IVAM UvA BV

Working with NP®-coatings at Nanopool GmbH

Annex to the Report *Nano in Furniture, State of the art 2012*

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Colophon

Title:	Working NP® coatings at NanoPool GmbH **Annex** of the report *Nano in Furniture -State of the art 2012*
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Working NP® coatings at Nanopool GmbH, Germany

Present: Mr. Sascha Schwindt

Meeting and nanoparticle exposure measurements, 27th March 2012

Nanopool GmbH has been founded ca. 10 years ago and is fully family owned. Their core business is the production and application of liquid-glass coatings. The coatings are either water-based or ethanol based, depending on the requirements of the substrate surface. The active ingredient of the coatings are SiO_2 molecules. Depending on the desired coating characteristics, the concentration of SiO_2 molecules is raised or lowered, or its surface is modified.

In a low concentration coating (2 – 10% of nano-SiO_2) a thin glass-membrane is formed at the surface of the substrate that is porous to gasses but highly hydrofobic and oleofobic such that a water-repellent, easy-to-clean layer is created, that allows to wipe-off:

- fingerprints
- graffiti and other permanent markers
- spills from coffee, wine etc

with only the help of a wet tissue, without leaving any residual stains.

When applied on metal, it furthermore acts as an oxidation protective layer. On laminate flooring systems, it adds to the durability of the material by preventing swelling by water, which is especially interesting in i.e. a kitchen *or bathroom* environment where the spilling of water on the ground is a regularity. Moreover, the dense flat layer hampers microbial growth, and prevents fungi or algae the grow (or 'eat') on the surface. In the case of wood, it even prevents termites from eating the wood away. And outside the direct scope of the furniture industry many other applications are thinkable that could benefit from this type of coating.

Nanopool is contracted by furniture companies in the last stage of their production process. The furniture manufacturer sends them their products (cushions, tables, cabinets, cupboards, chairs) to be treated, after which the product returns to the furniture manufacturer to be send to the customer. Alternatively, Nanopool trains the furniture manufacturer to use their coatings them self. In this case, the furniture manufacturer receives a 5-day course to learn the ins and outs of working correctly with the Nanopool-coating, how the product works, how to reach optimum coating performance and how to explain customers about the product. Over the years, they trained approximately 300 people from many different companies from Norway to Italy, to India, to New Zealand and Brazil. At this moment they are training a group of Furniture manufacturers which are working all over Europe about their products and potentials for furniture products.

At this moment, the main focus of Nanopool is on Hospital furniture and medical applications since in Germany, there is a serious germ problem in hospitals and therefore a clear market demand for solution. However, car, kitchen and office furniture are other markets in which they see growth potential. Bacterlon, the product available for this purpose of reducing bacterial growth at all sorts of surfaces has been tested by Nanopool for many different adverse effects on health and safety like skin sensitization, irritation, inhalation toxicity and cytotoxcity. All proved positive for ‘no-invasive’. Moreover, the product proved to comply to the European standard for food-safety.They furthermore received approval to use their coatings on medical implants (in this case, it is the implants producing manufacturer who applies the coating to deliver a ready-for-use product at the hospital).

One factor responsible for the low toxicity profile is the rapid polymerization of the SiO_2 molecules upon application. As soon as the SiO_2 molecules polymerizes, the ‘nanoparticle’ dimension of the material disappears and a nano-thick layer is formed. Consequently, possible exposure (of workers or of end-users) is no longer an issue. Preliminary results do suggest that once the coating has dried, no monomer nano-SiO_2 resides at the surface, ruling out a residual risk of monomer exposure of end-users.

Despite their certificates of safety, when Nanopool gets in contact with new customers though, they normally do not highlight the ‘nano’ in their product. It is their experience that customers in general do not appreciate the possible uncertainty on health and safety risks that are being associated to ‘nano’. However, once they get to know the product and get familiar with its characteristics, they are no longer frightened by the idea of applying a nanoproduct.

