« nano-inventory »

Intermediate report: a qualitative pilot study

Kaspar Schmid, Michael Riediker

26.05.2006

Institut universitaire romand de Santé au Travail
(Institute for Occupational Health Sciences)
Rue bugnon 19, 1004 Lausanne
Tél. +41 (0)21 314 74 21

General addresses and contact information for the „nano-inventory“

General address
Institut universitaire romand de Santé au Travail
Rue du Bugnon 19
1005 Lausanne
Suisse/Switzerland
Tel. +41 (0)21 314 74 21
Fax . +41 (0)21 314 74 30
www.iurst.ch

Nano-inventory - leader
Michael Riediker, Dr.sc.nat.
Head "Group Particles and Health" (NEW NAME)
Institute for Occupational Health Sciences
(IST = Institut universitaire romand de Santé au Travail)
Rue du Bugnon 19
1005 Lausanne
Suisse/Switzerland

Tel. direct +41 (0)21 314 74 53
Fax . +41 (0)21 314 74 30
Michael.Riediker@hospvd.ch

Nano-inventory
Kaspar Schmid, Dipl. Umwelt Natw. ETH
Institute for Occupational Health Sciences
(IST = Institut universitaire romand de Santé au Travail)
Rue du Bugnon 19
1005 Lausanne
Suisse/Switzerland

Tel. direct +41 (0)21 314 58 96
Fax . +41 (0)21 314 74 30
Kaspar.Schmid@hospvd.ch

Index:

1 Abstract

Background

Nanoparticles are particles smaller than 100 nm in at least two dimensions. They are interesting for industrial and medical applications since they have properties, which are different from those of the same substance at larger size. A large number of different types of nanoparticles and applications are currently being developed and introduced into industrial processes and consumer products.

Exposure to micro- and nanosized particulate matter (PM) from air pollution is associated with negative health effects such as physiological reactions in the lungs, pro-inflammatory and pro-thrombotic vascular responses, and interferences with the cardiac rhythm. Manufactured nanoparticles might cause similar responses. There is an urgent need to evaluate the risks of these particles to ensure their safe production, handling, use, and disposal. Three main elements are required for such a risk assessment: the number of exposed people, the type and quantity of exposure and the associated health effects. Studies about industrial exposure are still rare, and our knowledge about nanoparticle-exposures in Switzerland is insufficient.

Goal of this pilot study was to evaluate the feasibility of a questionnaire-based approach for studying nanoparticle applications in Swiss industries with regard to types and quantities of nanoparticles, protective measures and numbers of potentially exposed workers. Special attention was given to evaluate the information that could be obtained from the companies' safety experts, since they would have to fill the questionnaire during the main study.

Experimental design and methods

A qualitative telephone survey was conducted among two hundred Swiss companies. First, companies were identified that were likely to use nanoparticles. This selection was based on published technology reports, self-declarations, member lists of industrial associations, and the yellow pages. Questions were asked about applications and particle types, the potential exposure of workers to nanoparticles, and the current safety policy in the company. The quality of the answers was also evaluated.

Results

Swiss companies were found applying the following nanoparticles in considerable quantities (tons per year): Ag, AlO3, Fe-Ox, SiO2, TiO2 and ZnO2. Applications were identified in the following fields: coating, cosmetics, food (animal feed, sport food and food packing), metal, optics, paintings, powder production, surface treatment, and research laboratories.

The companies that used nanoparticles had a median of 130 total employees (mean of 350 total employees). The quantity of particles used per company showed a skewed distribution with a median of 100 kg per year and a mean of 40 tons per year. Production managers of upscaled productions tended to be less concerned about the use of nanoparticles in their company than those of smaller productions.

Conclusion

The pilot survey shows that nanoparticles are not fiction but already reality in the Swiss industry. Several types of nanoparticles are already used in very up-scaled productions, while others appear to be used solely in research. The companies contacted are probably not representative for the Swiss industry. However this pilot study allowed the identification of industrial sectors with established nanoparticle-use and gave valuable information about the knowledge of production and safety managers. It allows developing a questionnaire that will be used to obtain a representative and comprehensive picture of industrial processes, sectors and companies in which nanoparticles are applied.

2 Introduction

Definition of nanoparticles

Nanoparticles are particles smaller than 100 nm in at least in two dimensions. This follows definitions made by VDI and DIN (1) "particles < 0,1 µm thermodynamic diameter", the European Commission Committee (2) "particle with one or more dimensions at the nanoscale"[1], the Royal Society (3) "particles less than 100 nm" and the EPA (4) "in the length scale of approximately 1-100 nanometre range".

A definition of "less than 100 nm" is problematic. Many particles are sold only with an indication of their mean diameter or an approximate size distribution. Furthermore, in an up-scaled production, even a relatively low proportion of nanoparticles can lead to important concentrations of nanoparticles.

Applications of nanoparticles

The properties of materials, such as the conductivity or the chemical reactivity, change as their size approaches the nanoscale. Reports on the surface properties show that nanoparticles differ from bulk materials (5). Nanoparticles often have unexpected visible properties because they interfere little with visible light. These aspects make nanoparticles interesting for industrial applications. Industries in the field of nanotechnology have developed a great number of different nanoparticles in short time. These materials are increasingly being used for commercial purposes such as fillers, opacifiers, catalysts, semiconductors, cosmetics, microelectronics, and drug carriers (6).

Health concerns

The same properties that make these particles interesting for industrial application make them potentially dangerous with regard to negative health effects. In ambient air-pollution-studies particles in the size of PM2.5 or PM10 are shown to be harmful to human health. Nano sized particles are even suspected to enter the human body easier than micro sized particles. Different types of nanoparticles were shown to have adverse health effects (7). The surface of nanoparticles is larger and may therefore have a higher biological activity. There is a call for routine tests of nanomaterials: physicochemical characteristics, in vitro assays (cellular and non-cellular), and in vivo assays (8). It must be recognized that the influence of particle properties such as size and surface area on toxicology and physiochemical responses are not fully understood (9).

Exposure to nanoparticles

Industries already started with the development of mass production and handling facilities, this in spite of the limited knowledge about the risks associated with exposure to such particles (10;11). Currently, there are no official safety guidelines describing safe and responsible handling and application of nanoparticles. ISO launched work on nanotechnology standards in 2005 and the NANOSAFE1/2, a European project, is to develop risk assessment and management for secure industrial production of nanoparticles since 2003/5.

