the beam is scattered by the atoms in the path of the x-ray is studied. The scattered x-rays constructively interfere with each other. This interference can be looked at using Bragg’s Law to determine various characteristics of the crystal or polycrystalline material. Measurements are made in Ångströms, 1 Ångström = 0.1nm.

The use of XRD is often compared to the microscopy techniques. XRD avoids issues of representative samples and determining crystals as opposed to particles as discussed above. However XRD can be time consuming and requires a large volume of sample.

**Aerosol Time of Flight Mass Spectroscopy (ATFMS or TOF-AMS)**

ATFMS focuses an aerosol sample into a tightly collimated beam of light. The particle sizes can be calculated by measuring the velocities of the particles in the beam. The beam then hits a
heated tungsten surface and the non-refractory components of the sample vaporise. The vapours are then analysed for their chemical composition by electron ionisation mass spectrometry. Accuracy of the particle size information can be improved by first using an electrostatic classifier to separate different sizes of particles.

ATFMS is less efficient for smaller size particles and therefore though reported for use with aerosol nanoparticles the technique may still require further development.

**Aerosol Particle Mass Analyzer (APM)**

The APM is the only technique listed here that concentrates on the mass of the nanoparticles. It is a technique independent of particle size, shape, orientation or the properties of the gas surrounding the particle. It classifies particles based on their mass to charge ratio. The analyzer uses two cylindrical electrodes rotating around a common axis. The aerosol sample particles are charged and sent into the annular gap and kept rotating at the same speed. When voltage is applied to the inner electrode the particles experience opposing centrifugal and electrostatic forces. From the balance of these forces the particle mass can be calculated.

**Summary of Considerations**

- What is the aim of the measurement? (number, mass, particle size, surface area?)
- What type of sample is required for analysis? (aerosol, suspension, solid, liquid?)
- Does the technique require the sample to have certain properties or be prepared in a certain way?
- What amount of sample is required and will the sample be destroyed?
- How long will the analysis take?
- What are the costs involved in the measurement technique?

**References**

Azo nanotechnology  [www.azonano.com](http://www.azonano.com)


Kanomax www.kanomax-usa.com

Nanosight www.nanosight.co.uk

Scientific Committee on Emerging and Newly Identified Health Risks (March 2006). The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies – modified opinion (report)


Sympatec GmbH www.sympatec.com

TSI (Trust Science Innovation) www.tsi.com

XRD.US www.xrd.us

Pacificnano http://nanoparticles.pacificnano.com
Annex 4  Total overview of nano-products

In chapter 3 many different nano-products have been introduced. An overview of those products is given in the table below, listing their product type, name and supplier and where known the nano-material or nanoparticle the nano-product contains. In addition to this list, there were various internet sites found to host nano-products. To name a few examples:

1. www.nanoworld.dk presents an overview of many different nano-products for sale at the internet. These products range from nano-socks to multicleaners developed using nanotechnology.

2. The Woodrow Wilson Institute does maintain a database of products brought at the US market at www.nanotechproject.org/inventories/consumer/

3. The German have a site www.nanoproducts.de (or www.nano-portal.eu) that contains a specific section for construction products.

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<td>TiO2</td>
<td>?</td>
<td>?</td>
<td>KWS</td>
</tr>
</tbody>
</table>
Annex 5  Nano-materials in more detail

In the present report, focus is on nano-materials and nano-products and their uses in the construction industry. The basis of any novel properties of the materials and products is in most of the identified cases the addition of nanoparticles (with the exception of i.e. several insulation materials that consist of a nano-foam: nano-holes instead of nanoparticles). These nanoparticles though, could cause health and safety risks that cannot be predicted based on the existing knowledge of their larger structures. An increase in surface area (per unit mass), for example, will result in a corresponding increase in chemical reactivity and a decrease in particle-size and altered electronic properties will influence the way nano-materials behave in the environment and in the body of a human being.

In relation to the use of nanoparticles in food and feed products, the EFSA Journal (2009) 95 did present a comprehensive overview of the present state of knowledge (known’s and unknowns) with respect to the uptake and distribution of engineered nanoparticles in the body, typical target organs and health and safety aspects. According to this work and references therein, uptake and distribution through the human body and the toxic effect observed depends on the type and size of nanoparticle. From the studies available though, it is most often difficult to judge the nature and fate (i.e. aggregation/agglomeration, metabolites) of the particles in the body as a thorough particle characterization is minimal (or lacking at all in some cases). No long term toxicity studies do yet exist. Acute toxicity tests do show inflammatory responses as a result of oxidative stress mechanisms for most nanoparticles studied and do show indications of genotoxicity for some nanoparticles, including iron/platinum, cobalt/chromium (CoCr), ZnO, SiO2, TiO2, carbon black (CB), carbon SWNT and carbon MWNT.

