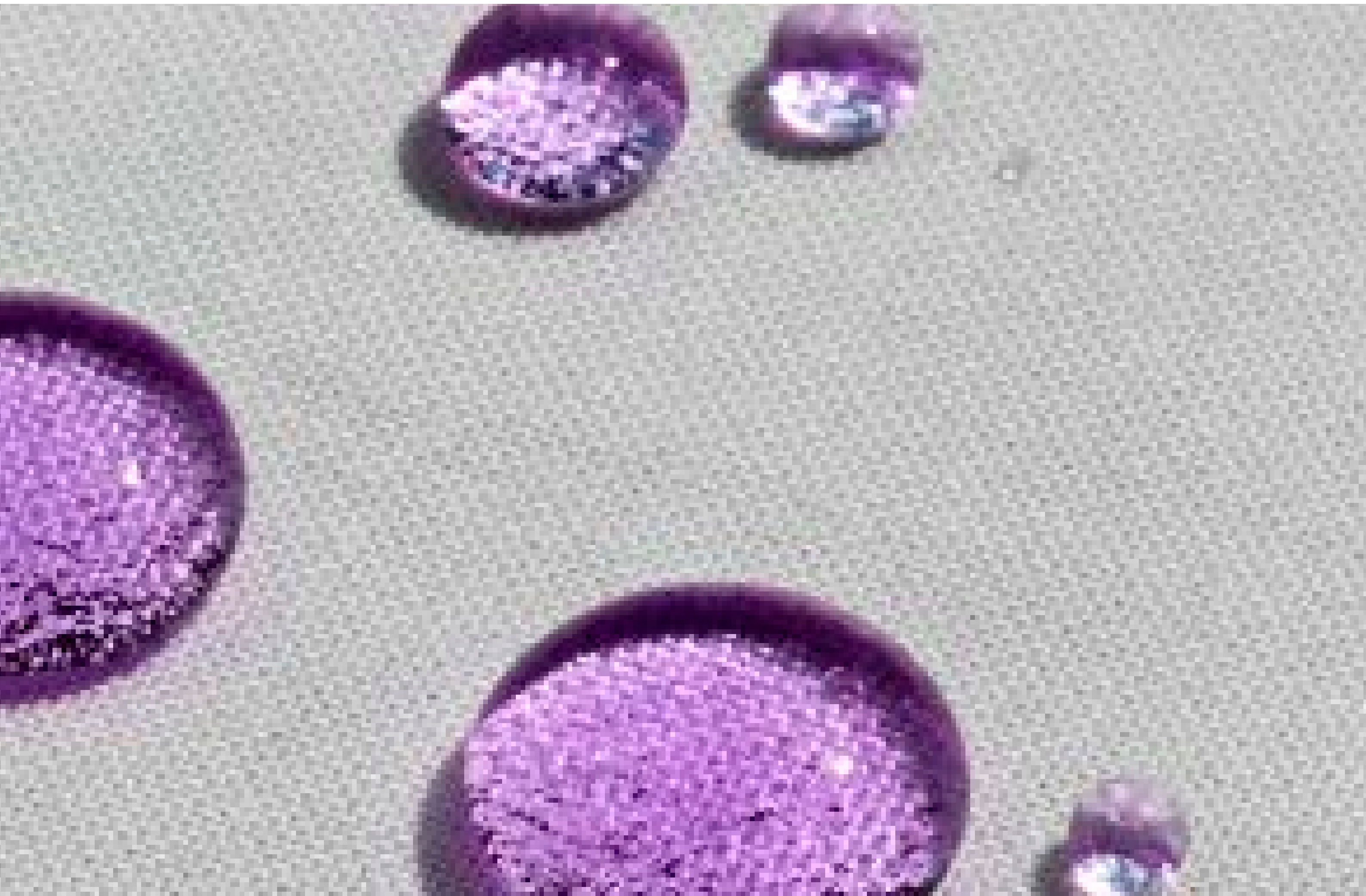
Bundesanstalt für Arbeitsschutz
und Arbeitsmedizin

NanoValid

Developing Reference Methods for Nanomaterials



Work system planning and risk assessment of fibres (CNT), which are handled in a laboratory

Field measurement report No 4

Imprint

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1 Abbreviations and acronyms

AGS	hazardous substances committee
ArbSchG	German Occupational Safety Act
ASR	German Technical Rule for Workplaces
BAM	Federal Institute for Materials Research and Testing (in Germany)
BAuA	Federal Institute for Occupational Safety and Health (in Germany)
BG ETEM	employers' liability insurance association for Energy, Textile, Electrical and Media products
BMAS	Federal Ministry of Labour and Social Affairs (in Germany)
CNF	Carbon Nanofibres
CNT	Carbon Nanotubes
DASA	German Occupational Safety Exhibition
DGUV	German Social Accident Insurance
DISC	Diffusion Size Classifier
FFP	Filtering Face Piece
GefStoffV	Ordinance on Hazardous Substances
GESTIS	Hazardous Substance Information System of the German Social Accident Insurance
HEPA	High Efficiency Particulate Airfilter
IFA	Institute for Occupational Safety and Health
MSDS	Material Safety Data Sheet
PPE	Personal Protective Equipment
STOP	Substitution, Technical, Organisational and Personal protection measures
TOP	Technical, Organisational and Personal protection measures
TRGS	German Technical Rule for Hazardous Substances

2 Summary

Within NanoValid, the BAuA laboratory for nanomaterials assessed and evaluated inhalative exposure to nanomaterials at different workplaces. The aim of these field studies was to check if the installed protective measures were effective and if a risk of the workers was sufficiently reduced. In all studies, the risk assessment combined measurements and a non-measurement approach in terms of an additional inspection of the specific workplace situation.
The present report summarises the results of a detailed risk assessment, gained during an internship. It describes the construction of a new test chamber for nanomaterials and the concomitant development and validation of an effective safety strategy.

This report presents:

- a work experience report by a safety expert (non-measurement method)
- an example for a guided dialogue (non-measurement method)
- a brief presentation to communicate the selected safety strategy to the appropriate decision making committees within a company

The focus of the report is on the assessment of the occupational safety and health aspects (**non-measurement method**). It describes basic settings at the workplace, hazards and risks, the development and the implementation of alternative solutions. The setup of a new exposure chamber required a high level of safety that ensures a safe handling of nanofibres. Therefore, all operational steps were systematically assessed by a safety expert. A relevant hazard from hazardous substances was identified which resulted in a need for urgent action in cases where the benchmark level for nanofibres was exceeded. A solution for the workflow and the cleaning of the exposure measurement devices and the Plexiglas tube of the test chamber was found in cooperation with the involved parties.
The brief presentation was originally used to present the developed safety strategy to a panel of safety expert. It supplements the work experience report and focusses on the communication of the main findings.

3 Introduction

The manual "Nano to go!" compiles information and training material for people, who are responsible for the implementation of occupational safety and health issues at a company level. It contains valuable information on safe handling of nanomaterials and other advance materials at workplaces.
In general, a specific workplace situation can be assessed either by using exposure measurements or by applying non-measurement methods like comparing the specific situation to standardised work routines and by using control banding tools. Since the reliability of the risk management depends highly on the quality of these approaches, it is important to provide professional advice on how to actually assess the workplace situation and how to perform adequate exposure measurements as potential efficiency control. "Nano to go!" aims to provide such advice in form of field study reports. The field study reports exemplify a way to address occupational safety and health issues when working with nanomaterials.

The present field study was performed at a laboratory, where a new exposure chamber was constructed, which required the concomitant development and validation of an effective safety strategy. The report describes basic settings at the workplace and the operational steps when using the new chamber. This is followed by risk assessment, target setting, development of alternative solutions, selection and implementation of a solution and the outline of a future efficiency control.

4 Work experience report of a safety expert

The topic of the work experience report is the occupational safety and health aspects of a work system planning in a research laboratory handling nanofibres.

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4.1 Abstract

The Federal Institute for Occupational Safety and Health (BAuA) has a nanomaterial laboratory in Berlin. In this laboratory, a nanofibre test center is being set up, where fibre dusts will be introduced into a closed test chamber via a new dust generation device. Some of the nanofibres and their dusts concern since they can have an effect similar to asbestos. The work system planning, addressed also occupational safety and health aspects during the workflow itself and especially during cleaning of the workplace and the work equipment. The aim was to develop protection measures which ensure the safe handling of the nanofibres by the employees. This was achieved by having an expert systematically accompany the definition of operational steps.
A relevant risk from hazardous substances was identified resulting in immediate action in cases where the benchmark level for nanofibres was exceeded. A solution for the workflow and the cleaning of the exposure measurement devices and the plexiglass tube of the test chamber was found in cooperation with the involved parties. Furthermore, an additional long-term proposal for a solution was proposed. This solution intends to minimize physical strains caused by the cleaning activity. The efficacy of the protection measures was controlled by an exposure measurement method. The implementation of the occupational safety and health aspects during planning and operating the test chamber enables the employees to handle nanofibres with a very high level of protection in the future.

4.2 Initial situation

Description of the company, where the internship takes place:
The Federal Institute for Occupational Safety and Health (BAUA) is a specialised federal research institution that reports to the Federal Ministry of Labor and Social Affairs (BMAS). As a federal institution at the interface between science and politics, BAuA has a broad spectrum of tasks with the aim to improve safety and health at work. BAuA's tasks range from policy advice, the performance of sovereign duties, research and development, knowledge transfer into practice through to the educational and instructional work done by the German Occupational Safety Exhibition (DASA). Over 600 employees work at the various sites in Dortmund, Berlin, Dresden and Chemnitz. The unit "hazardous substances management" in Dortmund focusses on, among others, research regarding simple assessment methods and protection concepts for activities with hazardous substances and protection measures for handling nanomaterials. The unit "health effects of hazardous substances", which is situated in Berlin, dedicates its research on, among others, the effects of nanomaterials on humans and personal and material-specific exposure measurements.

Action required during the internship:
BAuA's nanomaterial laboratory in Berlin is planning to produce higher amounts of nanofibre dusts than before.

