



USE OF NANOMATERIALS IN TEXTILE FINISHING

1. Case metadata

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2. Organisations involved

Schmitz-Werke GmbH + Co. KG

3. Description of the case

3.1. Introduction

The family-owned Schmitz-Werke is a large company employing approximately 800 persons. Six daughter companies represent the company in other European countries. Schmitz-Werke manufactures awnings, textiles for outdoor use and decorative textiles. It runs an integrated management system and certified quality and environmental management systems according to ISO 9001 and 14001 standards.

Schmitz-Werke decided to use a finishing agent for textiles containing nanomaterial in order to improve the quality of its awnings to repel water, dirt and oils by creating a self-cleaning surface. The finishing agent contains silic acid in nano form, with the silic acid particles incorporated as agglomerates.

The company has assessed potential risks from the use of the finishing agent and monitored the efficiency of the existing workers' protection measures at the workplaces in the concerned work areas (mixing station of the finishing agents, foulard and stentering frame) in the production facility of Schmitz-Werke. The assessment of potential releases of nanoparticles from the awnings (c.f. Section

3.3.5 on measurements) would also cover any workplace in subsequent processing sites outside the facility of Schmitz-Werke. In addition, potential risks were discussed with the employees and the customers and respective information related to further processing of finished textiles was forwarded in the supply chain¹.

3.2. Aims

To assess the health and safety issues that are relevant to the introduction of the new finishing agent into the production system; and to ensure that neither workers at Schmitz-Werke nor workers in the customers' production sites nor the final users of the awnings could be at risk from the use of nanomaterials.

3.3. What was done, and how?

In the context of its general quality and environmental management systems, Schmitz-Werke has established routines to introduce new products into its manufacturing processes, which were applied to the introduction of the nanomaterial as well. The routine is described in an internal electronic Wiki (intranet of the company). The routine consists of several steps, and a description of these follows.

3.3.1. Communication with suppliers

The safety data sheet of the nanomaterial containing finishing agent (dispersion) was assessed with regard to potential hazards for workers health. According to the classification rules for mixtures, the textile-finishing agent is not classified as dangerous. The safety data sheet's section on toxicology does not contain any specific information on silic acid. The recommendations on handling the product are based on the other (volatile) components of the finishing agent. The recommended measures are:

- Preventive skin protection and the use of gloves
- The use of goggles
- Use of respirators in case of high concentrations of the finishing agent (aerosols, evaporation) in the workplace air, in particular when occupational exposure limits could be exceeded.

In order to be sure that all risks are minimised for the workers, Schmitz-Werke consulted the supplier for further information specifically on the silic acid. The supplier confirmed in writing that:

- the primary particles of the silic acid (size range of 10 to 30 nm) are dispersed as agglomerates in the watery solution of the finishing agent,
- the agglomerates would later form a nanostructured surface layer on the fabric (provision of properties after application) and that,
- the formation of dusts is hardly possible for an aqueous product.

Furthermore, the supplier confirmed that the particles of silic acids are bound in a matrix on the fabric of the awning after application. The finishing agent contained binders, which lead to an additional fixation of the particles on the fabric. Therefore, a release of silic acid particles from the awning was stated to be very unlikely.

In addition, the supplier provided the results of toxicity studies with similar silic acids. The studies showed:

- No dermal, inhalative or oral acute toxicity
- At the 'technical maximum concentration', no mortality was observed after inhalative exposures in animal studies
- No irritation was observed for skin and eyes

¹ Normally the textiles are sold to companies which process the material and include it in awnings for use by consumers.

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- Animal tests did not indicate cancerogenic or reprotoxic effects after chronic exposure
- After chronic, inhalative exposure reversible effects were observed in the lung; however silicosis was not observed.

The content of the safety data sheet as well as the additional information of the supplier were assessed and Schmitz-Werke concluded that the handling and use of the finishing agent would in principle not cause risks to the workers, because the available information did not indicate any specific hazard.

Schmitz-Werke's company policy is based on a precautionary principle and being aware of knowledge gaps on nanomaterials in general, and the confusion and insecurity of workers regarding the use of nanomaterials; it was decided as essential and helpful to continue with a comprehensive assessment of the exposure situation, although the hazards were evaluated as low.