In the construction sector, only a limited group of nanoparticles are actually identified as being used in products. Those particles encountered most often are:

a. Titanium dioxide (TiO2)
b. Zinc oxide (ZnO)
c. Aluminum oxide (Al2O3)
d. Silicium dioxide (SiO2)
e. Silver (Ag)
f. Organo fluor compounds (CF-compounds)

In the sections below, the current state of knowledge on possible health and safety issues of some of these nanoparticles will be discussed (i.e. TiO2, ZnO, SiO2 and Ag). In addition to this, an overview will be given of CNT health and safety issues. Though CNT have not been identified in construction products in the current report, there is active research and development ongoing in this field and these nanoparticles might become an important ingredient of construction products in the future.

Carbon nanotubes
Carbon nanotubes (Figure 0-1) are cylindrical in shape with a diameter between 1-100nm and a length that can be up to several millimeters. CNT’s can be single walled (one shell of carbon atoms thick) or multi walled (more than one shell of carbon atoms thick). The Price of nanotubes depends on quality and material specifics and ranges from about €20 to €1000 per gram.

![Single-walled CNT and Multi-walled CNT](image)

Figure 0-1 Artist depiction of single-walled (SCNT) and multi-walled (MCNT) carbon nanotubes

Some remarkable properties of CNT’s are their high strength (~100 times the strength of steel whilst being 1/6th the density), tunable eclectically conducting properties and high thermal conductivity (along the tube axis). CNT’s are available commercially but selective and uniform production of CNT’s with specific dimensions and physical properties is still a challenge.

From a number of in-depth interviews, the information is obtained that, though research is ongoing, CNT are not applied to concrete materials (yet). Near future products are most likely to be expected in the field of (fire) protective coatings for textile, wood, steel, aluminum or concrete, and anti-fouling coatings for marine applications. Other applications like i.e. CNT enforced concrete products are probably further away from real market applications.

Health and Safety issues of CNT
At present, there is a lot of media attention for the potential health and safety risks of CNT’s. Especially leading has been the work by Poland et al. (2008) showing that MWNT of specific aspect ratio’s with respect to their diameter and length did induce similar inflammation and lesions characteristics in the mesothelial lining of the body cavity of mice as asbestos does. Their work does suggest a relation between the health effects of asbestos and those of CNT upon inhalation. However, great care should be taken when interpreting these results. The current suite of studies points at many different factors that play a role in the eventual toxicity pattern of CNT. First there is the number of walls of the nanotube (SWNT or MWNT), the aspect-ratio and its rigidity. Preliminary work in vitro and in vivo seems to suggest that especially those CNT that are rigid and longer than ~10µm pose a health risk that looks similar to the first stages of asbestos induced cancer (Poland et al. 2008, Pacurari et al.)
2008, Kostaleros 2008). Coupled to this, and complicating the discussion, is the observation that agglomeration of “short” CNT to long rod-like agglomerates of several micrometers seem to induce toxicological effects that relate to the effects observed for long (>10µm) and rigid CNT’s, and similar to the asbestos reference (Wick et al. 2007). This finding is especially interesting since in the application of CNT, one of the technical challenges faced today is to disperse them in the product (methods are e.g. the use of specific solvents, detergents, ultrasonication and the specific activation of the CNT surface) and prevent their agglomeration during the production process. Given this situation (see e.g. Kostaleros 2008), there is a severe chance that CNT containing products do contain a fraction of agglomerated material that might induce asbestos like effects, even though the CNT itself might be shorter than 10µm.

Besides size and shape, other factors influencing the toxicity of CNT are the concentration of defect sites at the surface of the CNT, influencing the oxidative reactivity of the CNT, and the presence of any active groups like for example carboxylic acids. The studies investigating the CNT toxicity do also show indications that small metal catalyst impurities in the CNT-batch do influence the toxicological character observed (Pulskamp et al. 2006). However, since not all studies did address these issues in a systematic manner, results remain inconclusive.

Still, even though results are inconclusive and more work needs to be done to better quantify CNT toxicity, there is enough scientific evidence to motivate that exposure to CNT material should be prevented and care should be taken to study the risks of such an exposure prior to production and use of any product.

**Metal Oxides**

**Health and Safety issues of Metal Oxides**

The toxicity of metal oxides nano-materials does vary significantly per material type. Just to name some, upon inhalation nano-TiO₂ is more effective in inducing oxidative stress than similar concentrations of nano-Fe₂O₃ (Bhattacharya et al. 2008) but crystalline nano-SiO₂ is much more aggressive than TiO₂, showing clear indications of carcinogenic effects (see NIOSH Draft2005; expected for publication in 2009). At this moment in time, it is therefore difficult to generalize any effects or to speak of ‘the toxicity of nano-metal oxides’ as each will have its own unique footprint.