For this reason, it has to be examined specifically whether the planned technical measures are suitable for the new exposure situation.
A new working system with a test chamber and a dust system is being planned. This work system design will integrate an existing dust system (Shaker) into a new technical plant. The new dust system allows for the even generation of a higher amount of nanofibres and an improved separation of fibres. Therefore, a new device was bought, the dust generator, which can generate homogenous fibre dusts.
The test chamber will facilitate the comparison of different dust measurement devices. The employees on-site seek support regarding occupational safety and health questions for setting up and operating the test chamber and the new dust generation system. Both activities, the workflow itself and the cleaning, will be considered here.

Problem definition:
Dust from biopersistent nanofibres, especially carbon nanotubes (CNTs) will be gathered. The different nanofibre types can vary regarding their toxicology and their shape. Some fibres are flexible and look like balls of wool, whereas others are stiff with their shape resembling asbestos fibres. These stiff nanofibres in particular can break and raise concerns.

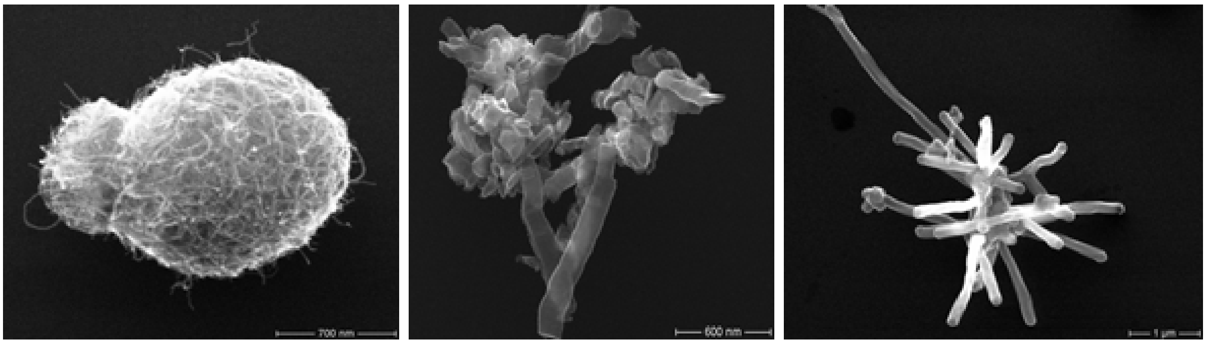

FIGURE 1: STRUCTURE OF DIFFERENT CNTS (PLITZKO, GIERKE, DZIUROWITZ AND BROSSELL 2010)

For nanofibres, health-based threshold values do not yet exist, but it is recommended that the exposure is limited to the range of asbestos fibres. However, measurements of the exposure level are difficult since nanofibres are far smaller than asbestos fibres and cannot be counted in a comparable way. In order to enable reliable exposure measurements, a standardisation of measurement techniques in the framework of projects is planned. For this purpose, it is necessary to compare devices from different producers. Since these devices measure homogeneous fibre dust amounts of a certain exposure level, dust from nanofibres will be previously gathered and fed to the devices. For this purpose, the engineers on-site will construct a test chamber.

Expected benefit for the enterprise:
A new technical system will be set up in the nanomaterial laboratory, which will enable safe handling of nanofibres, associated with the dust generation tests during the typical workflow, as well as during cleaning and maintenance. With the developed technical, organisational and personal protective equipment, health and accident hazards of the employees can be avoided. With the new dust generating system, measurement techniques willl be standardized and the dust amount evaluated in later projects. The measurement techniques will again enable an ongoing development of the occupational safety management system regarding handling nanofibres in the long term. The results will be included in the update of the state-of-the-art safety strategy.

4.3 Aim of the internship

The aim is to follow the construction of the new test chamber and to develop, determine and validate an effective safety strategy for safe handling of nanomaterials during the workflow and especially during the regular cleaning of the test chamber. The purpose is to protect the health of the employees.

4.4 Approach

The topics of the internship are "Safe operating and purchase of machinery, equipment and facilities" and "Purchase and safe handling of agents / hazardous substances".
An analysis of the operational steps, risk assessment, target setting, development of alternative solutions, selection of the solution, implementation of the solution and efficiency control are carried out:

- The analysis starts with differentiating the working system and the specifications of system safety. Potential hazards are subsequently identified.
- Risk assessment examines the risk factors "explosions" and "hazardous substances". The need for action regarding the risk factor "hazardous substances" will be determined using a benchmark level.
- Target definition sets a minimum target and an optimisation target.
- The development of alternative solutions is oriented to the hierarchy of measures according to the STOP principle (substitution, technical, organisational and personal protection measures). The focus is on technical measures. The activity "cleaning of the plexiglass tube" is especially considered, due to the expected higher exposure.
- Selection and implementation of the solution are performed in close consultation with the employees on-site. A solution is sought that will combine a high level of protection measures and a simple feasibility in practice.
- Efficiency control will be performed, using exposure measurement methods. This involves determining the inhalative exposure to nanoscaled fibres with a handheld measurement device.

4.5 Results of the internship

4.5.1 Analysis

During analysis, the individual component of the work system will be analysed and the specifications of the system safety will be described in order to identify the hazards. The risk factors, the sources of risk and the dangerous conditions will be determined afterwards.
A scheme of the new work system is given in Figure 2.

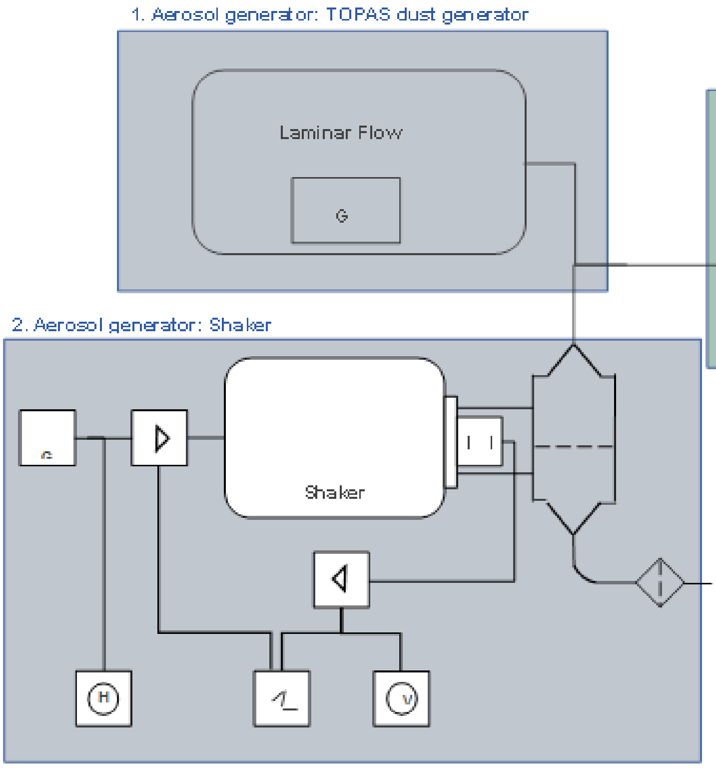

FIGURE 2: SCHEME OF THE DUST GENERATION SYSTEM

1. Dust generator (blue): open dust generator, located in a safety cabinet; 2. Dust generator (blue): closed shaker system; the testing chamber with the measurement devices (green) will be connected with the dust generators (Figure by Sabine Plitzko and Dr. Asmus Meyer-Plath).

TABLE 1: DESCRIPTION OF THE WORKING SYSTEM

WORK TASK	Work task is dust generation of nanoscaled fibres in order to compare exposure measurement devices.
HUMAN	1-3 middle-aged trained employees, normal physical constitution
WORKFLOW	1. shaker (old): Nanofibres are weighted on a ceramic frit, which is then clamped into the shaker. Dust is generated by adjusting the oscillation and an air flow. 2. dust generator (new): In parallel to the shaker, nanofibres are added through a funnel into the dust generator. The dust is generated coming from the device through a nozzle. The dust generator is an open system and will be located in a safety cabinet in order to ensure the system security. 3. The dust coming either from the shaker or from the dust generator willl be directed into a test chamber. The exposure measurement devices to be compared are located in this test chamber. For this purpose, the technical development needs to be instituted in the future. 4. At the end of the respective test procedure, the production unit of the dust generator, the test chamber, the safety cabinet and the exposure measurement devices are cleaned.
WORKPLACE	A typical laboratory workplace.
WORK EQUIP-MENT	The already established Shaker (a closed dust generator) is located in the laboratory. Addition-ally, the use of the open dust generator SAG 410/U is planned.
INPUT	information: information relating to the test procedure, various (partly not classified) nanofibres in low amount (milligram range), electricity: electric power (standard voltage)
OUTPUT	finely distributed, singular nanofibres, which are distributed in an aerosol; measurement data of the different exposure measurement devices, which are to be checked and compared; dust deposits at exposed surfaces of the aerosol generators and the walls of the test chamber.
WORK ENVIRON-MENT	The laboratory has an area of approximately 25 m^2. General exhaust ventilation exists. No further devices are present in the laboratory. Hence, hazards due to mutually influencing pro-cesses are not expected.