3.3.2. Internal procurement template and pre-test

The product was submitted to an internal procurement request in accordance with the management routine. This implied an additional check of the finishing agent with regard to potential hazards for workers and to water organisms. In addition, potential impacts on the company's compliance with legislation in the area of water emissions, air emissions and waste had to be assessed.²

In order to actually procure the finishing agent, it was necessary according to the management routine to assign a control band to the product defined in the German 'Easy-to-use Workplace Control Scheme' by the German Federal Institute for Occupational Health and Safety (BAuA). The workplace safety officer of the company assigned the control band. The product was assessed as follows:

- Classification: not dangerous (no R-phrases) → hazard class A
- Use amount: litres per day → medium group
- Release: boiling point between 50 and 150°C → medium group (use at room temperature)

The product was assigned to the control band 1 (low risk), which resulted in the preliminary conclusion that no additional measures were needed for its use. However, the Easy-to-use control scheme has not been developed with a focus on nanomaterials, which should be considered in its application. Therefore, Schmitz-Werke also conducted work to assess potential exposure levels.

3.3.3. Inclusion of information in the company's data base

All safety-relevant information was included in the company's data base system, during the testing phase of the product, to ensure that instructions and information are readily available in case of emergencies. The safety data sheet was scanned and saved. The identity of the hazardous components including their classification and labelling as well as any information on the safe use were entered into the data base. Based on this, instructions for the safe storage and use of the product at the workplaces were generated automatically. The workplace instructions were placed next to the storage places of the product and the workplaces where it is handled.

The hazardous components in the product were automatically entered into the company's hazardous substances inventory and the respective information was forwarded to the heads of the involved departments. Since the silic acid is not a hazardous substance, the nanomaterial is not included in the register of hazardous substances in the company.

3.3.4. Qualitative assessment of potential risks

² The product is not hazardous to the water environment and neither the silic acid nor other components of the product are subject to legal requirements under water legislation. No problems should arise related to air emissions because the existing regenerative afterburner is also appropriate for the use of the product containing nanomaterial.

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The production process was analysed in order to identify, whether an exposure and the type of exposure could occur to workers handling the nanomaterial-containing finishing agent. The production process was analysed and described as follows:

- The finishing agent is procured in containers, which are transported to their storage place. The containers are not moved from the storage until they are empty. They are secured with dripping pans and in case of leaks, an automatic alert is sent to the person responsible for this task, to take care of it.



- The storage containers are connected to an automated dosage system: the solution is extracted from the container using lances and directly introduced into the pipe system leading to the mixing vessel. The introduction of the lance is manual, but no direct contact occurs with the finishing agent.
- The different ingredients of the finishing agent for the textile awnings are pumped from the storage containers to a closed vessel for mixing. The piping system and mixing vessels are closed systems.

Figure 1: Automatic dosage system for textile finishing preparations

- The vessel is automatically emptied from the bottom and the finishing mixture is pumped to its place of use. The mixing vessel is automatically cleaned; manual work includes a visual inspection of the vessel and an additional cleaning with water, if necessary.
- The mixture containing the finishing agent is applied in a foulard. The textile is first continuously submersed and dragged through a bath containing the finishing agent. After that it is lead through a nip, which controls the amount of the finishing agent to be applied by squeezing the excess liquor into the submersion bath. The process is open and automatic. Therefore, no direct contact of the worker with the finishing agent is possible. Spills do not occur and the process is conducted at room temperature; hence any evaporation is very unlikely.



Figure 2: Application of textile finish in a foulard process

- After the application in the foulard, the textile is dried at high temperatures in stentering frames. These frames are closed systems operating at negative pressure. The volatile substances in the finishing agents and other auxiliaries used as well as the water vapours, are extracted through an exhaust extraction system, which is connected to a regenerative afterburner. Pollutants and hazardous substances are destroyed and the clean waste gas is emitted through the chimney to the environment. A release from the stentering frame into the workplace air is not possible due to the negative pressure in the closed system.

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- The awning textile is then reeled in after drying. As part of the quality control, those parts of the textile, which have production mistakes, are cut out and removed. At this time the nanomaterials are already bound into the matrix of the finish. Therefore, it is not expected that nanoparticles are released during this stage.
- The fabric is then further processed and put onto the awning frame either by Schmitz-Werke or by their clients³. During this process the fabric may be subject to mechanical stress when it is cut, sewn, glued, stretched, rolled etc. Since the nanoparticles are included in the matrix, it is assumed that no release occurs.