There is a scientific discussion going on about which parameters are essential to describe nanoparticle exposure. Mass, number, and surface area are the most often mentioned metrics. But also surface reactivity, charge, etc are frequently proposed with regard to toxicological questions. The UK Royal Society and The Royal Academy of Engineering recommended that the Health & Safety Executive (HSE) should review the adequacy of its regulation of exposure to nanoparticles, and in particular should consider the relative advantages of

[1] In the present report, nanoparticles are considered to have two or more dimensions at the nanoscale.

measurement on the basis of mass and number. In the meantime, they recommend that occupational exposure levels for manufactured nanoparticles should be kept as low as possible. They also recommended to treat nanomaterial as potentially hazardous, to seek to remove them from waste stream, to not apply free nanomaterial to the environment unless the benefits clearly outweigh the anticipated risks and to assess the potential impact of nanomaterial throughout their lifecycle (3).

2.1 What is missing, or not well researched?

Occupational exposure to nanoparticles is not a new phenomenon. In the past, heat-associated processes such as fuel combustion or welding accidentally produced nanoparticles that were quite short-lived due to agglomeration processes. The new nanoparticles, on the other hand, are produced on purpose, and many producers aim to develop nanoparticles with low agglomeration tendency. The number of industrial nanoparticle applications is increasing quickly.

In Europe, there is no specific declaration duty for nanoparticles. As a consequence, we have a limited knowledge about who is using nanoparticles in Swiss industries and what types of particles are used. Guidelines for the safe and responsible production, handling and disposal of nanoparticles need to be developed. For the development of such guidelines, more information is needed about the exposure resulting from different handling-methods of different nanoparticles with different protection measures. At the moment, the scientific basis for recommendations about the safe handling of nanoparticles is insufficient. Current recommendations are mostly based on analogy reflections.

Besides the uncertainties regarding exposure to nanoparticles, there is also very limited knowledge with regard to mobility, dispersion and distribution of nanostructures in different media (especially in air but also in water). New measurement strategies and modelling efforts are needed to provide adequate information for risk evaluations.

Special attention will have to be paid to up-scaled productions and their potential long-term consequences for health and ecology (12).

3 Objectives

3.1 Objectives of the nano-inventory

The principal aim of this study is to estimate the prevalence and extent of nanoparticles in the Swiss industry as well as the potential for exposure to engineered nanoparticles of the Swiss working population. One basic assumption of this research is that occupational cohorts are likely to have earlier and higher exposures than the general population, which makes them an interesting population for risk assessments. Studies on toxicological effects need to be combined with information about exposure. In the absence of solid exposure data no solid risk evaluation can be conducted.

For this purpose a nano-inventory will be created. It will show the number of companies from different industrial branches, the type of particles used and the number of potentially exposed people. This information will be combined with data about different protection measures for humans and the aquatic and atmospheric environment. This will allow an estimation of the potential exposure of the Swiss occupational exposure to nanoparticles. It can be combined in a later moment with exposure profiles of typical workplaces to estimate the exposure to nanoparticles. In addition, the knowledge about the amounts of nanoparticles being handled by individual companies can be useful for environmental risk assessments.

3.1.1 Objectives of the pilot study

This pilot study was conducted to evaluate the feasibility of a questionnaire-based approach, to investigate the availability of relevant data and to acquire a first impression about the use of nanoparticles in the Swiss industry. A selected, non-representative number of companies were interviewed by telephone about the following aspects of exposure: the type and quantity of nanoparticles, the level of potential exposure and the current safety-policy in the company.

The aim of this survey was to see if companies (specifically their security-managers) were willing and able to answer questions about their production with nanoparticles. Another aim was to identify different industrial sectors with nanoparticles-applications and the quantity of particles used in this selection in order to prepare a representative written survey.

4 Methods

The inventory of nanoparticle applications in Swiss industries will be created in two different steps. This report is about the first step, the pilot study.

a) Pilot study: a focussed telephone survey to give an overview about the nanoparticle use in the different industrial sectors, their application types and the feasibility of a written survey.
b) Main study: a questionnaire-based written survey of a representative sample among all industrial branches where the production or application of nanoparticles cannot be excluded with certainty. The survey will be conducted in collaboration with and mandated by BAFU, BAG, SECO and SUVA.

4.1 Design of the qualitative pilot study

Applications and addresses of potential users and producers were looked up using an Internet search. Syndicates of industrial sectors in which applications were suspected were contacted to obtain their membership-lists. A direct application search and the yellow pages complemented the list. About two hundred companies were contacted by telephone.