FIGURE 3: DUST GENERATOR SAG 410/U[1] FROM TOPAS1 (TOPAS GMBH 2009), ARROW: NOZZLE

[1] Manufacturer brand of the company Topas

TABLE 2: SPECIFICATIONS OF THE SYSTEM SAFETY

DEVICES	CE label and declaration of conformity are available. The noise emission is according to the state-of-the-art of noise reduction. dust generator: meets the requirements of the Machinery Directive 2006/42/EG (Directive 2006a), the Electromagnetic Compatibility Directive 2004/108/EG (Directive 2004), the Low Voltage Directive 06/95/EG (Directive 2006b) shaker: meets the requirements of the Machinery Directive 98/37/EG (Directive 1998) including the Application guidelines 93/68/EWG (Council Directive 1993) and the Low Voltage Directive 06/95/EG (Directive 2006b) safety cabinet: built according to standard EN 14175-1 up to standard EN 14175-3 (Beuth-Verlag 2003, 2004)
WORKPLACES	entrance: easily accessible, no containers in the way, emergency exit easily accessible space for movement: sufficient freedom of movement working environment: Noise, vibrations are avoided, general hygiene measures, climatic conditions in the comfort zone with approximately 20 - 22 °C air temperature body posture: ergonomically designed according to the state-of-the-art work equipment: easily accessible, clearly arranged Human: no particular conditions for performance are to be considered
WORKING TIME	working time of the employee: 8 hours per working day, activity at the device: maximum 2 hours per day, in addition a daily break of at least 30 minutes.
PPE	Individually adjusted, used by one person only, no mutual interference of PPE. PPE under hygienic conditions. reduction of the dust exposure: minimization as far as possible, hence an FFP3 mask or Mask with P3 filter and CE label for opening the system.
WORKING ENVIRONMENT	visibility: lamps with at least 500 Lux nominal illuminance (according to the German Technical Rule for Workplaces ASR 3.4 (ASR A3.4 2014), minimum illuminance value of 500 lx for laboratories and measurement places) and daylight, ratio window to floor at least 1:10. Working area: sufficient space
THRESHOLD VALUES	For nanomaterials, no health-based threshold values exist yet. Benchmark levels for stiff fibres are the recommended limit from the Institute for Occupational Safety and Health (IFA) of the German Social Accident Insurance (DGUV) with 10000 fibres/m^3 and the threshold value for asbestos also with 10000 fibres/m^3 (TRGS 517 2013; IFA 2014).

Hazard identification

A number of risk factors can be present in a laboratory. The most important **risk factors** identified in this working system are **hazardous substances** and **fires and explosions**.

There are several **other risk factors**, which cannot be excluded (mechanical hazard, electrical hazard, hazard from physical factors).

Regarding the mechanical hazard from moving parts, these are a) unprotected mechanical moving parts, which are exposed if the enclosure of the dust generator is opened for instance for dust removal (toothed belt, drive wheels, motors) and b) specifically moved mechanical parts, since the bottom of the Plexiglas tube can be moved up and down automatically for opening / closing and crushing of fingers is possible.

The **electrical hazard** refers to a potential electrostatic discharge of the dust generation, which can be caused during the dispersion process by friction leading to an electrostatic charge of the dispersion nozzle and dust. Hence, during cleaning and maintenance the hazard of electric shock could be possible.

The **hazard from physical factors** focusses here on a potential inappropriate load distribution of the musculoskeletal system caused by standing too long. This can, in principle, cause spinal damage, a higher energy consumption and a higher heart rate.

In case of all hazards, no additional need for action was determined. For instance regarding the hazard by physical factors, the standing activity has a duration of no longer than 2 hours per day and fatigue is prevented by various workplaces with changes of body posture and with relaxation breaks.

The following considerations focus on **hazards from hazardous substances** and **from explosions**. For these hazards, the explanatory model on the causes of accidents (explosions) and work-related diseases (hazardous substances) is applied. According to this model, an accident or a work-related disease is caused by a complex structure of causes, which mesh like the links in a chain. A safety strategy can start at different sites to reduce or prevent a hazard. The components of this structure of causes are:

- the **human** with his/her individual performance conditions,
- the **source of risk** with injury or disease causing factors,
- the **dangerous condition**: does not (sufficiently) prevent the collision of human and a certain risk factor,
- the **supporting condition**: a specific unforeseeable incident, where the hazard becomes effective,
- the **hazard**: situation or state, where a damage to health can take place.

The factor human was already looked at in table 1 "Description of the working system". No specific performance-related conditions for the employees working at the actual workplace are given.
The **source of risk** regarding the hazard by hazardous substances is associated with stiff nanoscaled CNTs (nanofibres). The source of risk regarding the hazard by explosions is caused by the structure of the CNTs from carbon atoms. Dust will be gathered from these CNTs, whereby carbon black can form explosive dust-air-mixtures according to the substance database GESTIS (Hazardous Substance Information System of the German Social Accident Insurance) (GESTIS 2014).

FIGURE 4: MODEL OF THE CNT STRUCTURE FROM THE SPECIAL EXHIBITION "NANO! USES AND VISIONS FOR A NEW TECHNOLOGY" (BAUA/FOX/VÖLKNER)

The **dangerous condition** regarding hazardous substances refers to a regular cleaning of the working system in case of a nanofibre type change, whereby the employees can come into contact with nanofibres and inhale these fibres. The dangerous condition regarding an explosion is in this case the dust generated by an intentional dust generation within the test chamber, which, without regular cleaning, may accumulate within the test chamber.
Supporting conditions are coincidental and not directly foreseeable like technical faults or inattentiveness. The hazard cannot be removed when the supporting condition is eliminated, but only the probability of coincidence can be minimized.
A **hazard** from hazardous substances exists since the CNT fibres are under suspicion of having an asbestos-like effect both due to their appearance under the microscope and to first animal-experimental indications. However, dust of CNTs is generated in a very low amount (up to a maximum of 5 mg per total test chamber volume of approximately 400 l), which is sufficient for the standardisation. It has to be determined if a potential hazard from explo-

sions exists. A detailed evaluation of both hazards can be found in the section on risk assessment (following pages).

TABLE 3: RISK FACTORS AND ASSOCIATED REGULATIONS

RISK FACTOR	REGULATIONS / RULES
1. HAZARD FROM HAZARDOUS SUBSTANCES	■ German Occupational Safety Act (ArbSchG), § 4: Attack health hazards at source (ArbSchG 2013). ■ German Ordinance on the use of personal protective equipment: Wear personal protective equipment (PPE) in case of a hazard if technical and organisational protection measures are not sufficient. (PSA-BV 1996). ■ German Hazardous Substances Ordinance (GefStoffV): The employer has to ensure the instruction of the employees. Part of the course of instruction is an occupational-medical and toxicological advice (GefStoffV 2013). ■ Announcement 527, No. 5.2 (Announcement 527 2013) and Technical Rule for Hazardous Substances (TRGS) 526 (TRGS 526 2008): The employees are instructed about the hazards from an increased exposure to nanomaterials, about hazards by fire and explosion as well as about general and activity-specific hazards in laboratories and the respective protection measures. ■ Announcement 527, No. 4.2.4: Asbestos-like properties are to be assumed for in preventive for fibrous nanomaterials (Announcement 527, 2013). ■ TRGS 910: Therefore, an acceptance concentration of 10000 fibres/m3, which is applied for asbestos, is used (TRGS 910, 2014).
2. HAZARD FROM FIRES AND EXPLOSIONS	■ Industrial Safety Regulation: Work equipment shall be designed against a hazard from fire, heating the work equipment, or release from gas, dust, liquids or other substances in order to protect the employees. Work equipment shall be designed to avoid any hazard from explosions (BetrSichV, 2011). ■ German Occupational Safety Act, § 5, Hazardous Substances Ordinance, § 6, TRGS 800 (Fire protection measures): The fire hazard has to be evaluated within the risk assessment (ArbSchG 2013; GefStoffV 2013; TRGS 800 2011).

4.5.2 Risk assessment

Risk factor hazardous substances:

The risk factor hazardous substances is considered. A hazard can be caused by inhalation of CNTs, which are suspected to be asbestos-like and hence carcinogenic. A high severity of damage is assumed since lung cancer can lead to permanent damage and to death. The probability of occurrence depends on the carcinogenic properties as well as on the duration and level of exposure. Although there is no legally binding occupational exposure limit, there is an acceptance risk of 10,000 fibres/m^3 for asbestos (TRGS 910 2014). Furthermore, the IFA from the DGUV published a benchmark level of 10,000 fibres/m^3 for those CNTs, where WHO fibre properties (i.e. length minimum 5 µm, diameter-length-ratio of 1:3) cannot be excluded (IFA 2014). In most cases with carcinogenic substances, no threshold can be determined and no health-based occupational exposure limits are available. For this reason, general, not substance specific, threshold limits were determined in the TRGS 910 (acceptance and tolerance risk) for handling carcinogenic substances. Accordingly, no additional protection measures are demanded below the acceptance risk (10,000 fibres/m^3 for asbestos) because of the remaining low additional cancer risk (TRGS 910 2014). Additional measures are not reasonable if the value lies below the background concentration (TRGS 910 2014). Therefore, there is only need for action when the benchmark level for nanofibres is exceeded.

Risk factor explosions:

At first, the risk factor explosions is considered. For this reason, it is checked if one should expect an explosive atmosphere to be generated and if the amount of this explosive atmosphere would be hazardous (TRBS 2152 2006). An explosive atmosphere can be generated by an air-dust-mixture with combustible dust of a minimal concentration of approximately 15 g/m³. Dust explosions can be avoided if the value falls reliably below the lower explosion limit (Merkblatt T 054 2009).

A maximum of 100,000 fibres/cm³ are dusted within the testing chamber. Since CNTs are very light, their weight corresponds according to the calculation of Dr. Meyer-Plath, an in-house physicist, to a maximum weight of 5 mg in the 400 l testing chamber volume. The weight depends on the fibre type (single wall, multi wall etc.). According to Mr. Krietsch, an expert from the German Federal Institute for Materials Research and Testing (BAM), concentrations of less than 1 g/400 l are not relevant for the explosion protection. In his experience, the lower explosion limit of CNTs is with 30 - 60 g/m³ far beyond this amount. A regular cleaning is planned in order to avoid dust deposits, also for other reasons like the improvement of the test results.

Since no increased hazard of explosion exists according to the opinion of the experts in the field, the identified risk is regarded as acceptable. The query scheme in the TRBS 2152 (TRBS 2152, 2006) shows that no explosion protection measures are required if an explosive mixture or a hazardous explosive atmosphere cannot be generated. As long as no significantly higher fibre amounts are being dusted in the testing chamber, **no further action** is required.

4.5.3 Target definition

The aim is to protect the employees from harm and to provide a safe and healthy workplace. Therefore, the minimum target is to reduce the potential hazard of cancer by CNTs in the first trial experiments with the testing chamber by complying with a fibre concentration below the acceptance limit 10,000 fibres/m³ as far as possible.

The optimisation target is to sustainably and reliably reduce the potential hazard from CNTs in any experiments to either background concentration (no increase during activity) or to the value of 500 fibres/m³ (according to TRGS 519, No 14.5 (TRGS 519, 2014), withdrawal of protection measures (approval)). If the background concentration is higher than 500 fibres/m³, then compliance with the background is regarded sufficient.

