



RISK ASSESSMENT AND MANAGEMENT IN HANDLING NANOMATERIALS IN POWDER FORM

1. Case metadata

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manual emptying of bags

2. Organisations involved

Thor GmbH

3. Description of the case

3.1. Introduction

Thor GmbH manufactures different specialty chemicals, such as flame retardants, additives for the cosmetics industry (emollients, silicones and quats) or in-can and film preservatives for paints and coatings. Thor GmbH employs approximately 450 persons in its production site in Speyer, Germany. It runs an integrated management system and is certified according to ISO 9001:2008 and 14001:2004 standards.

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The company uses pyrogenic silic acid in powder form with a primary particle size of 5 to 30 nm¹. The particles form aggregates of a size from 70 to 500 nm and agglomerates from 1 to 10 µm as ingredient in its products. For the production of products containing silic acid at nano scale, it is manually filled into a mixing vessel containing a water-based dispersion. Workers could be exposed to and inhale dusts from opening and emptying bags and by the transfer of materials to the vessel. Dermal contact is possible also.

Thor GmbH conducted a risk assessment at the respective workplace in the production site in Germany² with the aim of avoiding and minimising exposures. The head of production, workers at the workplaces and the health and safety specialist were involved. The results of the assessment showed that the implemented technical, organisational and personal protection measures are effective in helping to minimise the potential risks that could arise from the silic acid. This was confirmed by air measurements at several similar workplaces.

3.2. Aims

To conduct a risk assessment and implement measures to protect workers from the risks of handling nanomaterials at the workplace. Dermal and inhalative exposures should be avoided as much as possible. Furthermore, manual activities should be performed with few burdens on the body as possible.

3.3. What was done, and how?

The responsible expert for workplace safety in the company carried out a detailed risk assessment at the workplace where the filling of materials took place. The workers carrying out the filling of materials were involved, as well as the head of the respective production department and the head of the research and development department.

3.3.1. Assessment of hazards

The safety data sheet of the supplier was analysed with regard to the hazardous properties of the substance and information on safe storage, handling and use. Section 2 of the safety data sheet states that silic acid is not classified as dangerous according to current legal criteria. The use of personal protective equipment is only recommended in case of dust formation during the handling of the material. Furthermore, the exposure limit values for dusts should be monitored.

In Section 11 of the safety data sheet, test data are provided indicating that silic acid does not cause acute toxic effects after oral intake. Furthermore, it does not cause irritation to skin or eyes. It is not skin sensitising and an Ames test did not display mutagenic effects. No silicosis or other adverse effects via inhalation are stated to have been observed in humans. According to the manufacturer, its X-ray amorphous supports these findings.

The 'Easy – to- use Workplace Control Scheme for Hazardous Substances' was applied to determine the required protection level for the use of the silic acid:

- Hazard group: Silic acid belongs to the group A because it is not classified as dangerous and there are no indications on toxic properties.
- Release category: The silic acid is provided as powder and the formation of dust clouds is generally possible. Therefore, the release category is 'high'
- Use amount: The amounts used per one activity are in the range of 120 kg/a.

¹ According to information from the manufacturer.

² Risk assessments are also conducted at the other sites; however the specific material is only used in this production site..

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According to the Easy-to-use Workplace Control Scheme, the protection level 2 (medium risk group, basic measures are necessary) is to be implemented. This corresponds to the implementation of technical measures.

3.3.2. Assessment of potential exposures

The process at the workplace with manual handling of powders was systematically analysed. The content of the analysis and the results of the assessment are provided in the following:

- Provision of raw material: the raw material is delivered in bags of 8 X 15 kg on pallets, which are secured by plastic foils on the outside. According to regular checks, the sacks are normally fully intact and not broken or torn in any place. Sometimes, powders are observed on the pallets between sacks, which, due to the intactness of sacks, are likely to stem from the manufacturer.
These powders do not become airborne (tested by fanning the material). This is because the silic acid aggregates (approximately 150µm) and occurs in agglomerated form in the final product.
- Manual filling of vessel: A pallet truck positions the pallet at an ergonomically fortunate height for the worker next to the manway opening of the mixing vessels. The worker opens the sacks with a knife and empties the content into the vessel in a slow and controlled manner. A chute is not used. The silic acid is present in form of aggregates (150 µm) and agglomerates of even larger sizes (visible grains). Therefore, no dust is formed from the material dropping into the vessel.
- Sack / bag disposal: The empty paper sacks/bags are disposed of into waste bags stored directly at the workplace.
- Start of Mixing: The mixing is started in the vessel already during the sack emptying process in order to ensure homogeneous distribution of the silic acid. During the mixing, the aggregates and agglomerates of the silic acid are destroyed and primary particles of a size of 5 – 50 nm may be restored. This leads to the formation of dusts, which partly are released from the vessel through the manway opening.
- Mixing: after the filling of the mixing vessel is ended, the vessel is closed for the actual mixing process.
- Packaging: The final product is a liquid and the nanomaterials are contained in a dispersed form; hence, no dust can be formed anymore. It is automatically filled into containers. No dermal contact is possible and no evaporation likely due to the low vapour pressures.
- Cleaning: The mixing vessel is cleaned between production of different products. Cleaning is carried out automatically and no manual cleaning operations are carried out. The silic acid remaining in the vessel after production is present in dispersed form, hence, no inhalation is expected to take place.