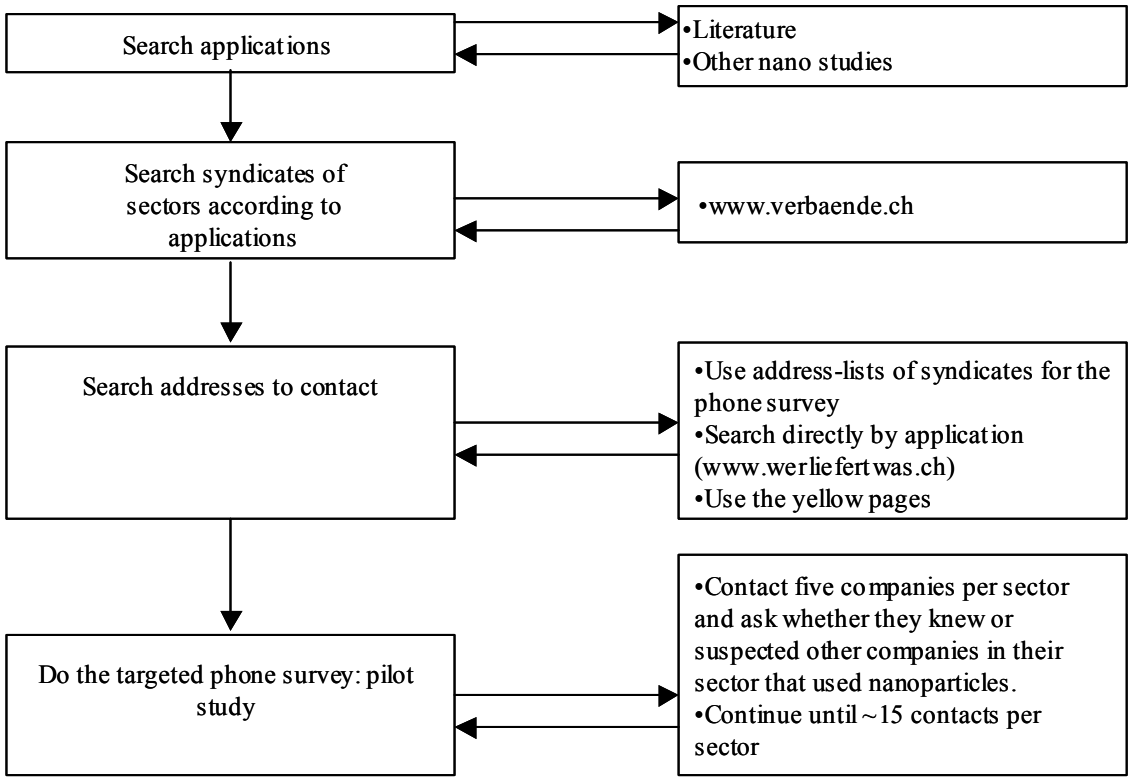

Figure 1: process chart of the pilot study

4.2 Methods of the qualitative pilot study

4.2.1 Search for nanoparticle applications

A literature review was conducted to identify presently known applications of nanoparticles.

4.2.2 Address search

First, companies were searched with self-declared use or production of nanoparticles (web page), and by an address collection from the program TopNano21[2], which lists companies in the field of nanotechnology (not necessarily nanoparticles). Company addresses of sectors with known applications were found using the list provided on a website about Swiss syndicates: www.verbaende.ch. In other sectors, companies were identified with the help of a product-based search engine: www.werliefertwas.ch. Additional companies were found with the yellow pages: www.gelbeseiten.ch.

4.2.3 Structured telephone interviews

In each sector initially five of the identified companies were contacted by telephone. The security manager or another person in charge (such as the head of the company, the line responsible, the production manager etc.) was interviewed with the help of an open questionnaire[3]: the type of application, some key elements for the estimation of a potential exposure and the actual safety policy in the company (see also Table 1). The questions included the duration and frequency of the application processes as well as the quantities of nanoparticle used. At the end, the interviewed person was asked whether he/she knew or suspected other companies in his sector to use nanoparticles. The hereby identified companies were contacted until a number of about 15 contacts per sector was reached. This approach was chosen to obtain as many "positive hits" as possible.

Table 1: Short description of the fields of questions used in the guiding form to conduct the telephone interviews. The full list of questions is in the annex (in German and French).

Fields of question	*Examples of questions asked in the telephone interview*
Types of nanoparticles	What type of nanoparticles is used?
Key elements for exposure estimation	How many persons are present and therefore potentially exposed? What are the used protection measures to lower the exposure? What kind of manipulation is done with the particles? What is the quantity of nanoparticles used per day?
The actual safety policy	How often are workers informed about the safety risks of nanoparticles? Which is the highest-ranked management-level that takes care of the topic nanoparticles and safety?

2 www.temas.ch/nano/nano_homepage.nsf/vwAllByKey/Vision|de, Top-Nano21, last access: 24.05.06
3 The whole open questionnaire is shown in the appendix; German version

5 Results of the qualitative pilot study

5.1 Source identification

The sources mentioned in Table 2 were chosen to obtain a comprehensive picture of nanoparticle applications. Several other sources, to include international webpages, were searched. However, they did not propose other, not yet mentionned application types.

Table 2: Sources to identify potential applications of nanoparticles in the industry.

University/ Organisation	*Link*	*Last accessed*
University of Ulm	http://wwwex.physik.uni-ulm.de/vortraege/StudiumGenerale/Nanot_0.htm	24.05.06
Technologiezentrum GmbH, Düsseldorf	http://www.zukuenftigetechnologien.de/11.pdf	24.05.06
INM: Institute for New Materials, Saarbrücken	www.inm-gmbh.de/htdocs/technologien/schwerpunkte/schwerpunkte_de.htm	27.02.06

Table 3 shows syndicates of sectors with an address-list with more than 15 contact addresses. The search was conducted by the Internet database www.verbaende.ch, a database of syndicates. Other databases used were the database to search a company by a product type www.werliefertwas.ch and the yellow pages www.gelbeseiten.ch.
Supposedly, not all company sectors were identified. In addition several applications were identified for which no contacts were found, see chapter 5.3.

Table 3: Sectors with potential applications found by the syndicate search page www.verbaende.ch, by the yellow pages www.gelbeseiten.ch and by the product based company search page www.werliefertwas.ch

By the syndicate list www.verbaende.ch	*By the yellow pages www.gelbeseiten.ch*	*By the database www.werliefertwas.ch*
Printing production	Tyres	Filters
Paint production	Milling	Gravure printing
Cosmetics production	Powder-Production	Dyeing factory
Varnish production	Coating	Clock industries (complementary)
Paper production	Batteries	
Chemical production		
Plastic production		
Cleaning agent production		
Feeding stuff production		
Food science		
Microelectronic production		
Sensors		
Clock production		
Construction materials		

5.2 Identified application-fields in Swiss companies

The following application-fields, indicated by the literature sources, were found in the Swiss industry. Table 4 shows the different sources and the corresponding possible application fields. The fields of possible applications are sometimes larger than the applications identified by the survey but they lead to the presumption that other applications in the same field may be used in similar companies.

Table 4: Fields of application found in Switzerland by the targeted telephone survey, (source that defined this application: VDI = Technologiezentrum, Düsseldorf - Germany[4], Uni Ulm = University of Ulm - Germany[5], INM = Institut für neue Materialien of Saarbrücken – Germany)

Possible application fields	*Found in the sector*	*Source*
Pharmaceutical research	Research	Uni Ulm
Fine mechanic, optics, analytics	Surface coating	Uni Ulm
Lubricants	Optics	Uni Ulm
Chemical-mechanical polishing	Else	VDI
Chemical or physical particle production (colloids, pigments, dispersions, powder)	Powder production	Uni Ulm
Corrosion-inhibitor	Surface coating	Uni Ulm
Ceramics	Else	Uni Ulm, VDI
Paintings and Pigments (hybrid and effect)	Paintings	Uni Ulm
Functional coating, anti-adhesive and defogging agents, Scratch-resistant coatings	Surface coating	Uni Ulm, INM
Varnish-effects and varnish-follies	Paintings	Uni Ulm
Super hard alloys	Metal treatment	Uni Ulm
Food production (milk, juices, brewery)	Food	INM
Sunscreen	Cosmetics	VDI
Cleaning	Cleaning	VDI

Figure 2 shows the number of companies and their distribution in the industrial sectors, which have been identified by the targeted survey. The proportion of companies with and without nanoparticles is clearly influenced by the targeting structure of the pilot study and does not necessarily reflect the real proportions. Some of the sectors may be over- or underestimated.