Also, their customers (i.e. textile manufacturers, but also manufacturers from the furniture industry aren’t enthusiastic by the idea of exposing themselves as companies using nanocoatings on their products. This, being a consequence of the world-wide social debate on nanotechnologies, focusing primarily on the risk aspects and the uncertainties therein.

Exposure measurements Nano (27th March)

Measurement strategy:

The exposure of the worker to airborn nanoparticles was determined in real-time using the portable NanoTracer by Philips Aerasense. The NanoTracer measured both the average number of nanoparticles in the air and their average diameter. The NanoTracer doesn’t provide any information regarding the chemical composition of the nanoparticles. One NanoTracer was positioned “at the worker” to probe the amount of nanoparticles present in the breathing zone of the worker. A second NanoTracer was positioned in the Far Field, 1 – 5 meters away from the worker to monitor changes in the background concentration of nanoparticles in the room. The position of the two Nanotracers is shown in the picture of Figure 1.

The shape and chemical composition of the nanoparticles was analysed off- line by SEM/EDX spectroscopy (Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy).

 

Figure 1 Positioning of the two NanoTracers and the Filter for passive sampling of airborn nanoparticles for chemical analysis by SEM/EDX. Left photo: On the table one finds the Far Field NanoTracer. Right photo: At the shoulder of the worker one finds the in-let "tube" of the NanoTracer for personal exposure measurements (the actual NanoTracer is carried at the back of the worker) and the circular "batch" for passive SEM/EDX sampling.

To allow for this off-line analysis, a carbon filter was used to collect any airborn nanoparticle present in the breathing zone of the worker during the work activities. The carbon filter was placed in a small petrish dish and positioned at the shoulder of the worker in close proximity of the place where the NanoTracer did monitor the amount and average diameter of the nanoparticles in the breathing zone of the worker. The position of the batch is shown in the picture (right one) of Figure 1. For more information on the measurements, their interpretation and their implications for working in a precautionary safe manner with nanomaterials, one should consult the report *Nano in Furniture, state of the art 2012*.

Measured activities:

1. Spray-coating of a dentist chair cushion. Ethanol based coating (2-10% nano-SiO_2) use of ca. 2 ml of coating m^{-2} of treated surface. Application: spraying on a small whipping cloth by a low pressure manual pump at short distance. Application of the coating on the surface of the dentist chair cushion with this wetted cloth. This to obtain a maximum thin glass-layer on the surface of the textile to reach optimum performance.

2. Cutting of a Nylon textile, treated with a Nanopool SiO_2 molecules coating, with normal scissors.

3. Spray coating of an office chair with water-based coating (2-10% nano-SiO_2) with a consumption of ca. 20 ml /m². After spraying the coating, the surface was brushed with a soft hand brush in order to homogeneously spread the coating over the textile fibers and 'rub-it-in'.

No ventilation was present in the room. No personal protection was worn other than protective glasses and a lab coat. Room dimensions were approximately 5x12x3.5 = 210 m^3. In case of bigger samples to be treated, applications are performed in a ventilated and larger area. This room was in use for another project at the moment of the visit.

Table 1 Overview of average exposures to nanoparticles during spraying activities using NP water or ethanol based liquid glass coatings or cutting treated textile

Marker	Av. amount of particles N cm-3 (FF)	Av. diameter (nm) (FF)	Av. amount of particles N cm-3 (PS)	Av. diameter (nm) (PS)	Comments
A	6.914	143	7.914	119	Manual spraying. Spray on cloth, wipe-on procedure. Ethanol based coating
B	8.859	121	8.375	114	No-spraying, coating first dripped on cloth, wipe on treatment
A&B	7.920	132	8.191	116	A & B together
D	7.581	123	7.934	98	Cutting treated textile (nylon) with normal scissors
F	6.927	130	8.763	88	Manual spraying directly on an office chair followed by brushing of the treated textile. Water based coating
G	7.337	115	6.678	95	Background

Figure 2, Figure 3 and Table 1 present the results of the three different exposure measurements conducted during Wipe-on coating of textile, Spray-on coating of textile (including brushing) and cutting of treated nylon. Figure 2 and Figure 3 show the average amount of nanoparticles present in the room during the time of work and the average diameter of the particles, respectively. 'PS' indicates the personal sampling in the direct breathing zone of the worker (at a distance of approximately 10 cm from his mouth). 'FF' represents the Far Field measurement taken at a distance between 1 to 6 meters away from the worker. When studying the graphs, they show a very constant and stable indoor air without turbulence or other 'sudden' disturbances on the nanoparticle-level.