4.5.4 Development of alternative solutions

A number of protection measures have to be considered regarding the whole work system, for instance recommendations for cleaning the safety cabinet. The development of alternative solutions is based on special protective measures for activities involving hazardous substances that are carcinogenic, mutagenic or toxic to reproduction according to the § 10 German hazardous substances ordinance (GefStoffV, 2013) as well as on the derivation of additional protection measures according to the Announcement 527 (Announcement 527, 2013).

At the starting point, general measures for the regular workflow were considered:

- **Substitution**: A substitution of CNTs is not possible in this case, since a targeted dust generation also from the critical stiff fibre types is required for the standardisation of fibre measurement devices for nanomaterials. Hence, the first tests will be performed with flexible fibres until the effectiveness of the protection measures is confirmed by measurements.
- **Technical measures**: Technical measures are a closed system and a prohibition of air return. The design of the closed system is planned on-site in close consultation with the safety expert. The closed testing chamber contains an exhaust air pipe with a HEPA H14 filter, which can be changed every 5 - 10 years in a completely closed envi-ronment. Soiling of the filter can be detected with a differential manometer, which measures the pressure in front of and behind the filter. The velocity of the air flow in the exhaust air pipe is controlled electronically with a bypass. The air flow in the testing chamber is automatically increased after the respective tests in order to achieve a particularly good exhaust. When the testing chamber is opened, a local exhaust ventilation called Dustbox® with a HEPA H 14 filter in order to exhaust the lower area is attached. The filter class of the Dustbox® is authorized for the asbestos removal.
- **Organisational measures**: The organisational measures include the demarcation of the workplace and the minimisation of the exposure duration. In order to avoid dust deposits, the working place and the dust generating devices will be wet wiped regularly. Since a higher exposure during cleaning of the testing chamber is expected, a focus is here on the design of the protection measures. As soon as the lower lid of the testing chamber is opened, the exposure measurement devices are transported in a protection bag for further cleaning within the safety cabinet and are cleaned by wet wiping.
- **Personal protective equipment**: If an increased exposure can be expected for a short-time, despite technical and organisational protection measures, than half masks with P3 filter or FFP3 half-face respirators are to be used for handling fibrous nanomaterials according to the announcement 527, No 4.4.2 (Announcement 527, 2013).

Alternative solutions for cleaning the testing chamber:

When the testing chamber is opened for cleaning after the respective test, contamination with fibres of the inner plexiglass tube walls and of the measurement devices is possible. There are different options:

1. brushes and wipers system: The cleaning is performed automatically with water and cleaning agent.
2. adhesive film: An adhesive film layer, which is conductive if necessary, is applied prior to the respective tests. In this case, the plexiglass tube is to be wet wiped before the respective test in order to enable a simple and air bubble free application. The adhesive film would be removed after each respective test.
3. polymerfilm: a polymerfilm is manually applied before the test. The fibres will be deposited on the film. It still needs to be examined if a release of fibres during the polymerfilm removal is possible and if this needs to be avoided by a second film layer. Here, several polymer products are available on the market (for instance, cleaner for vinyl records, for digital camera sensors, but also for asbestos removal). The solution with the polymerfilm has 3 options:

a) application by spraying
b) application by brushing
c) automated application: an automatic brushing system, which drives along the inner wall of the plexiglass tube.

The polymerfilm must have certain material properties, for instance: compatible with plexiglass, water-based, fully removable and suitable for vertical surfaces. For occupational safety reasons, it is important that the polymerfilm has, if possible, no hazardous properties (not toxic, eye irritant etc.) and that it is electrostatically conductive in order to avoid an electrostatic charging of the plexiglass tube. An application by brushing is preferred compared to an application by spraying in order to reduce the exposure. The application is only preferred if it is technically suitable, i.e. the polymerfilm can be applied lump-free.

4.5.5 Selection of the solution

Criteria for the selection of the solution are:

I. a high level of protection measures, current state of the art,

II. technical feasibility of the solution in time before the planned project start,

III. good practical feasibility,

IV. simple and effective disposal possible,

V. preferably without any burdensome personal protective equipment (PPE).

TABLE 4: CRITERIA FOR THE SELECTION OF THE SOLUTION

	I.	II.	III.	IV.	V.
SOLUTION 1 (BRUSHES AND WIPERS)	yes	no	no	no	no PPE
SOLUTION 2 (ADHESIVE FILM)	limited	yes	no	limited	PPE required
SOLUTION 3 (POLYMERFILM)	yes	only a) and b)	yes	yes	dependent on product and procedure

solution 1: The cleaning with a brushes and wipers system can only be a long-term solution since the construction is not possible before the planned project start. The disadvantage of this solution is the required high amount of water, which will generate a lot of contaminated water with difficult disposal.
solution 2: It is assumed that the air bubble free manual application of an adhesive film would be rather difficult in praxis. For occupational safety reasons it is additionally disadvantageous that fibres can possible come off the adhesive film during the removal process and that hence an inhalation by employees is possible. Since PPE is probably required for this reason, a solution without burdensome PPE is preferred.
solution 3: In comparison with the adhesive film, the polymerfilm has the advantage that a cleaning of the measurement devices located inside the tube is probably easier, if they can be coated and subsequently cleaned by removing a polymerfilm.
This solution has three options:

a) **application by spraying**

b) **an application with brushes or paint rollers** is favoured over an application by spraying in order to reduce the exposure.

c) an **automated application** is preferred for the long term. A possible construction consists of a brush system, which moves along the inner wall of the plexiglass tube. On the one hand, this has the advantage of improving the process organisation and on the other hand, a new hazard can thus be avoided. This new hazard might be caused during the manual application possibly due to a forced posture of the employees (height of plexiglass tube, inner tube difficult to access) or even due to work in the restricted space of the inner tube (diameter 65 centimeter).

After the above consideration, **solution 3** is selected since it optimally meets all criteria. The solution is being discussed with the measurement engineers on-site, with the occupational health physicians, with a representative of the staff committee and the safety representative and is judged very positively. Material samples for approximately 10 products for solution 3 (peelable polymerfilm) were ordered and tested (see figure 5).

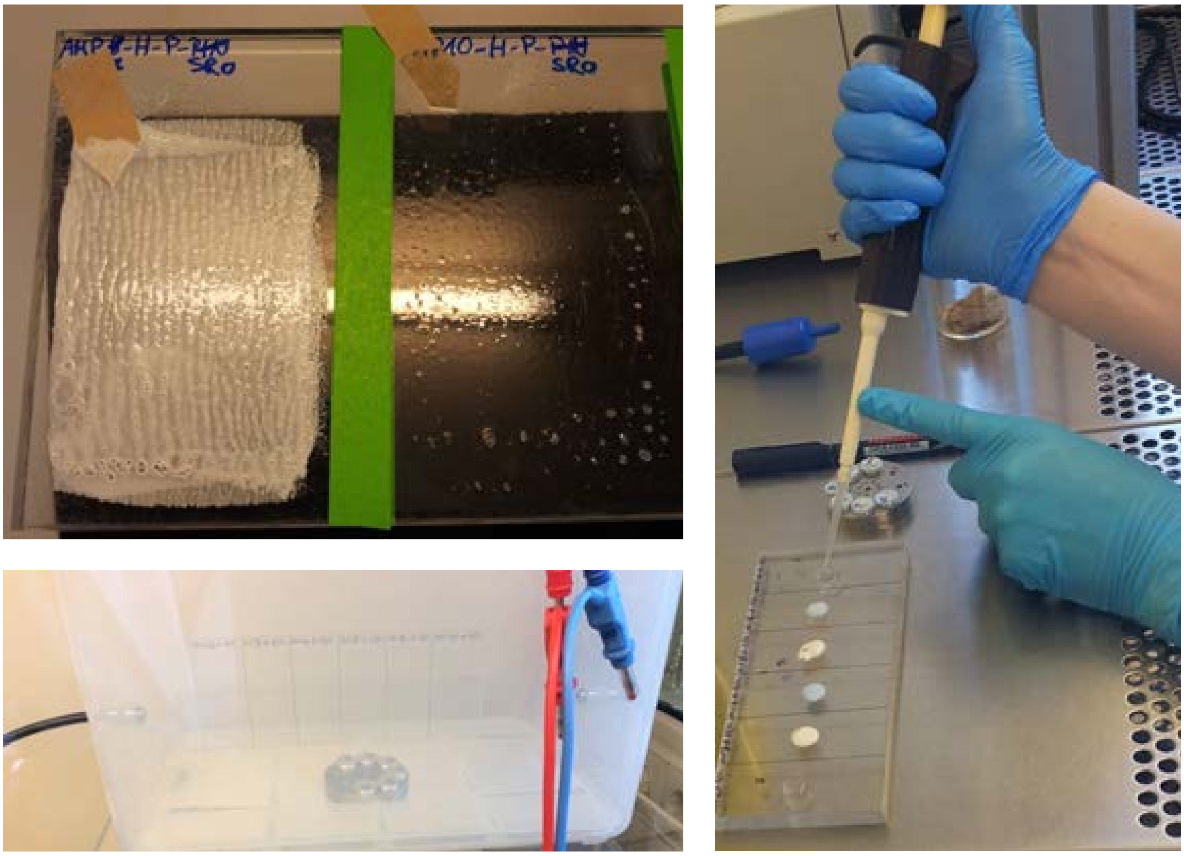

FIGURE 5: TESTING THE SUITABILITY OF DIFFERENT MATERIALS FOR THE APPLICATION OF A POLYMERFILM (MIRIAM BARON, BAUA)

top right – peeling experiment with 2 polymer films on a plexiglass plate coated with an antistatic foil. The plate was arranged vertical in order to test if the respective product is sufficiently viscous.

bottom right – Dust generation on a Plexiglas plate coated with CNT fibres. The dust generation takes place in a closed plastic box in a safety cabinet.

left – Application of material samples on the Plexiglas plate after the dust generation experiment.