**Titanium dioxide**

Probably the most widely used nano-additive in construction nano-products today is titanium dioxide (TiO₂) (see Figure 0-2 for an example image of the anatase TiO₂ form). In its microscopic form, TiO₂ has been widely used as white pigment (particle size ~300 nm). Nano-TiO₂ particles are transparent (particle size <100 nm) for visible light but are still able to absorb UV-light or use the energy of the UV-light to photo-catalyze the degradation of i.e. NOx or organic air pollutants. Nano-TiO₂ is added to paints, cements, glass, tiles, or other products for hydrophilic, UV-blocking, sterilizing, deodorizing and anti-fouling properties.
Typically two forms of nano-TiO₂ are observed to be used: rutile TiO₂ and anatase TiO₂. As will be shortly addressed below, there are indications that suggest that health and safety aspects of these two morphologies might differ. It is therefore important to distinguish between the two in the construction products used. For those nano-products indicated in this study, it is often not possible to positively identify what nano-form is used from the product information supplied.

The toxicity of nano-TiO₂ is one of the best studied among all engineered nanoparticles. As has been note previously, the toxicity of its two morphological structures, anatase and rutile TiO₂, seems to differ. Most toxicological studies though, do not specify the exact morphology studied and it is therefore difficult to interpret and further quantify the extent of this differences. However, in the studies that do differentiate between the two, anatase is generally found the most hazardous of the two forms. One example of such a study is done by Sayes et al. (2006) showing results that suggest anatase TiO₂ can be about 100x more toxic to in vitro cell cultures than an equivalent sample of rutile TiO₂.

![Electron micrograph of (anatase) titanium dioxide (TiO₂) nanoparticles](image)

Figure 0-2 Electron micrograph of (anatase) titanium dioxide (TiO₂) nanoparticles

The International Risk Governance Council (IRGC 2008) does conclude in one of their recent reports that nano-sized TiO₂ exposure to the intact skin probably doesn’t affect human health, although critical notes are to be made on the possibility to penetrate damaged skin (SCCP 2007). This detail might be of particular interest when one realizes that damaged skin does involve scratches and abrasions, but also includes damages such as sunburns. For construction workers, these type of damages to the skin are not uncommon.

The IRGC though, did investigate the potential health risks of nano-TiO₂ as a consequence of skin-contact in the context of its presence in several cosmetics products including transparent sun creams. As these creams might be used by construction workers, this source of (occupational) nano-TiO₂ skin-exposure is to be taken as seriously as the potential skin-exposure to nano-TiO₂ from working with coatings, cement or concrete.

Via inhalation exposure, indications are found that TiO₂ is able to induce adverse effects. A comprehensive overview is given by NIOSH (Draft2005). TiO₂ might (under certain conditions) show genotoxic potential and does show inflammatory effects upon inhalation. This latter effect seems linearly related to the surface area of the
particles per unit mass and is dependent on the exposure duration and concentration and is seen to be reversible in some studies. This same overview furthermore presents some indication of carcinogenic effects in lung tissue induced by long term exposure to anatase TiO$_2$ (but not to rutile TiO$_2$). More recent in vitro studies support this, showing that anatase TiO$_2$ induces oxidative stress reactions in human lung tissue that are observed to result in DNA damage (Bhattacharyya et al. 2008). Very recent toxicological work by Simizu et al. (2009) furthermore does indicate the possibility for anatase TiO$_2$ to affect the development and function of the early central nervous system development of unborn mice after prenatal inhalatory exposure of their mother, hinting at the possibility of reprotoxic effects in humans.

Anatase TiO$_2$ is the form typically applied for photo catalytic applications$^{96}$. Since this material property is attributed to TiO$_2$ in a suite of different construction nanoparticles it is important to be aware of the fact that this substance might have adverse effects on human health and protective measures against inhalation should be taken. Skin protection is probably also advisable, although health hazards via this exposure route are likely to be less severe than when the particles get inhaled.

**Zinc oxide**

ZnO nanoparticles are used in coatings to absorb UV-light. The particles are less opaque than similar particles of TiO$_2$. ZnO absorbs both UVA and UVB rays of UV-light. It is the broadest spectrum UVA and UVB absorber that is approved for use as a sunscreen by FDA, and is completely photo stable. Like TiO$_2$, ZnO also has photo-induced anti-microbial and anti-fungal activities.