The average diameter of the particles measured lays around the 100 nm and is seen to vary (on average) between 88 nm to 143nm for the different activities looked at. Within the measurements, there seems to be no correlation between an activity occurring and an average particle diameter observed. This also seems to be the case for the total amount of nanoparticles measured in the air. From these measurements there appears to be no correlation between the work activities performed with the nanocoating or the nano-treated nylon and the amount of nanoparticles observed in the air near the worker (PS) or further away (FF) in the

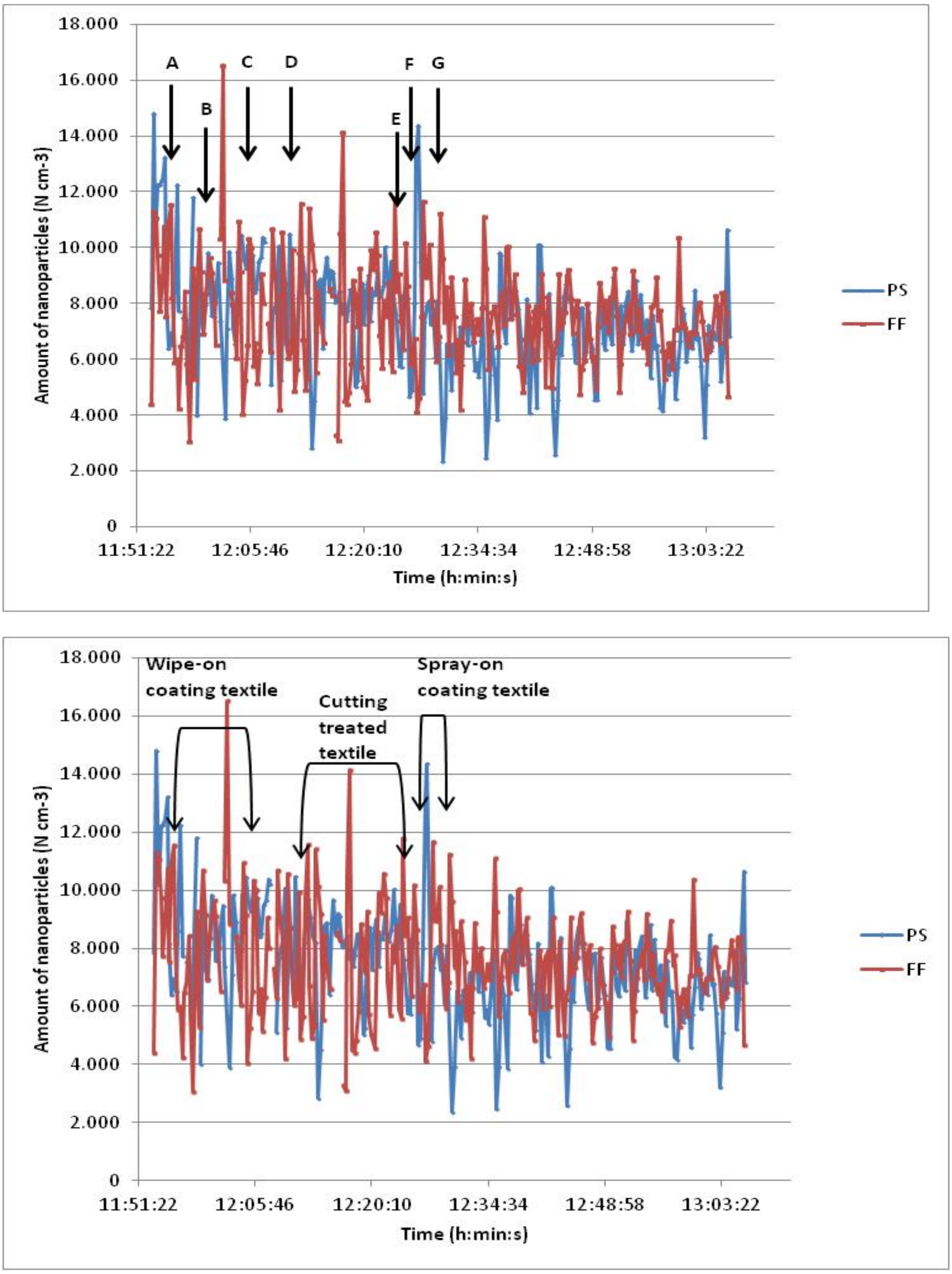