Note that several companies are present in two or more sectors. The sum of the individual bars does not equal the number of the identified companies. The total number of identified companies with nanoparticles is 56. The same limitation applies to the sum of companies without nanoparticles (132). Some of the identified companies with nanoparticles do not have an actual production but only buy and resell products with nanoparticles. Companies buying and reselling products with "free" nanoparticles (powders or liquids) were considered to use nanoparticles. Surface-treated solids or solid-matrix applications such as wire production (no manufacture in Switzerland) were considered as "no nanoparticles".

[4] http://www.zukuenftigetechnologien.de/11.pdf, last access: 24.05.06
[5] http://wwwex.physik.uni-ulm.de/vortraege/StudiumGenerale/Nanot_20.htm, last access: 24.05.06

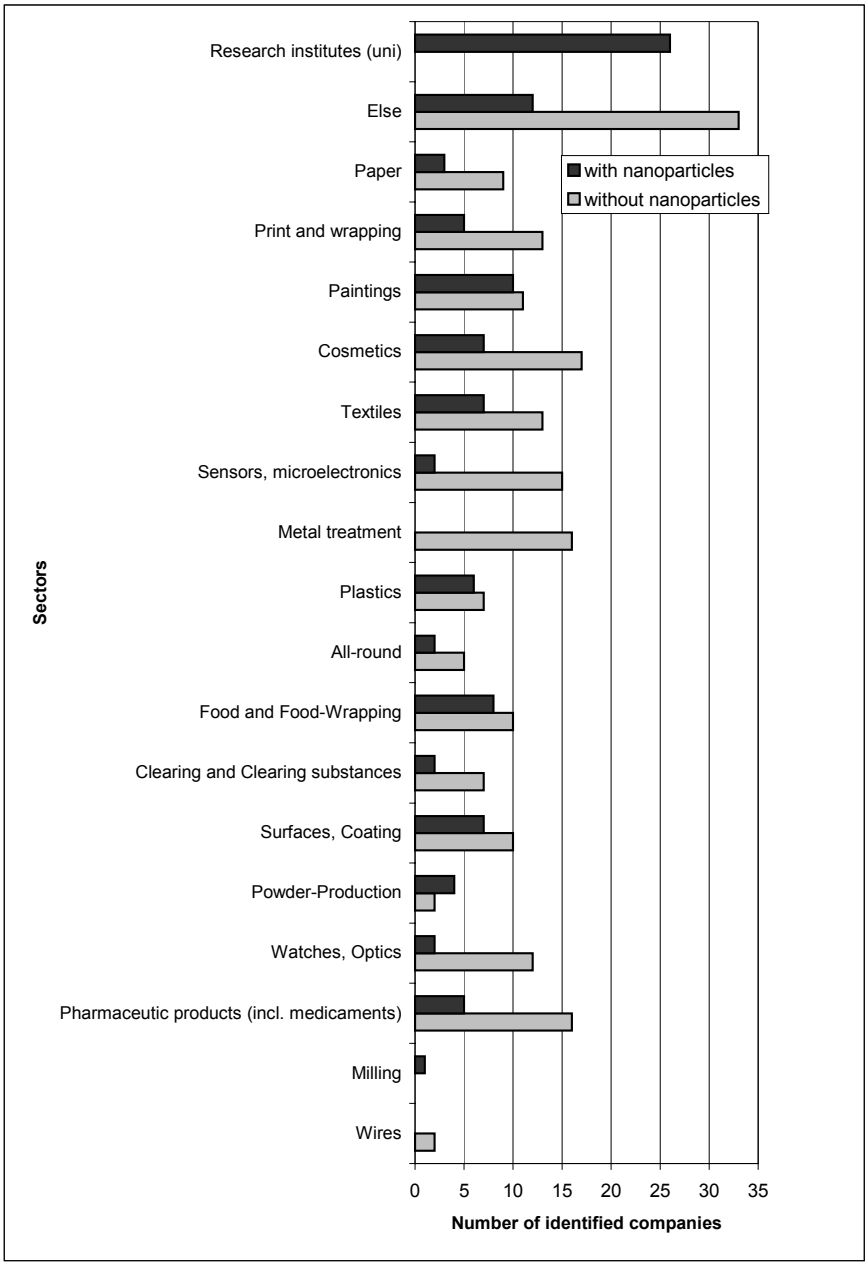

Figure 2: Number of Swiss companies per sector with nanoparticles according to the non-representative telephone survey. The survey finished February 2006.

About 20 types of nanoparticles were identified that are used by the companies interviewed. The application methods were characterised as liquid, powder or else. Table 5 focuses on the types of nanoparticles. For eight types of nanoparticles, only one company was found. SiO2 and TiO2 are the two predominant nanoparticle types. Up-scaled usages (kilo-tons per year) were found for iron oxides, TiO2 Ag, AlO3, and Carbon black nanoparticles. The strict size-limit was weakened for counting the companies: particles smaller than 1000 nm were considered in six companies as potential nanoparticles (see Table 6). There were slightly more liquid than powder applications (30 and 25, respectively). The number of total employees shows that also very small companies can use large amounts of nanoparticles (e.g. silver-particles). Note that in several companies, more than one type of nanoparticle was identified and that some companies just sell and resell a product with nanoparticles.

Table 5: Different types of nanoparticles found in use in Swiss companies by the targeted telephone interview, quantity of used nanomaterial and total number of employees in the companies. Some applications were also mentioned without further specification: Pigments, cellulose, diamond and (unspecific) Metal-Ox. The particle size distribution curves are unknown, therefore particles with an average size of less than 1µm were considered (see *-marks) as nanoparticles.