Based on a comparison of the material properties (if possible elastic, antistatic, suitable for vertical application, removable without residues) and the hazardous properties, the following 4 products were chosen for further testing:

- **"Selvol™ Polyvinyl Alcohol 09-523 Solution[2]":**
  - The polyvinyl alcohols of the company are among others incorporated in adhesives and coatings as stabilisers of emulsions.
  - The product is not classified as hazardous. It contains 0.9 % methanol with the occupational exposure limit value of 270 mg/m³. If this threshold level is met, no further safety measures are required.
- **"Carboline ALARA 1146[3]":**
  - The product is used for the surface decontamination of radioisotopes.
  - According to the material safety data sheet (MSDS), the product is irritant to eyes and skin above a concentration of 10 mg/m³. Hence, if this value is exceeded, PPE has to be worn. If this product will be chosen, then it needs to be checked with an effectiveness control if this threshold value is securely complied with.
  - This product was ordered despite of its hazardous properties, since it is assumed to be technically very well suited.

[2] Manufacturer Brand of the company Sekisui Chemical Co., Ltd.
[3] Manufacturer brand of the company Carboline Company and trademark of the company Carboline Deutschland

- **"Aqua Abziehlack Kronen® 392 [4]":**
  - The product is a peelable protective film for smooth, non-absorbent surfaces.
  - According to the MSDS, it has no hazardous contents.
- **"E-D-Abziehhaut T [5]":**
  - The product is a peelable water-based film, which is usually applied for spray cabin protection.
  - The product is not classified as hazardous. It contains 0.1-1 % methanol. When below the occupational exposure limit value, no special respiratory protection is required.

It is an important selection criterion if the nanofibres will be bound by the polymerfilm and cannot be released from the matrix during the removal. An efficiency control can be performed by an examination with the scanning electron microscope. For the short-term timeframe, the option b) application with "brushes or paint rollers" will be chosen with one of the mentioned products. In the long-term, the option c) "automatic application" will be examined with regard to, how often the chamber needs to be cleaned and hence how high the physical strain of the employees is in praxis.

4.5.6 Implementation of the solution

The solution to clean the inner wall of the plexiglass tube with a removable polymerfilm (short-term: manual application, long term: automated application) with preferably low toxicity will be presented to the employees on-site during an occupational safety meeting at the earliest possible date. A high level of protection is adequate for an effective protection of the employees in case of asbestos-like fibres.
Automated cleaning is recommended in order to reduce physical strain from wearing personal protective equipment and working in a narrow tube or the application on the outer side of the tube, whereby the brush inside needs to be transported with a telescopic bar to the upper part of the tube. Furthermore, one can expect time-saving of approximately 50 % during the cleaning process.

4.5.7 Efficiency control

The efficiency control will be performed using metrological determination methods. This will involve determining the inhalative exposure to nanoscaled fibres with a handheld measurement device.
The efficiency of the protection measures against an inhalative CNT exposure will be controlled. Although the planning of the testing chamber with the technical implementation of the selected solution is already well advanced, the subsequent efficiency control is not performed within the restricted timeframe of the internship. The level of exposure will be compared to the background concentration and to the intended minimum and optimisation target. Therefore, the fibre concentration within and outside the testing chamber will be measured during the regular workflow and during cleaning. The measurements will be performed with the handheld measurement device DiSCmini[6] (Diffusion Size Classifier). The background concentration at the workplace without the activity will be measured in advance. Next, the concentrations of the nanofibres will be measured during typical handling (dust generation in the closed system) and during cleaning.

[4] Manufacturer brand of the company Paul Jaeger GmbH & Co. KG
[5] Manufacturer brand of the company Erich Drehkopf GmbH
[6] Manufacturer brand of the company Matter Aerosol AG

5 Dialogue guide for occupational safety and health aspects for handling nanomaterials

DIALOGUE GUIDE FOR OCCUPATIONAL SAFETY AND HEALTH ASPECTS FOR HANDLING NANOMATERIALS (NM)		
Company / Institution:	Contact data: Contact person:	Date:

Question 1: Are NM

☐ Produced

☐ Processed

☒ Released during production / processing

in your company / institution?

Intentional release of fibres for research purposes

Question 2: How many employees come into contact with NM in your company / institution?

☒ < 10 ☐ 10 to < 50 ☐ 50 to < 100 ☐ ≥ 100

Question 3: In which form are the NM produced / processed / released?

☒ Fibre

☐ Dust

☐ Aerosols

☐ Liquids

Question 4: Which NM is (are) produced / processed / released during the working procedures?

Carbon nanotubes

Question 5.1: What is the quantity of NM handled on a daily basis?

- [x] g/day (ml/day)
- [ ] kg/day (l/day)
- [ ] t/day (m^3/day)

Question 5.2: What is the quantity of NM handled on a yearly basis?

- [x] g/year (ml/year)
- [ ] kg/year (l/year)
- [ ] t/year (m^3/year)

Question 6.1: Are MSDS for the produced / processed nanomaterials available in your company? (Can the MSDS be shown? Can they be delivered? Are they accessible for all employees?)

[x] Yes [ ] No

Question 6.2: Do the MSDS refer specifically to NM?

[x] Yes [ ] No

Question 6.3: Do the MSDS contain the following information?:

- [x] Does the classification of the hazardous properties (see below) refer specifically to the nanoscaled form?

- [x] Are threshold values for alveolar dust (A-dust) and / or particle number concentration given?

- [x] Morphological information (form, structure, i.e. is it for example a stiff fibre...)

- [x] Solubility in water (g/l range → well soluble, below 100 mg/l → unsoluble)

- [ ] Information about dustiness / dust number

- [x] Information about human toxicity
  - [ ] Acute toxic (R23, R24, R25; H301, H311, H331)
  - [ ] Chronic toxic (R48)
  - [ ] Carcinogenicity (carc. 3) (R68)
  - [ ] Irritating to skin (R38; H315)
  - [ ] Sensitisation by inhalation (R42, R43; H317)

Unfortunately only carcinogenicity was tested with AMES test, which is not applicable for a fibre structure toxicology statement.

Question 7: Do you include NM safety information in training courses and occupational-medical and toxicological advice?

☒ Yes ☐ No

Are there any specials?

Question 8: Which of the following operations are performed on NM?

☒ **1.** mixing and dispersion
⇢ **Control guidance sheet 215:** Mixing of solids with other solids or liquids (additional measures)

☒ **2.** filling and bagging
⇢ **Control guidance sheet 204:** Removing waste from a dust extraction unit (additional measures)

☒ **3.** charging and decanting

☒ **4.** weighing

···❯ **Control guidance sheet 214:** Weighing solids (additional measures)

....

....

☐ **5.** spraying

....

....

☐ **6.** coating (of surfaces)

....

....

☒ **7.** other

Cleaning...

....

···❯ **Control guidance sheet 240:** Dust workplaces (principles)

Question 9: Which of the following protection measures are used when handling NM?

Technical protection measures – ventilation:

☒ Function and efficiency is regularly inspected, at least once per year.

☒ Before starting work, the ventilation is switched on and tested.

☒ The ambient air movement is across or away from the employee.

☐ Is data on the amount of alveolar dust (A- dust) and / or particle number concentration at the workplace available respectively does data on the fibre amount exist?

- ☐ Yes
  - ☐ How high was the exposure?
- ☒ No → *not relevant*

Which of the following technical measures are used when working with NM?:

- [x] Local exhaust ventilation (LEV)
- [ ] Fume hood
- [x] Glove box
- [x] Safety cabinet

Which of the following technical measures are used when working with NM in form of aerosols:

- [x] Closed facility
- [ ] Closed spray booth with automated change of moulded part
- [ ] Open spray booth, the spray dusts are captured by exhaust ventilation
- [ ] If spraying is performed manually, the spray lance is as long as possible. The drop size is preferably >100 µm (no inhalable mist)

Control guidance sheet 100: General ventilation (minimum requirements)

Control guidance sheet 200: Local exhaust ventilation (source extraction) (additional measures)

Control guidance sheet 301: Glove box (closed system)

Technical protection measures - processes:

- [x] Low-dust drop and dump areas
- [ ] Low-dust processing and disposal methods

Intentional generation of dust for research purposes

Organisational protection measures:

- [ ] Hazardous substances are clearly labelled
- [x] Containers for waste disposal are clearly marked and labelled

- [x] Surfaces are easily cleaned
- [x] Possibilities for dust deposits are minimised.
- [x] Wet cleaning is mandatory.
- [x] Industrial vacuum cleaners are available.

Type of filter:

- [ ] M
- [x] H

- [x] Appropriate clean-up equipment for leaking or spilled agents are available and easily accessible.
- [x] Cleansing wipes are not kept in pockets.
- [x] Dusty protection clothes are not shaken out or blown off
- [x] In case of dusty activities, only clean filtered air (filter type H) is recycled.
- [x] Bulk goods and open containers are covered.
- [x] Dusty agents are stored in closed containers.
- [x] Basic occupational hygiene standards are adhered to.

→ **Control guidance sheet 110:** Inhalation - Basic Safety Precautions (Principles)

....

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Personal protective measures:

- [x] Instructions on how to use, maintain and properly store protective equipment, are readily available.
- [x] Chemical-resistant gloves are used.

Type: *Nitrile*

- [x] Protective equipment is correctly stored in a dedicated area.
- [x] Is protective clothing worn?

  Material of protective clothing (if a high amount of material is handled)

  - [x] Dust: Type 3
  - [ ] Aerosols: Type 4

- [x] Is a respirator used for short-term activities?