Figure 2 Nanotracer data (no background subtracted, no smoothing of the raw data): Number of nanoparticles measured per cm^{-3} (y-axis) at the production facility of Nanopool GmbH, Germany, during the visit (time, x-axis) on the 27th of March 2012. The markers as they appear in **Table 1** and the corresponding work activities are indicated in the graphs.

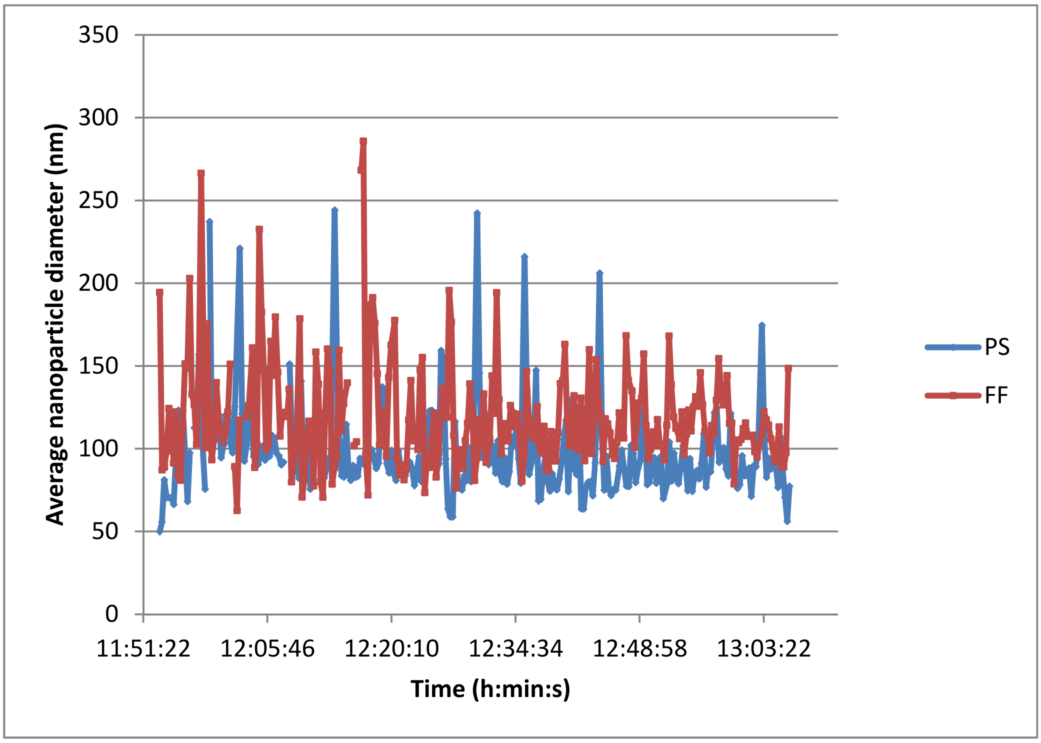

Figure 3 Nanotracer data (no background subtracted, no smoothing of the raw data): average diameter of the nanoparticles measured per cm^{-3} (y-axis) at the production facility of Nanopool GmbH, Germany, during the visit (time, x-axis) on the 27th of March 2012.

same room. The average concentration of nanoparticles per activity is seen to vary between 6.900 N cm^{-3} and 8.900 N cm^{-3}, which is similar to the background concentration measured after the work was finished.