Identified nanoparticles types	*Number of companies*	*Employees total in all companies*	*Quantity used per year [kg]*	*Liquid (L) or Powder (P) or Solid (S*
Ag	3	22	3'100	3xL
All sort	3	171	2	2xL, 1xP
Al-ox	2	1720	5	1xS, 1xN/A
Betanten	1	150	1'000	1xL
Carbon black	4	75	1'000'000	1xL, 2xP, 1xN/A
Carbo nanotubes	1	N/A	1'000	1xN/A
Fe-ox	2	135	365'000	1xL, 1xP
Liposome	1	N/A	70'000	1xP
Mincor	1	71	N/A	N/A
Polymer	3	460	102'500	3xL
Sio2 (*)	16	3000	7'300	8xL, 7xP, 1xN/A
Sio2 with carboxyl groups	2	835	300	2xL
Sio2 solgel	1	1	1	1xL
Tinosorb (**)	2	230	400	2xP
Tio2 (***)	10	680	400'000	4xL, 5xP, 2xN/A
Zno	2	230	70'000	2xP
N/A	11	4551	500	5xL, 2xP, 2xS, 1xN/A

(*) Tree companies declared to use SiO2 particles with an average size between 100nm and 1µm
(**) Tinosorb has an average size of 200nm
(***) One company declared to use TiO2 with an average size smaller than 400nm

Figure 3 shows the distribution of the quantities of nanoparticles used per year by the companies that use or produce particles (without research institutes and pure re-sellers). The class definitions were less than 100kg/a, which is more a research sector than a production; until 1000kg/a, which resembles a small production; until 5t/a, which still resembles a small production; until 25t/a representative for an up-scaled production of a small company; and until 100t/a respectively more than 100t/a represents a very up-scaled production. The range was very large from "some grams" per year to one thousand tonne per year[6]. The majority of the companies using or producing particles had less than a tonne per year. The mean quantity was 40 tons, the median 100 kg. Several companies were identified that can be classified as "re-sellers". Of these 17 re-sellers, 6 bought and sold pre-packaged solid products containing nanoparticles e.g. surface treated metal parts (therefore not registered in this report), 11 bought and sold products that had been treated

[6] The top producer declared the production as "pilot plant".

abroad with nanoparticles (therefore registered in this report), some of the companies did not comment the quantity of used nanoparticles. No information about the quantities of nanoparticles contained in these products (e.g. textile coatings) was available.

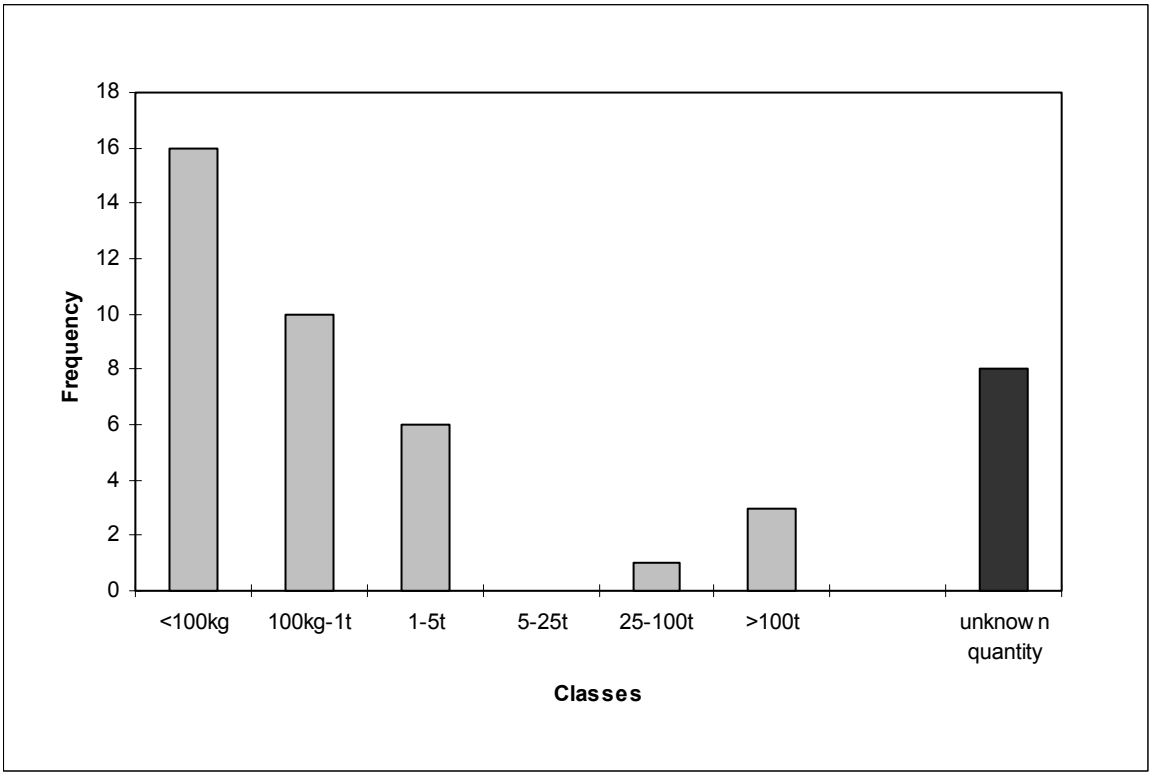

Figure 3 Frequencies of companies with different quantities of nanoparticles use per year (n=44). Research institutes (n=26) and pure re-sellers without reworking of the product (n=6) are not shown.

The size of companies using nanoparticles was estimated from the number of the total employees. The size of companies is presented in Figure 4. It shows a peak of "middle"-sized companies. The federal definition of company sizes is as follows (Bundesamt für Statistik, 2001) – micro is smaller than 10 employees, small <50 employees, middle <250 employees and big >250. Two additional groups were created to differentiate between the big companies: <500 employees and >500 employees.