The toxicity of nano-ZnO is much less well studied than that of TiO$_2$ but toxicological studies do show indications of oxidative stress reactions in lung tissue and oxidative DNA damage (Lin et al 2009; EFSA 2009). In an environmental setting, a comparative study by Adams et al. (2006) investigating the toxicity of TiO$_2$, SiO$_2$ and ZnO to bacteria in water does show indications that ZnO nanoparticles are potentially slightly more toxic than both TiO$_2$ and SiO$_2$. However, unlike these, the toxicity of ZnO did not seem to be effected by the presence of (UV) light, whereas the toxicity of both TiO$_2$ and SiO$_2$ did increase when a (UV) light source was present. As TiO$_2$ is typically considered to be an effective bactericide to disinfect water, it should be noted that both ZnO and SiO$_2$ can also act as bactericides in similar concentrations. This observation is not directly relevant to assess the occupational health risks of construction workers, but is important to take into account in relation to environmental health and safety when treatment of spills, cleaning and maintenance activities or wear of the construct are considered.

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>UV/light stability</th>
<th>Anti-microbial</th>
<th>Anti-static</th>
<th>IR-absorption</th>
<th>Magnetism</th>
</tr>
</thead>
</table>

Silica
When addressing health and safety aspects of nano-silica, there is a big difference between amorphous or crystalline nano-SiO₂. According to a recent report by the IRGC, synthetically produced nano-SiO₂ is water soluble and non-toxic. However, depending on the method of production, amorphous SiO₂ can be contaminated with crystalline SiO₂, which, depending on the fraction of crystallinity, does effect the toxicity of the total sample. Merget et al. (2002) did present a comprehensive review on the toxicity of amorphous SiO₂. Amorphous silica fume is normally treated with similar human risk factors related to toxicity as non-nano non-toxic silica dust. It has been observed to cause fribrogenic effects upon occupational exposure and defined exposure safety thresholds for inhalation lay in the range between 4-10 mg/m³. Crystalline silica on the other hand with its needle like structure and sharp edges (typical length of 200nm and less and diameter of about 20nm) is very toxic and is known to cause silicosis upon occupational exposure. Between the two, amorphous silica is most widely used. Applications of crystalline silica fume are found for example as additive in paints or coatings (see also section 0). Amorphous silica fume is the form normally used in cement and concrete. Amorphous silica fume does however contain small amounts of crystalline silica (varying between 0.1 and 60% depending on the production process), with the exception of high grade synthetic amorphous silica fume that is for example used in cosmetic or food products. In contrast to amorphous silica fume, for crystalline silica fume much lower threshold limit values (as low as 0.05 mg/m³) have been proposed. It is therefore essential to be informed by the product manufacturer about the potential crystalline silica fume contamination in order to take appropriate safety measures.

Nano-silver

Little is known about the toxicity of nano-silver for humans and the environment. Wijnhoven et al. (2009) reviewed today’s available knowledge and knowledge gaps. They hypothesize that the toxicity of nano-silver is proportional to the activity of the silver-ions released by the nanoparticle. This hypothesis has been derived from the general toxicity observations for the regular metal that relate toxicity to those forms of silver that release silver-ions. Regular silver is relatively non-toxic: the release of silver-ions is typically too low to cause a health effect. However, upon long term exposure, soluble silver-compounds are observed to accumulate in small amounts the brain and muscles. Silver-ions are in fact toxic to the environment and aquatic organisms. 1-5 microgram l\(^{-1}\) of bio-available silver-ions is already toxic for the most sensitive organisms. However, under normal conditions for regular silver polluted environments, this concentration is not reached.

For nano-silver pollution though, there might be a risk of exceptional silver-ion release, leading to an increased bioavailability. The limited work available does show indications that nano-silver does exhibit a different biological activity and does show different physico-chemical properties than the regular silver metal (non-nano) due to a higher surface-to-mass ratio. Various toxicity studies show that silver nanoparticles influence reproduction and development, do cause DNA damage, stop cell growth and cause cell damage in mammalian cell cultures. However, sufficient data on environmental fate patterns of nano-silver is missing.

With respect to human health hazards, Wijnhoven et al. (2009) reviews that inhaled nano-silver particles have been observed to be taken up in the lungs, enter the body and appear in the blood. Furthermore, nano-silver that enters the body via the nose has been observed to reach the central nerve system and the brain. Ingestion via the mouth has been seen to result in uptake of nano-silver particles in the gastrointestinal tract and accumulation of these particles in various tissue. And finally, dermal uptake through damaged skin has been observed, though it is uncertain if nano-silver or only the silver-ions did penetrate the skin. Target organs typically involve the liver and the immune system. As has been noted previously, the hypothesis is that exposure to the silver-ion is responsible for at least an important part of the toxicity observed. However, Wijnhoven et al. (2009) do stress that the knowledge available is still to scarce to be conclusive, especially also because in the toxicity studies available, often a detailed description of the fate of the nano-particle in the organism after exposure and uptake (!) is missing.