SEM/EDX analyses of the airborne concentration of nanoparticles present during wipe-on coating and cutting of treated nylon textile show that SiO_2 is no observable fraction of the nanoparticles present in the breathing zone of the worker during his activities with the nanocoating. These results are in line with the NanoTracer data, showing that the present activities of low-energy spraying of a nanocoating and the manual cutting of textile do not result in a measureable increase in the nanoparticle exposure of the worker.

Figure 4 shows a typical SEM spectrum (Back Scatter Electron Modus) and the chemical analysis of various “spots” on the SEM image of the batch taken during low energy spraying of the nano-silica coating (activity 1). Based on the nanocoating applied, one would expect the process induced nanoparticles to contain a high fraction of silicium (Si). From the chemical element analysis could be concluded that Silicium was only a minor fraction of each spot, presenting no more than 20% of the elemental weigth. This result therefore suggest that silica nanoparticles where not emitted by the process to a detectable extend.

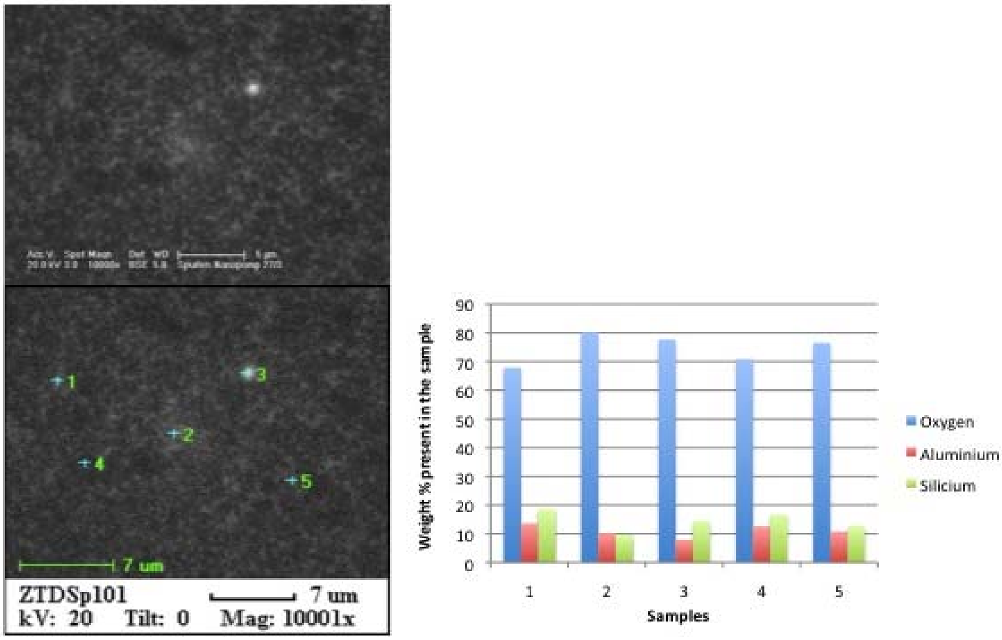

Figure 4 Personal exposure to nanoparticles during manual low-energy spraying of a Silica based nanocoating: left: SEM image in the "Back Scatter Electon" Modus, which is especially sensitive to highlight "heavy" atoms like silica. No. 1-5 point at the 5 different locations at the sample for which chemical analysis was done. Right: overview of different main elements present at each location. Oxygen was dominantly present in each sample. Silicium was only a minor (weigth) fraction, suggesting that the nanoparticles found in the air do not contain high levels of SiO2.