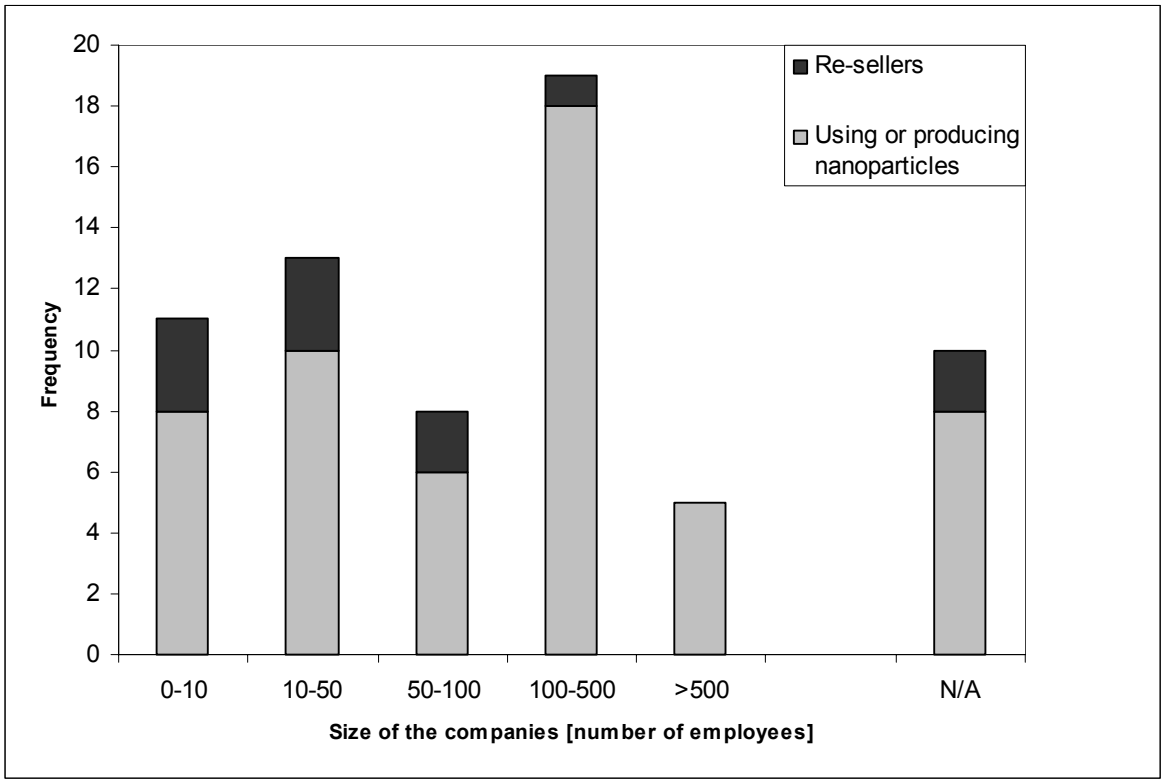

Figure 4: Distribution of the size of companies, which stated in the telephone interview to use nanoparticles. Re-sellers shown in the graph bought and sold products that had been treated abroad with nanoparticles.

Table 6 shows the quantities and applications of the seven most used nanoparticle types sorted by sector. The row "carbon black" is probably incomplete – most of the security managers did not realize that carbon black is also a nanoparticle because it is used since years. Carbon black can be used as pigment, in paintings, in plastics and even in electronics etc[7].

Table 6: Quantity of nanoparticles identified in the different sectors with different types of nanoparticles [estimated weight/year] and a short description of the application.

Sector	*SiO2*		*Fe-Ox*		*TiO2*		*Ag*		*ZnO2*		*AlO3/ AlO2*		*Carbon black*	
Milling	g-kg	tests	g-kg	tests	g-kg	tests	g-kg	tests	g-kg	tests	g-kg	tests		
Pharmaceutical products (medicaments)	t	dental composites, pigments, rheologic additives												
Powder-production	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	kt	glue
Surfaces, Coating	g-kg	ceramics, wood-surfaces					t	varnish						
Cleaning and Clearing substances					kg	stabilisator elutriation								
Food and Food-Wrapping	kg-t	fluxing agent separating agent, carrier												
Plastics			kt	un-defined	kg-kt	undefined								
Metal treatment			kt	un-defined										
Sensors, microelectronics											kg	fire-protection		
Textiles	kg-t	coating												
Cosmetics	t	coating of UV-protection particles			kt	UV-protection			kt	UV-pro-tection				
Paintings	g-t/a	varnish, hydrophoby					t	anti-micro-biotic coating						
Paper	kt	binder/ retention agent									kt	inkjet-paper (>100nm)		

[7] http://de.wikipedia.org/wiki/Industrieru%C3%9F

Table 7 shows the protection measures used. Most of the companies working with nano-powder use several types of protection measurers and many of those working with nano-liquids use only personal protective equipment. The protection types were: separation (the application of closed environments like closed machines or separated rooms); airflow (the use of a fume cupboard or a suction device); filter (the use of some air filtering system); personal protective equipment (the use of masks, gloves, eyeglasses etc.). Few other protection types were indicated. All companies that use powders had protection measures, most of them several (see Table 10 in the appendix for the strategies of individual companies). Only four companies with liquid-only applications provided respiratory personal protective equipment (not detailed in Table 7). Three companies with liquid or solid application types used no protection at all.

Table 7: Protection measures used for the different application types, identified by the targeted telephone interview.

Application type versed protection type	*Separation*	*Airflow*	*Filter*	*Personal protective equipment*	*Other protection*	*No protection*
Liquid	4	4	4	14	1	2
Liquid & powder	1	2	2	2	0	0
Powder	10	11	8	11	2	0
Solid	1	0	0	1	0	1
Else (e.g. metal coating)	1	0	0	0	0	0
Total	17	17	14	28	3	3

5.3 Sectors that may use nanoparticles but were NOT contacted in the pilot study

For several nanoparticle applications, no target companies were identified (e.g. no hospital was identified that routinely uses nanoparticles) or companies contacted gave the information that they would not have such applications.

Table 8: Possible sectors and applications that were not contacted during the telephone survey

Sector	*Possible Application*
Fire protection materials	Fire extinguishing agent, fire barriers
Pharmacy/medicine	Medical targeting, drug-delivery, magnetic particles, implants, Magnetic Resonance Imaging contrast agent
Electronics	Quantum construction elements, digital memory, background lights, electro conductive coatings[8]
Material science	Fullerenes/Carbon NanoTubes, integral parts of cars and engines, materials for light constructions, gasholder, membranes, high speed embossing processes
Laboratory tools	Chromatography, bio detection and labelling, bio magnetic separations, catalytic converters
Surface applications	Photo catalysts, anti graffiti, thermal spray coating

[8] One company stated, that particles are not yet used in production. Instead, airborne nanoparticles are considered as a source of quality problems.

5.4 Ranking of the interview-partners' concern about nanoparticle-exposure in their company

The interview-partners' concern about nanoparticle-exposure in their company was noted during the phone call. This subjective impression about the knowledge and the way the interview-partner answered the questions was the base for Figure 5.