3.3.3. Implemented prevention and exposure reduction measures

- Above the manway opening of the mixing vessel, a funnel-shaped exhaust hood is installed, which extracts vapours and dusts. The airflow of the extraction system is 1 m/s.
- Inside the mixing vessel an inner exhaust system exists which extracts air via vacuum pumps during the filling process of the vessel.
- The mixing vessel is closed after being filling. As the final product is a liquid, no dust emissions occur when opening the mixing vessel after production is finished.

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- The worker filling the mixing vessel wears protective clothes (overalls used once), gloves and a respirator with an ABEKP³ – combination filter. The ABEKP filter contains an integrated particle filter (P3) and provides protection against vapours and dusts.
- Workers are trained regularly on health and safety at the workplace. In this context, workers are also instructed on checking the functioning of the exhaust ventilation, the correct position when emptying sacks; i.e. keeping the head away from the area between manway opening and exhaust hood and the use of personal protective equipment.

3.3.4. Requirements for workplace safety

No occupational exposure limit value (OEL) exists for silic acid in powder form. In the company and at any workplace general good industrial hygiene is to be implemented always. The general OEL for dusts (3 mg/m³ alveolar fraction; 10 mg/m³ inhalable fraction) is used as orientation of an acceptable exposure level.

3.3.5. Decision making on measures

Thor GmbH used the protection guidelines by the German Federal Institute for Occupational Safety and Health (BAuA) to check whether the implemented measures at the workplace are sufficient or not. According to guideline 210, the following organisational and technical measures should be in place:

Table 1: Checklist of implementation of measures at protection level 2

Recommended measure	Check	Comments
No storage of materials at the workplace exceeding the daily used amount	✓	
Facilitation of lifting and handling loads	✓	
Controlled emptying enabled through tipping mechanisms of machinery	(✓)	Lifting the sack to the manway opening and controlled, slow manual emptying. No additional technical equipment used.
Exhaust ventilation at opening with airflow > 1 m/s	✓	In addition, an inner extraction system is installed inside the vessel.
Connection of mixing to exhaust extraction		The inner and outer exhaust systems are connected to the exhaust air pipes. During mixing, no air extraction takes place (not needed as not dusts or fumes are generated during/after production (liquid product at room temperature))
Extraction system with short pipes, no long sections with flexible pipes	✓	In place
Explosion protection	(✓)	Not necessary, no explosive
Workplace is not located close to doors, windows or aisles	✓	Implemented
Hall ventilation ensures replacement of air extracted by local ventilation	✓	Implemented
Functioning of extraction system is easily controlled, e.g. via manometer or measurement of volumetric flow rate	✓	Respective devices for controlling functioning of system exist
Extracted air is released at safe location	✓	Air is released to waste gas washer

³ Provides protection against vapors of organic compounds (A), inorganic gases and vapors (B), sulfur dioxide and hydrogen chloride (E), ammonia (K) and particles (P)

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Recommended measure	Check	Comments
The installation is controlled visually once a week	✓	Maintenance plan exists
The extraction system is controlled once a year and compared with its performance standards	✓	Maintenance plan exists
The workplace is regularly cleaned, spills are removed, sacks are disposed of safely	✓	Implemented
Protective clothes and street wear must be kept separate	✓	Protective clothes are disposed of after activity
No food at the workplace	✓	Implemented
Additional measures in case the workers work alone	✓	It is not allowed to work alone
Measures are taken for actions in case of incidents, accidents and emergencies, first aid measures are available	✓	Company standard on incidents etc.
Medicinal prevention is to be implemented; including workplace hygienic consultations and instructions	✓	Regular instructions and training

It was concluded from the above illustrated check that the existing measures and workplace organisation is in conformity with the guideline for the activity.

Thor GmbH implements the use of personal protective equipment, such as protective clothes, gloves and respiratory protection with air filters in addition to the recommended measures. These measures should ensure that any potential inhalative exposures from emissions that are not directly extracted by the local exhaust ventilation and any dermal contact with the material are prevented. This corresponds to the precautionary approach.

3.3.6. Consultation and information of workers

The workers carrying out the filling of the mixing vessel were consulted in the process of assessing the exposure level to the silic acid. They were interviewed on how the process is carried out in detail and provided information on any particularities with regard to the protection level and work routines. The consultation did not reveal any surprising information.