  Type of respirator? Type of filter?:

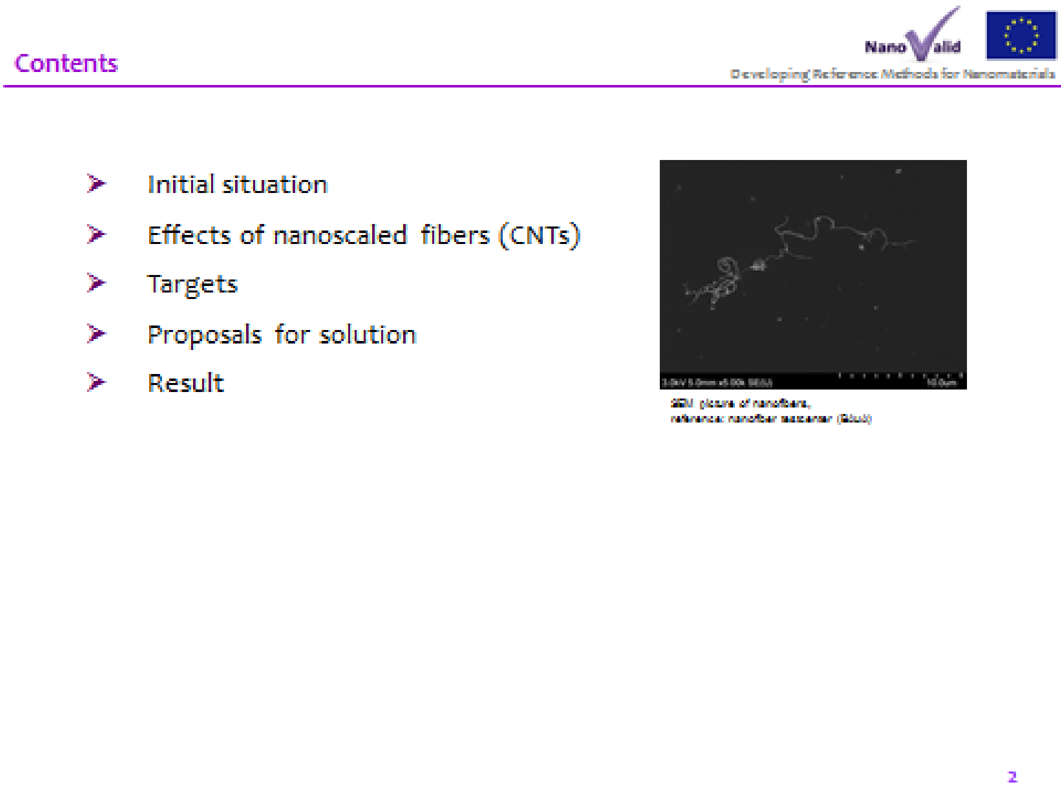
  - [ ] P2
  - [ ] P3
  - [ ] FFP2
  - [x] FFP3
  - [ ] Other

6 Brief presentation: Occupational safety and health regarding activities at a testing chamber, which generated nanofibre dusts

Slide 1:

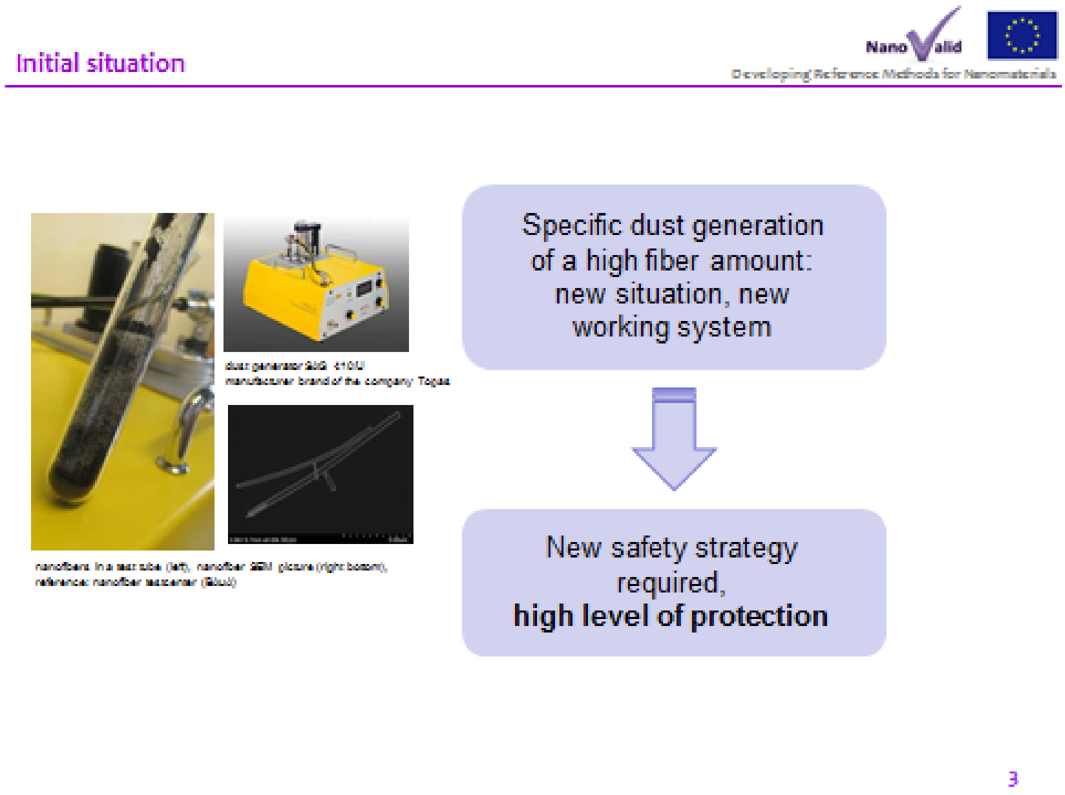
I would like to thank you for the possibility to present you the topic „Occupational safety and health aspects regarding a work system planning in a research laboratory handling nanofibres.

Slide 2:



- At first, I describe the initial situation and the actual difficult situation.
- Then I address the issue of various hazards and risks.
- This leads to targets and solution proposals.
- Finally, I present you the result on what solution we selected.

Slide 3:



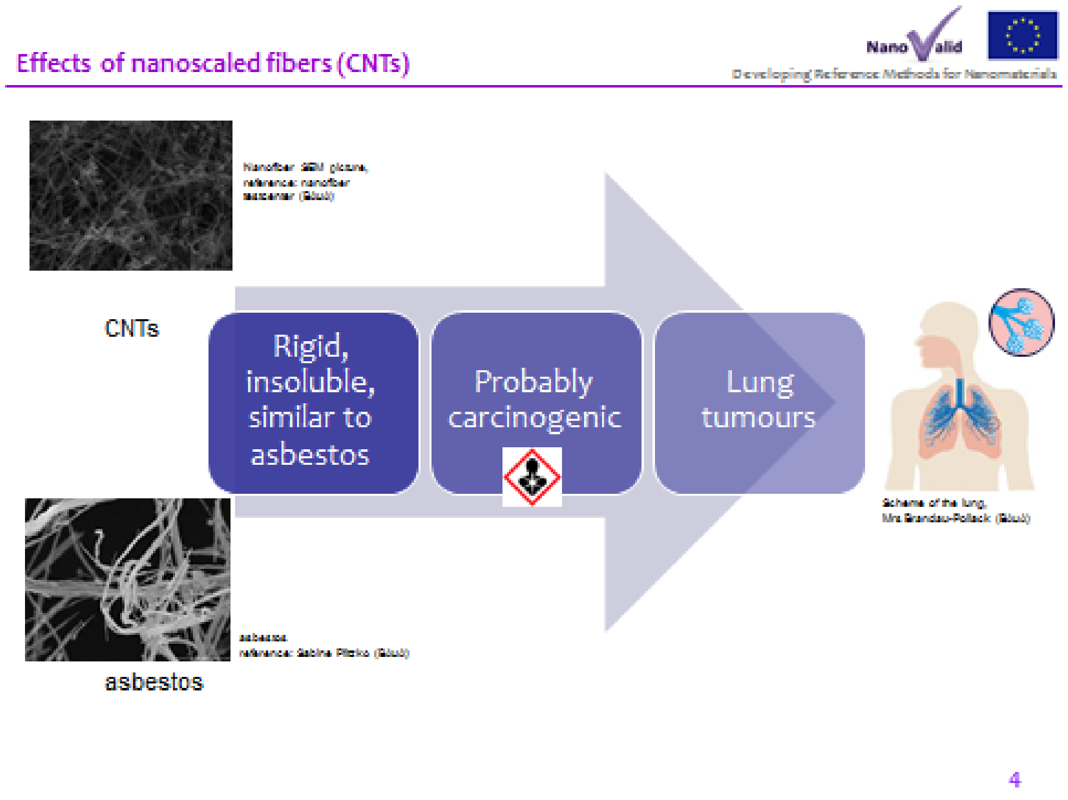
- The **initial situation** is the planning of a new work system.
- We generate nanofibre dusts, namely carbon nanotubes (CNTs).
- These fibres can have the same effects like asbestos.

The **current situation** is as follows:

- In our nanofibre testcenter we would like to generate nanofibre dusts with a dust generator.
- The dust generator can generate many uniform and well-isolated nanoscaled fibres.
- Hence we have a new situation, a new work system and for this we need a corresponding safety strategy.

- With these nanoscaled fibres we need a very high level of protection for the safe handling by the employees.

Slide 4:



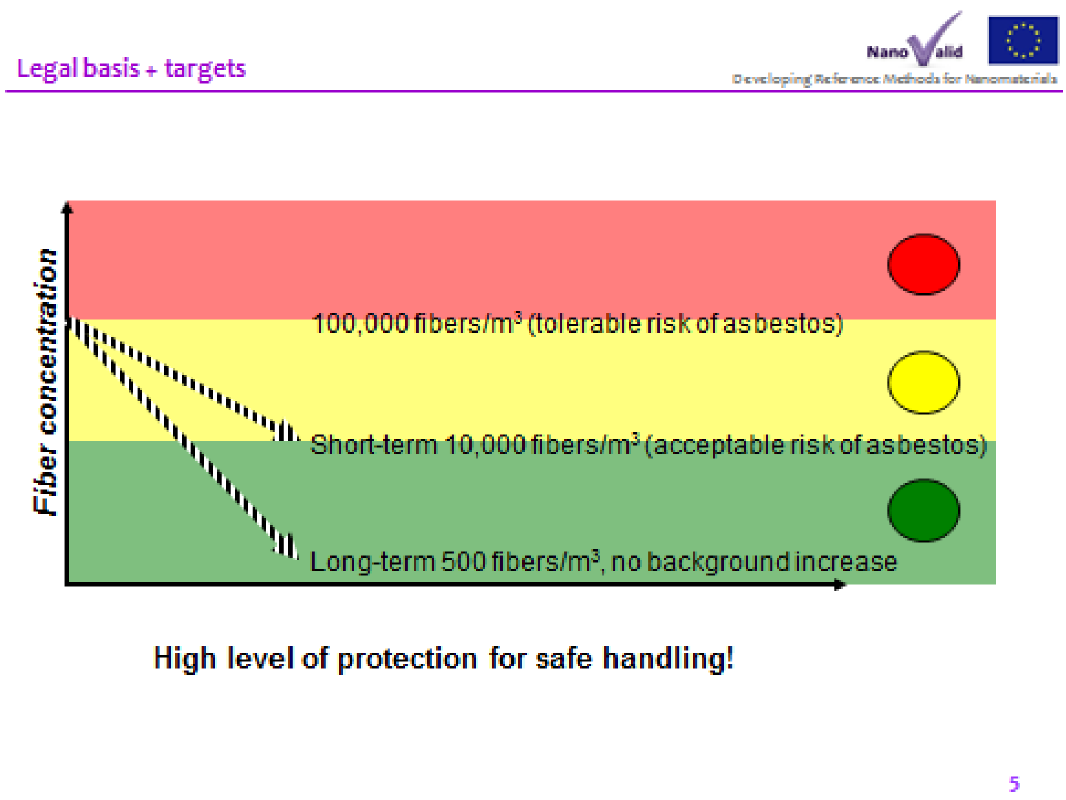
Therefore, we have a difficult situation with a **need for action**:

- We have a hazard by hazardous substances namely nanofibres.
- Nanofibres may have different shapes and can have different hazardous properties. Some fibres are flexible like balls of wool, but others are rigid and look similar to asbestos fibres. These fibres can break.
- There is growing evidence that they do not only look like asbestos fibres, but also cause the same problems like asbestos fibres.
- Hence, the source of risk is the rigid, insoluble nanofibres. The health risk results from their potential asbestos-like effects.
- In conclusion, we generate dusts from very hazardous fibres in a high amount.
- In this case the release of fibre dust, which can be inhaled by the employees, is the dangerous condition.

Effects:

- What do you think can happen, if the employees on-site do inhale these fibres?
- The fibres can be carcinogenic and can cause lung tumours.
- At first, one is unaware of it, but the effects can be there nonetheless.
- If we do nothing, there is a risk that the hazards manifest themselves much later. For this reason, we take precautions!

Slide 5:



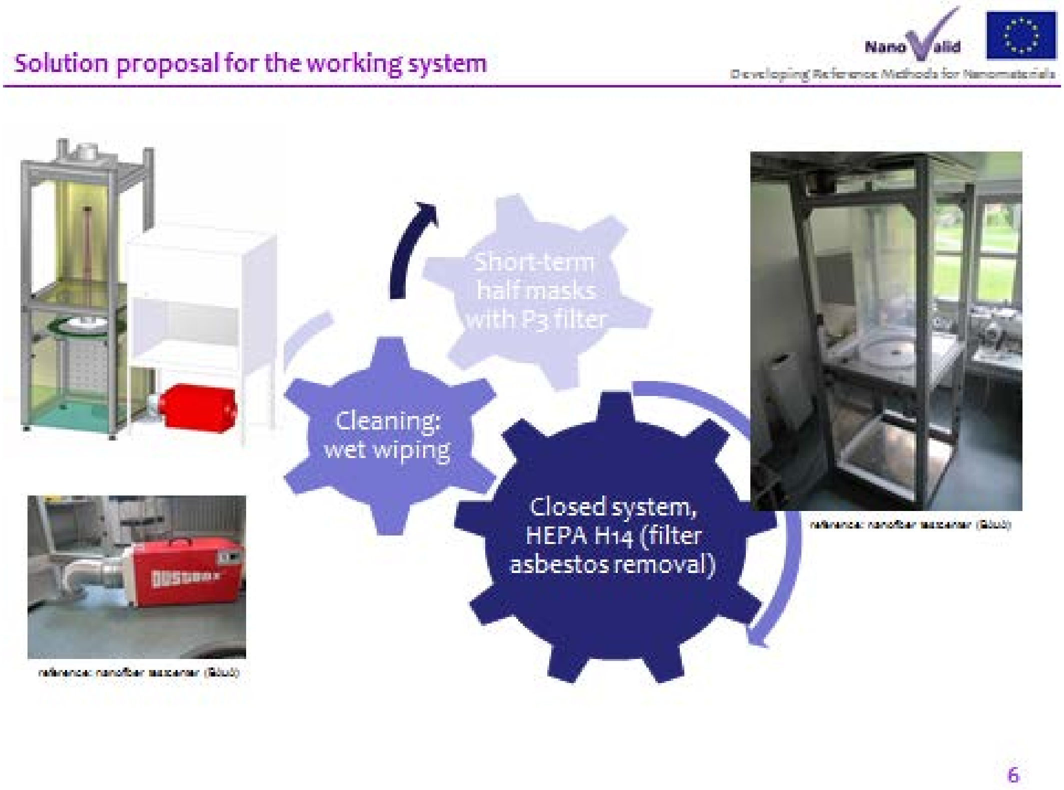
The **legal basis** is the following:

- Usually, for many substances we have occupational exposure limits.
- However, in this specific situation, we have no binding health-based limit values specifically for nanofibres – but we have benchmark levels.
- In the German Technical Rule for Hazardous Substances (TRGS 910, 2014) "Risk-related concept of measures for activities involving carcinogenic hazardous substances", we have a value for long-term exposure to asbestos of 10,000 fibres/m^3.
- And exactly this value is proposed for nanofibres both from the German Social Accident Insur-ance (DGUV) and from the German hazardous substances committee (AGS) in the Announcement Manufactured nanomaterials (Announcement 527, 2013). Both hence agree on that concentration.

What should be the **target** then?

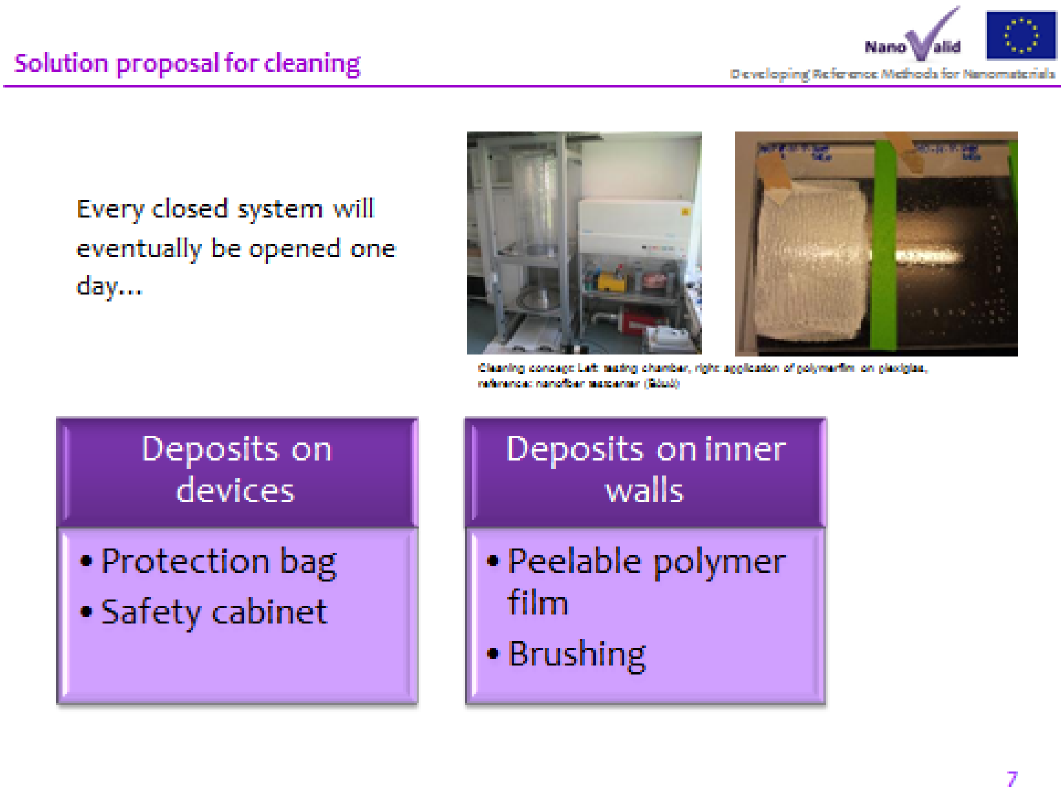
- One should start with the benchmark level.
- It is our **minimum target** to comply with this value of **10,000 fibres/m^3**, already from the first application with rigid fibres.
- This value is the same like for asbestos. However, a further value exists for asbestos of **500 fibres/m^3** (TRGS 519 2014, Asbestos: "Demolition, reconstruction or maintenance work") for the clearance measurement of renovation works. This our **optimisation target**.
- Permanently and in the long term, the aim is that:
  - The background concentration caused by the process is not increased,
  - A value of 500 fibres/m^3 is not exceeded. For asbestos, this value is taken for the clearance measurement (re-pealing further measures) of renovation works.

Slide 6:



- What would be the **solution proposal** then? We have a series of protective measures according to the TOP approach.
- Technical measures: The testing chamber is a closed system with an exhaust with a HEPA H14 filter. The filter is authorised for the asbestos removal.
- Organisational measures: The work area is cleaned regularly by wet wiping.
- Personal protective equipment: In case of a short-time higher exposure, which can be caused due to the activity for instance during cleaning, half-face masks with P3 filter are worn.