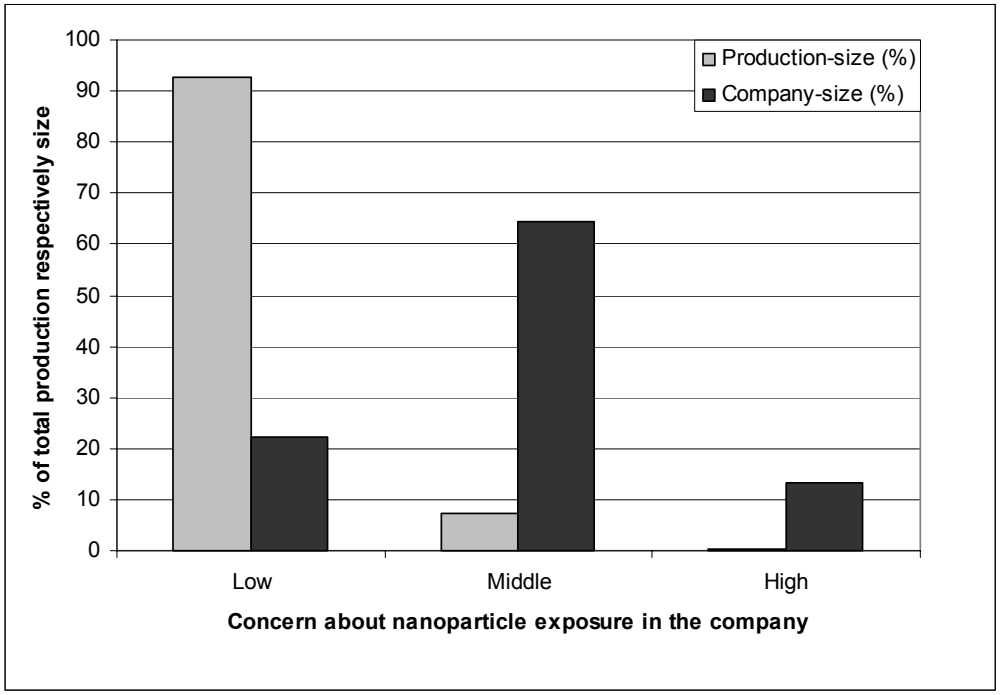

Figure 5: After each telephone call the interview-partners were rated regarding their concerns about nanoparticle exposure in their companies.

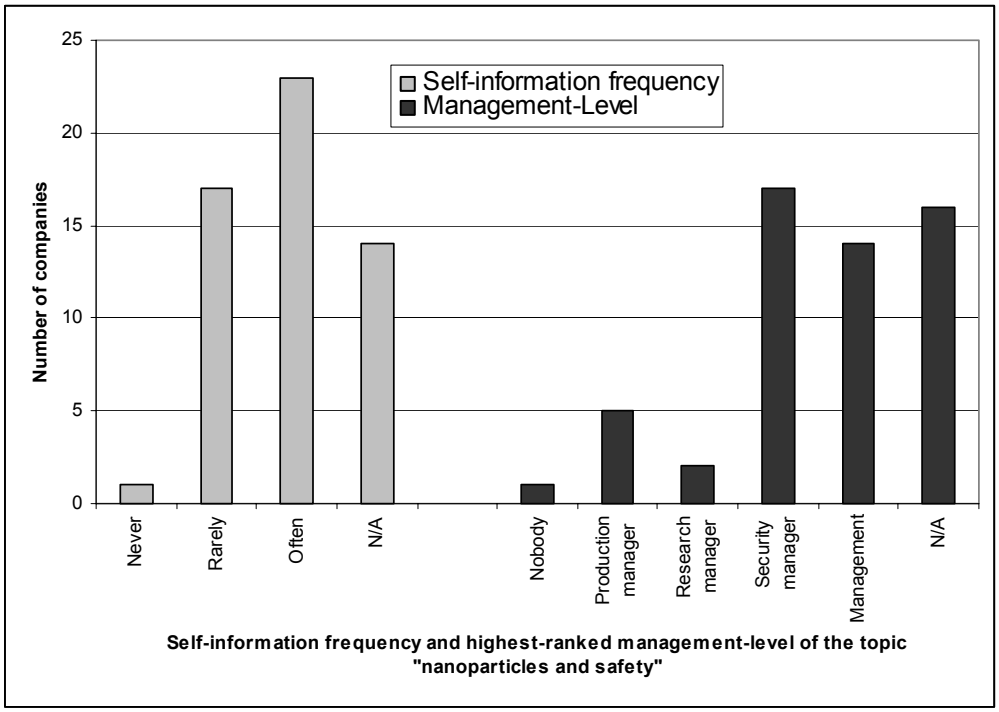

Figure 6: Self-information frequency of the respondents and level of the highest-ranked management that takes care of the topic "nanoparticles and safety".

6 Discussion

In this targeted survey, 55 of approximately 198 companies reported the presence of nanoparticles and 44 companies had applications or productions of nanoparticles. The quantities of nanoparticles used ranged from a few grams to very up-scaled productions with thousands of tons. The majority of nanoparticle applications were on a small production scale. An up-scaled production was found for Ag, AlO3, Fe-Ox, SiO2, TiO2 and ZnO2. Applications were identified in the fields coating, cosmetics, food / animal food / food packing, metal, optics, paintings, powder production, research and surface treatment. Most companies were middle-sized with 50-250 total employees. The protection means seemed to be adapted to the used type of application (liquid, powder, solid etc.). Most liquid application protections assumed that nanoparticles would not become airborne (no airways protection).

Almost all safety managers of all sectors answered our questions about nanoparticle applications and protection measures. Many of them gave detailed information. This pilot study gave a first impression about types and quantities of the nanoparticles used in the investigated Swiss industrial sectors. Additional information was obtained about who was using the nanoparticles (in terms of company-size), how they were using them (in terms of protection means) and what sort of application was used.

Most likely not all sectors and applications using or producing nanoparticles were identified. The results of the pilot study are not representative, only qualitative. In most cases the company management was not contacted to confirm the responses of the safety manager. Nevertheless the information about the occurrence of nanoparticles in the investigated sectors is interesting. It shows that nanoparticles are already a reality. It supports the need to establish a “nano-inventory”.

The pilot study evaluated the feasibility of a question-based survey and the types and quality of data that can be obtained about the use of nanoparticles in the Swiss industry. The results of the pilot study will help to design a representative survey with good power. It allows a layered survey that targets different sectors.
The quantitative results of the “nano-inventory” from the upcoming main-study will assist the identification of fields that seem important for occupational health protection, prevention and research. It may also be helpful to analyse environmental risks.