The most important results of the first qualitative analysis were:

- Dermal exposures of workers to the finishing agent may only occur, if at all, during the change of the lances from an emptied container into a new, full container with the textile finishing agent or during cleaning of the mixing vessels. It is prescribed in both cases that workers wear protective clothes, in particular gloves.
- Dermal exposures of worker with the finished textile are likely. It was not clear if the nanoparticles are actually fully bound to the finishing matrix, or not.
- Inhalative exposures are not likely during the process, because the textile-finishing agent is used in closed systems. The processing temperature in the only open process is so low (room temperature) that evaporation is not likely. A formation of aerosols is not observed.
- The highest likelihood of an inhalative exposure exists at the stage of tailoring, because here the fabric is submitted to high mechanical stress (dust formation is possible).

3.3.5. Measurements

Although information on the silic acid in the nano dispersion did not indicate a hazard for workers, Schmitz-Werke has conducted measurements of the workplace air. On the one hand, it should be ensured that any exposure is minimised in accordance with the precautionary principle (also exposure to non-dangerous products should be low). On the other hand, the concerns of workers with regard to the exposure to nanoparticles were considered seriously.

The manufacturer of the textile-finishing agent had tested the use of the product on textiles for technical and functional reasons inside his company. According to the manufacturer, a similar risk analysis of workplaces and uses had been conducted and no concern was identified. This was a first indication to Schmitz-Werke that the product can be used safely.

Nevertheless, Schmitz-Werke contracted an external laboratory to carry out sampling and analysis for exposure measurements in the area of the welding machines. The welding machines impose the highest mechanical stress to the fibre in the tailoring processes. The sampling was conducted during normal operation of the welding machines, as confirmed by an active worker stating that the 'process and activities were conducted as always'. The sampling time was two hours and the sampling volume was 0.4 m³ (0.2 m³ for the alveolar fraction).

The concentration of fine dust particles in the samples was 0.51 mg/m³ (inhalable fraction) and 0.74 mg/m³ (alveolar fraction). Both values are well below the occupational exposure limit value of (10 mg/m³ / 3 mg/m³). At the time of the measurement there was no method to distinguish the particle sizes or identify, whether or not the measured dusts (partly) consisted of silic acid or not.

Four years after the exposure measurements were done, an analytical institute developed a new method by which particle sizes can be determined exactly. Schmitz-Werke commissioned the institute to carry out measurements on the release of nanoparticles from the awning fabric under mechanical stress. For this, samples of the fabric were tested under

³ Companies that manufacture awnings sourcing the awning textile from Schmitz-Werke. The processes are similar at the clients' sites and at Schmitz – Werke: the awning textile is customised, cut, sewn and glued.

- a) highly abrasive conditions by very quick machining and,
- b) mechanical destruction.

One sample was used with and one sample without the nano-finish. Air samples were taken from the testing chamber within which the fabric was subjected to the mechanical stress. The air samples were analysed by SMPS/CPC⁴ and a particle size distribution in the range from 15 to 670 nm could be obtained.

In both textile samples no release of nano-particles was observed due to abrasion.

In the sample where mechanical stress led to the destruction of the fabric, from both samples particles were released. The nano-finished fabric sample released approximately 20 times more particles than the sample without the finish (in total approximately 2,500 / m³ compared to 130 particles per m³ in the non-finished textile). The particle from the finished fabric had sizes from 150 to 650 nm.

The type of released particles was not analysed. The sources of the particles could therefore not be determined. Apart from the possibility that the particles were released from the nano-coating, also the fabric itself and materials introduced during the processes could be a possible origin of the fine dusts.

In total, the release of particles from the finished textile was evaluated as rather low and in no way of concern. The measured concentrations were well below the existing occupational exposure limit values for fine dusts.

3.3.6. Communication with workers

Schmitz-Werke communicated internally and externally the different aspects of the nanomaterial use. The employees of Schmitz-Werke were informed via the workers' council and the company expert on workplace health and safety about the (planned) use of the new product. Information on the hazards of the silic acid particles in the finishing agent was provided. The workers' questions were answered, concerns replied to and the results of the measurements at the workplace announced. Furthermore, the results of the qualitative risk assessment were announced in detail. In addition, in an employees' meeting, the topic was discussed.