Figure 5 shows a typical SEM spectrum (Back Scatter Electron Modus) and the chemical analysis of various "spots" on the SEM image of the batch taken during manual cutting of nano-silica coated nylon textile (activity 2). Based on the activity, one would expect small pieces of textile, maybe small fibers that are released when the textile is cut. One would furthermore expect these fibers to contain small amounts of silica (Si). On the batch, No nanoparticles could be found containing heavy elements. These fibers were observed and analyzed in more detail. From the chemical element analysis could be concluded that Silica was only a minor fraction of each spot, presenting no more than 4% of the elemental weigth. The presence of Sodium, Potassium and Chloride and Sulphur on the other hand do hint that the fibers observed are of biological origin. Maybe a (human) hair. But not a nylon fiber with a silica coating.

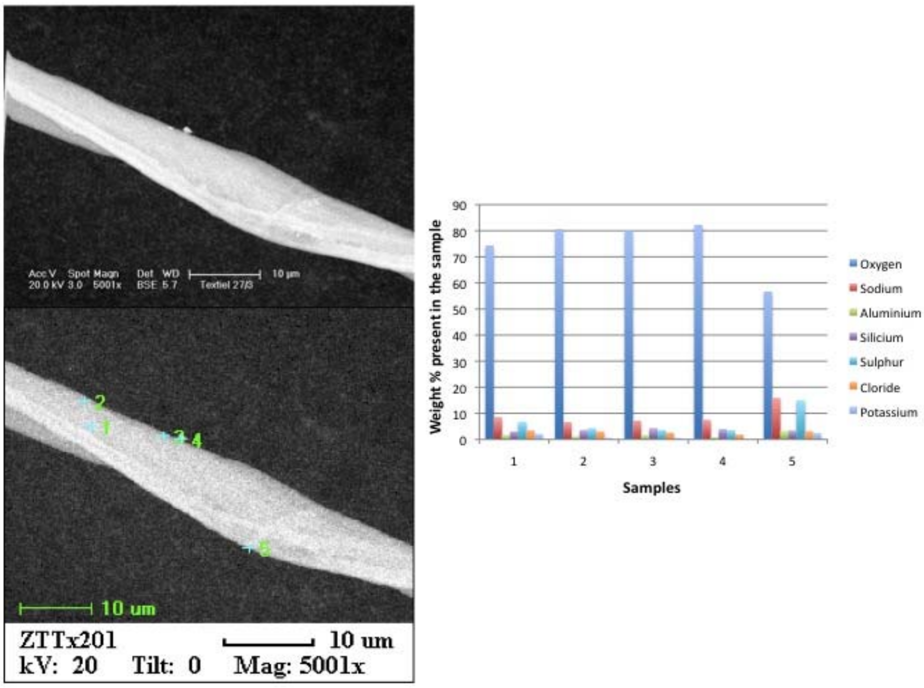

Figure 5 Personal exposure to nanoparticles during manual cutting of nylon textile treated with a a Silica based nanocoating: left: SEM image in the "Back Scatter Electon" Modus, which is especially sensitive to highlight "heavy" atoms like silica. No. 1-5 point at the 5 different locations at the sample for which chemical analysis was done. Right: overview of different main elements present at each location. Oxygen was dominantly present in each sample. Silicium was only a minor (weigth) fraction. The presence of Sodium, Potassium and Chloride and Sulphur suggest the fiber observed is a (human) hair and not a nylon fiber with silica.

Conclusion

The results from the NanoTracer and the SEM/EDX analysis both suggest that the current work activities do not give rise to any detectable exposure to nanoparticles of the worker involved. Treating the textile with the liquid glass coating and cutting treated nylon using manual scissors did not lead to elevated number concentrations of nanoparticles in the workplace air. There is however a significant risk of skin exposure when the coating is sprayed onto the whipping cloth. Exposure is well controlled wearing gloves and protective clothing. Preferably, this is done by nytril gloves and non-woven (Tyvek) clothing. These results so show first evidence that under the present conditions workers can work safely with these materials.

It should be stressed though that exposure characteristics may change when the intensity of the work increases. Also when workers work less careful than the worker involved here, exposures may increase. It is therefore advisable to assess the workers exposure to nanoparticles also during i.e. the larger scale processes.

For further and more in depth conclusions related to the European study *Nano in Furniture*, it is referred to the report, *Nano in Furniture, state of the art 2012*.