All workers at Thor GmbH are regularly, and at least once a year, informed about handling of hazardous substances at workplaces. As the company handles diverse materials with hazardous properties, e.g. active substances in biocidal products, the general awareness and knowledge of handling hazardous substances is comparatively high.

Due to the high level of awareness as well as a certain routine in handling hazardous substances and mixtures, the workers were not particularly concerned about the nano-scale of silic acid particles handled.

3.3.7. Checking the effectiveness of measures

The effectiveness of the implemented risk reduction measures, in particular the local exhaust ventilation was controlled using workplace air measurements at similar workplaces in the company with similar working activities and conditions.

Based on the qualitative assessment, the emission of dusts from the mixing vessel during the bag-emptying process was identified as the most critical process regarding workers' safety. Samples were taken at similar workplaces, where dusty materials are handled in a similar way than the silic acid. Sampling was done close to the worker to simulate the situation directly in his breathing zone. The sampling duration was 190 minutes. The samples were analysed with regard to ultra fine dust particles.

The results of the analyses carried out at similar workplaces showed a dust concentration of less than 0.55 mg/m³ (inhalable fraction). All the measured values were below the occupational exposure limit value of 10 mg/m³. From these results, it is concluded that the exhaust extraction system works effectively and ensures that workers are protected against air exposures to nano-particles.

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Due to a lack of respective standard measurement methods, it was not possible to determine the identity of the particles. Although nanoparticles may not be sufficiently addressed by dust measurements and although the mass concentration may not be an appropriate metric to determine the relevance of exposures, the efficiency of the implemented exhaust extraction is regarded as sufficient because:

- The workers use respiratory protection during filling of the vessel and,
- The silic acid is regarded as non-hazardous based on measurement results and long-time experience with handling the material in different contexts.

In addition, the processing conditions and risk management measures were compared to the recommendations for working with synthetic nanomaterials by the German Federal Institute for Occupational Health and Safety and found sufficient too.

3.3.8. Evaluation of the process

Thor GmbH assesses its workplaces on a regular basis; hence the entire process benefited from existing procedures.

The applicability of the Easy-to-use Workplace Control Scheme for Hazardous Substances was ensured by checking:

- The exclusion criteria inside the guidance are not met – none of them relate to the size of particles
- The method is regarded as applicable by the authors of the guide⁴

3.4. What was achieved?

The assessment of the workplace resulted in the following achievements:

- The available installation including the technical measures to reduce exposures of workers were analysed and found appropriate for handling input materials in powder form, such as the silic acid looked at in this example.
- The knowledge level of hazardous properties of the silic acid is fairly high due to the thorough analysis of the safety data sheet and additional communication with the supplier
- Workers continuously made aware of wearing personal protective equipment and implementing workplace routines as recommended.
- Due to the overall precautionary approach, a high level of protection for the worker is ensured by the combination of technical and organisational measures.

3.5. Success factors

The process is regarded as successful in particular because the workers at the specific workplace, the production manager and the workers in research and development as well as the health and safety expert were involved in the analysis of information and the evaluation of existing protection measures. This ensured that all available knowledge was used and the results of the assessment are well accepted by all parties.

Another success factor is seen in the high awareness level of the workers at Thor GmbH, which is achieved through the training and instructions on handling hazardous substances.

⁴ This is e.g. stated in a press release by the German Federal Institute for Occupational Safety and Health (BAuA) <http://www.baua.de/de/Presse/Pressemitteilungen/2011/01/pm004-11.html?nn=1652694> (German)



Finally, the information on hazards of silic acid is comparatively good. This regards the information in the safety data sheet but also general and publicly available information.

3.6. Further information

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3.7. Transferability

The process of emptying sacks into vessels or containers is carried out across many sectors and in the context of different activities. It is one of the core activities in the chemical sector and therefore, appropriate installations and prevention measures are likely to be in place. In other manufacturing sectors, feeding dusty input materials into their processes and machines are only a side activity and hence less attention may be paid to workers' protection. However, exposures resulting from the dusting at these workplaces may be much higher as at the core activities due to the high concentrations that could occur.

The method of analysing workplaces and comparing existing measures with control guidelines can be applied to various processes in different sectors. Apart from the German Easy-to-use Workplace Control Scheme for Hazardous Substances, similar tools are available from other national institutions. Hence, the process can be transferred to other sectors easily.

4. References, resources:

- Schutzleitfaden 210, available at <http://www.gefahrstoffwissen.de/gefahrstoffwissen/Schutzleitfaeden.htm>
- Easy-to-use Workplace Control Scheme for Hazardous Substances available at http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/workplace-control-scheme.pdf?_blob=publicationFile