Slide 7:

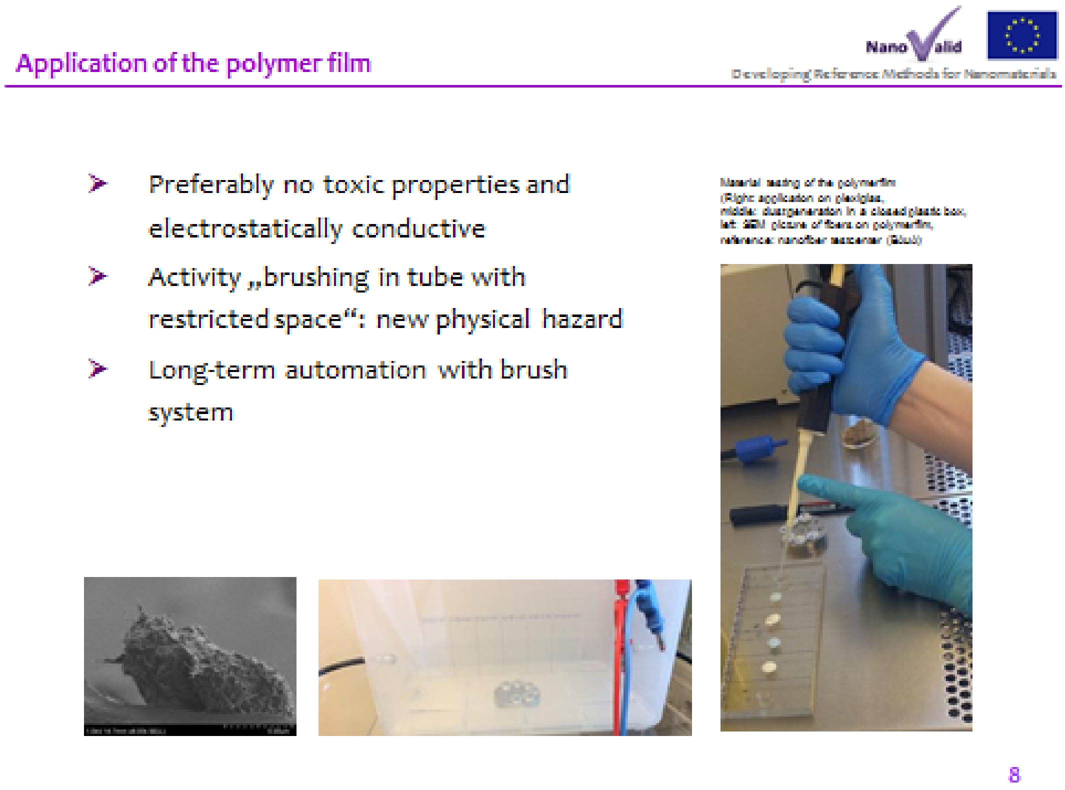


We focus especially on **cleaning**, since the system is opened then, and the employees could inhale fibres:

- difficulty 1: Single fibres can attach at the devices within the testing chamber. For this reason, if the system is opened for cleaning, the devices are transported to a safety cabinet in a plastic bag.
- difficulty 2: During the workflow, fibres can attach at the inner walls of the Plexiglas tube. Therefore, also the inner wall needs to be cleaned.

The **solution proposal** to meet these difficulties is a peelable polymer film. The fibre dust deposits on this polymer film, which can be peeled and removed after the experiment.
This idea to apply this cleaning concept when working with nanomaterials, is completely new. My colleague working on-site in Berlin had excellent implementation ideas for this concept.

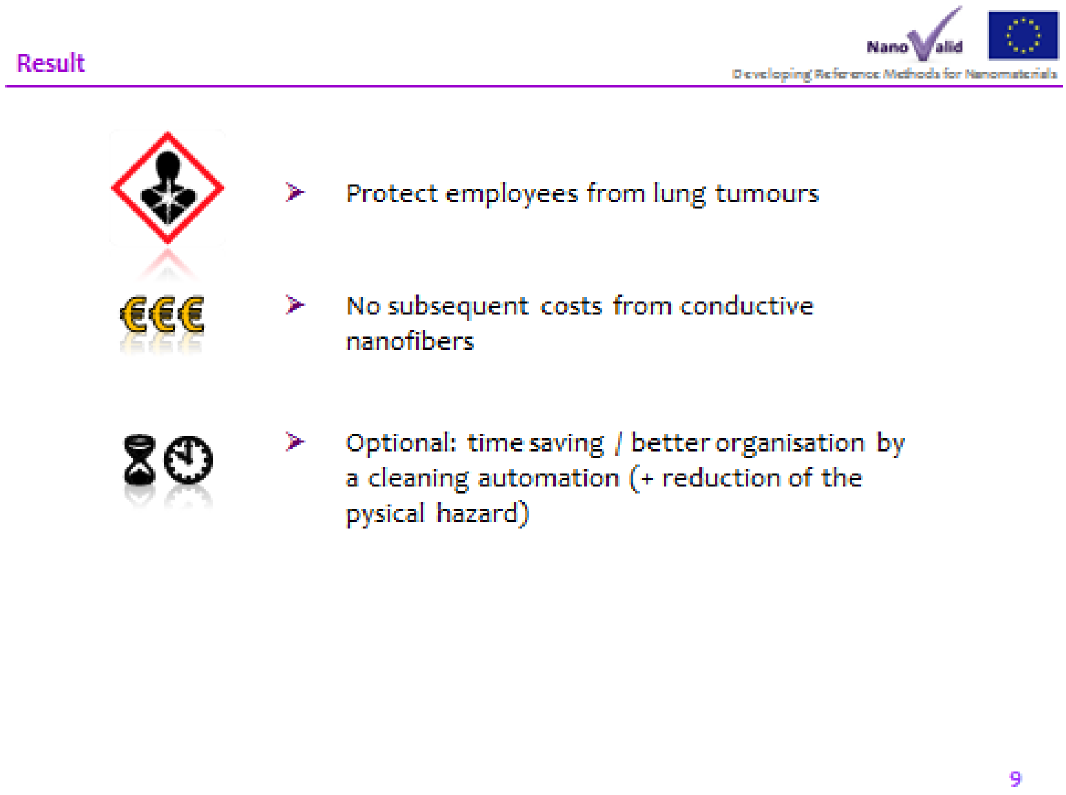
Slide 8:



- It is essential that:
  1. the film is compatible to Plexiglas, can be brushed vertically and can be completely removed afterwards.
  2. Preferably, the film has **no hazardous properties** (not toxic…) and is preferably **electrostatically conductive** in order to avoid an electrical charge of the Plexiglas tube.
- Therefore, we tested material samples from different producers.
- We could confirm the effect in before-after pictures.

- We have thus a new cleaning activity. Due to this activity, the employees can be optimally protected.
- In this way, we can solve the problem of the **hazard from fibres.**
- However, one should also take care of the hazards, which can be caused by this activity itself. As you can imagine: for the manual application the employees
  a) have to work cramped in a narrow tube with a diameter of 65 cm or
  b) brush the product from the outside to the inner wall, whereby the brush needs to be brought in with a telescopic pole to the upper area of the tube.
- We would hence have a physical hazard caused by forced posture.
- Therefore, it is the short-term goal to minimize the hazard from the inhalation of fibres.
- In the long-term, physical hazards can have negative effects.
- What can be done? In the long-term, an automated application should be sought. A brushing system can be constructed by the engineers on-site for this reason. The brushing system would automatically move along the inner wall of the plexiglass tube.

Slide 9:



- These proposals for cleaning provide a number of **benefits**:
- With a high level of protection, the employees are **effectively protected** against these asbestos-like fibres, which can cause lung tumours.
- Dust distributes so that **follow-up costs** can be the consequence. The applied fibres are electrically conductive. Dust deposits of these fibres are hence undesired on electrical devices. Therefore, it is important to keep the area clean.
- If in the long term we succeed to automate the cleaning process, we can not only protect the employees against physical hazards by working in a narrow tube, but we can also **improve the process organisation** and clearly **save time**.

Slide 10:

Developing Reference Methods for Nanomaterials

I therefore ask you to approve to the implementation of these measures!
Thank you

Contact email: baron.miriam(at)baua.bund.de

I would like to thank my colleagues from the nanofiber testcenter in Berlin
Barbara Dettlaff, Nico Dziurowitz, Dr. Asmus Meyer-Plath,
Sabine Plitzko and Carmen Thim for the pictures and the possibility to support them
in the generation of the testing chamber and the cleaning concept!

10

- We need a very high level of protection for the safe handling of the employees with these nanoscaled fibres! – and we can achieve this with a cleaning concept with a polymer film, which can be automated in the long-term.
- I kindly ask you to approve this safety strategy.
- I would like to thank my colleagues from the nanofibre testcenter in Berlin for their support in the safety concept regarding nanofibre handling in a newly generated work system.

7 Conclusions

7.1 Specific conclusions for the firm

In the long-term, an automated cleaning of the plexiglass tube is preferred, in order to develop the occupational safety and health in a sustainable way. Research on the hazardous properties of nanomaterials is a current and much discussed scientific topic and the prudent and continuous adaption of the occupational safety and health to new findings and benchmark levels is essential. Much attention is given to comprehensive occupational safety and health in the operational actions. Therefore, activities at the testing chamber can only be started if the hazard after implementation of the safety measures is not higher than in the other laboratory areas, where CNTs are examined. This means that the exposure during cleaning will not be higher than during the other activities. For this reason, no additional action, which exceeds the regulations and agreements already taken, is needed regarding the cooperation with partners. In any case, the employees are informed about the possibility of a precautionary examination by the occupational health physician.

7.2 Specific conclusions for the safety expert

The cooperation with the employees involved on-site was very good. Concerted joint action resulted in appropriate solutions, which received general approval. After planning the new work system, the safety expert will support the colleagues in the improvement of the selected work system and protection measures for a continuous optimisation of occupational safety and health. In the context of efficiency control it can be tested whether the selected safety measures have decreased the hazard by hazardous substances to the targeted residual risk. Regarding the mechanical hazard from intentionally moved machine parts, a cover at the bottom of the plexiglass tube is planned in order to avoid crushing fingers, thus following a standard safety strategy.

The future installation of an automated cleaning process will be accompanied by a safety expert. It is planned to reassess the level of physical strain from the activity "cleaning the testing chamber" and to determine effective protection measures, which are accepted and supported by the employees on-site. The selected solutions will be presented to the in-house occupational safety committee.

The risk assessment for the testing chamber as developed in this internship will be integrated into other, already existing instructions, e.g. the task-area related "dust laboratory instructions". All protection measures will be combined and adapted accordingly.

7.3 General conclusions

Measurements are an important tool for experts in order to deduce model situations which can be transferred on comparable workplaces. Small enterprises that cannot afford expensive measurements, can compare their settings to these model situations. This provides a good starting point to assess their own situation and enables a comprehensive view on the quality of their occupational safety and health strategy and installed protective measures.

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