Information on the safe handling of the finishing agent was made available in the form of workplace instructions at the respective workplaces⁵. The content of the safety data sheet was published on the company's intranet and placed in the internal data base system for all persons who are involved with the production processes and the protection of workers' health in the company.

Schmitz-Werke also regularly conducted appraisal interviews, workplace instructions and training on the safe use of hazardous materials at the workplace. During these sessions, workers were informed on how to handle the nanomaterial and they could discuss their concerns with the responsible persons. Information was also provided to health and safety managers and workers' representatives.

3.3.7. Communication with clients

At first, Schmitz-Werke's customers, who further process the awning fabrics, were sceptical with regard to the nano-finish. At the time the finish was introduced, there were frequent reports and announcements in the media highlighting knowledge gaps and risks from the use of nanomaterials. These reports were not very well-founded and scientifically researched, which resulted in a lot of insecurity and confusion of the public about nanomaterials. Schmitz-Werke observed especially high concerns among workers who could come in direct contact with the nanomaterial and the end users of the awnings. The later were afraid that the nanoparticles could trickle down on them, when sitting under the awning.

Schmitz-Werke forwarded the measurement results on the release of nanoparticles from the fabric during mechanical stress to their direct and indirect customers to meet these fears and to provide

⁴ Measurement devices for nanoparticles: Scanning Mobility Particle Sizer and Condensation Particle Counter

⁵ Mixing station of the finishing agents, foulard and stentering frame

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relevant information. In most cases the customers could be convinced that no risks result from the nano-finish on the awning for their workers or consumers, because release is very low, even under worst-case scenarios.

3.4. What was achieved?

- The thorough analysis of information on the nano-product showed that at the current state of knowledge no risks could occur for workers of Schmitz-Werke and their customers.
- The qualitative analysis, the measurements of fine dusts at the workplaces and of the material under mechanical stress showed that only under extreme conditions nanomaterials are released from the fabric.
- Forwarding information from the hazard analysis, risk assessment and measurements to the employees convinced the workers of the harmlessness of the product use. It strengthened the trusted relationships in the company and well-being at the workplaces.
- The release of the measurement data from mechanical stress tests to the customers; increased their trust in the product safety and the safety in the further processing of the textile fabric.
- The entire process lead to the smooth introduction of a new product into the production process at Schmitz-Werke. The produced awnings have already reached a relatively high share of the total production and could be established successfully in the market.

3.5. Success factors

The core success factors for of the process were:

- Established routines for the introduction of new products, which include the collection, assessment and thorough analysis of information on hazards and risks regarding workers health.
- Early and active communication of the product hazards to the employees, regular information of the concerned workers protection experts in the company on the state of analysis and the potential risks.
- Measurements at the workplaces although no hazardous properties of the used nanomaterial were identified.
- Active communication of the nano-dispersion's benefits with regard to the product quality (better technical properties, higher environmental performance through less cleaning needs of the fabric) inside the company and at the customers.

3.6. Further information

Schmitz-Werke (www.schmitz-werke.com), contact person: Mr. Bosse (bosse@schmitz-werke.com)

In the scope of the Commission on Nanomaterials of the German Government, Schmitz-Werke has conducted an analysis of aspects related to the benefits and potential risk of nanomaterial containing products according to an instrument developed in one of its working groups. In the assessment, the environmental benefit achieved by the lower frequency of cleaning the awning compared to the conventional awning was described. Disadvantages of using the product could not be identified neither for the environment nor for workers or consumers. The results of the analysis are available (only in German) on the Internet

(http://www.oekopol.de/de/themen/chemie/nano/nano_material/17_Bericht_TG2_NanoKommission_Chancen_Risiken.pdf).

3.7. Transferability

The structured process of analysing the hazardousness of a material or product as well as the qualitative and quantitative exposure assessment is applicable to all workplaces where hazardous materials are handled and used. The used instrument 'Easy-to-Use Control Scheme' for a first identification of control bands is applicable to all chemical agents, including nanomaterials. The procedures are not only useful for the textile but for any industrial sectors.



The measurements on releases of nanoparticles / fine dusts under high mechanical stress are a relatively new method and can be applied in principle to all textile fabrics.

4. References, resources:

- Easy-to-use Control Scheme for Hazardous substances:
http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/workplace-control-scheme.pdf?__blob=publicationFile&v=2⁶
- <http://www.schmitz-werke.com/>

⁶ The English version has not been updated. A more recent version is available in German.