7 Literature

(1) Kommission Reinhaltung der Luft im VDI und DIN. Bewertung des aktuellen wissenschaftlichen Kenntnisstandes zur gesundheitlichen Wirkung von Partikeln in der Luft. report 2003.

(2) SCENIHR. scientific committee on emerging and newly identified health risks. report 2005.

(3) The Royal Society & The Royal Academy of Engineering. Nanoscience and Nanotechnologies. report 2004.

(4) EPA. Impacts of Manufactured Nanomaterials on Human Health and the Environment. report 2003.

(5) Hoet PH, Bruske-Hohlfeld I, Salata OV. Nanoparticles - known and unknown health risks. J Nanobiotechnology 2004; 2(1):12.

(6) Nel A, Xia T, Madler L, Li N. Toxic potential of materials at the nanolevel. Science 2006; 311(5761):622-627.

(7) Donaldson K, Stone V, Tran CL, Kreyling W, Borm PJ. Nanotoxicology. Occup Environ Med 2004; 61(9):727-728.

(8) Oberdorster G, Maynard A, Donaldson K et al. Principles for characterizing the potential human health effects from exposure to nanomaterials: elements of a screening strategy. Part Fibre Toxicol 2005; 2:8.

(9) NIOSH. Approaches to Safe Nanotechnology. NIOSH-Report 2005.

(10) Maynard AD, Baron PA, Foley M, Shvedova AA, Kisin ER, Castranova V. Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material. J Toxicol Environ Health A 2004; 67(1):87-107.

(11) Aitken RJ, Creely KS, Tran CL. Nanoparticles. report 2004.

(12) Colvin VL. The potential environmental impact of engineered nanomaterials. Nat Biotechnol 2003; 21(10):1166-1170.

8 Appendix

8.1 Guide for the pilot study telephone survey (German and English)

Telefonat:

Datum.....
Firma:.....**Grösse der Firma: #Angestellte:**.....
Person am Telefon:.....

1. Kommen im Unternehmen Nanopartikel zum Einsatz?

□ **Ja** weiter zu 2
□ **Nein** Frage nach, ob sie wirklich keine Einsetzen, Frage nach Carbon black, nach Metalloxiden, Pulver, etc. Frage nach Metallverarbeitung, Frage nach regelmässiger Metallverarbeitung (Schmelzen, Schweissen, Laserschneiden etc.), wenn alles nichts, dann vielen Dank ;)

Branchenübliche Stoffe gezielt nachfragen?.....
.....
.....
.....
.....
.....
.....
.....

2. Mich interessiert auch welche Arten von Nanopartikeln zum Einsatz kommen? Es geht nur um eine grundsätzliche Evaluation, keine Firmengeheimnisse...

a, Substanz: carbon black, SiO_2, AlO_2, TiO_2, Pharmakologische Dinge, andere?
.....
.....
b, Form: □ Pulver, □ Flüssig, □ sonstwie
c, Menge etwa: .....(g, kg, t /d)
d, Dauer pot exp.: .....(nur 1x/d, ständig), (regelmässig, ab und zu)
e, **Anwendungszweck** / Einsatz: .....

Kommentare:
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....
.....

3a. In welcher Art kommen die Arbeiter mit Nanopartikel in Kontakt?

a, Art der **Anlieferung** □ Pulverfass, □ Flüssigtank, □ Feststoff, □ Sack etc...
b, Art der Verarbeitung Gibt es **Umschüttung**? □ Ja □ Nein
c, Art Beteiligte: Anlieferung/Verarbeitung/Reinigung(ext/int)/Verpackung
.....
d, **Zahl** Beteiligte: Wie viele sind überhaupt während Prozess in der Nähe?
.....

3b. Gibt es Schutzvorkehrungen?

Pulver Welches sind die Typen der Luft-Schutzvorkehrungen?
□ Trennung, Organisation etc.....
□ Druck, Luftzug, Kapelle etc.....
□ Filter, Reinluftfilter etc.. .....
□ PSA (pers. Schutzausrüstung, welcher Art? .....
.....

Filter wohin gehen die Partikel, wenn ein Filter verwendet wird? Wer wechselt oder unterhält die Filter?
□ Firmeninterner Wechsel
□ Externe Firma (ev. Namen?).....
□ Gar kein Filter? Nur Abluft? Wohin geht die?.....

4. Jede Firma hat ihre eigene Sicherheitspolitik... sind hier Nanopartikel ein Thema?

□ **Ja**: Wie häufig beschäftigt sich der Sicherheitsverantwortliche mit Nanopartikel?.....
□ **Ja**: Arbeiter wird regelmässig informiert: etwa.....

□ **jein**: Ab und zu mal wieder Infoblatt oder ähnliches
□ **Nein**: Niemand beschäftigt sich damit

Etage: Welches ist der höchste Chef, der sich je mit Sicherheitsfragen um Nanopartikel kümmert?.....

5. Gibt es einen Arbeitsmediziner oder Arbeithygieniker in Ihrer Firma?

□ **Ja** / □ **Nein** Arbeitsmediziner □ **Ja** / □ **Nein** Arbeitshygieniker

6. Dürfen wir sie nochmals kontaktieren, um ev. Probemessungen machen zu können?

□ **Ja**: Kontaktadresse?
□ **Nein**: Vielen Dank für die Auskünfte!

Kommentare:.....
.....
.....
.....
.....
.....
.....

Survey: Application of nanoparticles

Date
Institute: **Size of the institute (#employees):**
Person responding:

1. Do you use nanoparticles in your institute? For example inorganic: SiO_2, TiO_2 or organic pigments like carbon black etc. or new materials?

☐ **yes** please continue with question 2
☐ **no** thank you for sending back this questionnaire

2. What sort of nanoparticles do is used?

a, substance: Carbon black, SiO_2, AlO_2, TiO_2, pharmaceutical, else? ☐
b, form: ☐ powder, ☐ liquid, ☐ else (solgel, solid, etc.)
c, quantity (aprox.): ☐ mg, ☐ g, ☐ kg, ☐ t /per day
d, period: ☐ 1x/day, ☐ continuous, ☐ once in a while
e, purpose of application: ☐

3a. What kind of contact do employees have with nanoparticles?

a, form at delivery ☐ powder tun, ☐ liquid tank, ☐ solid, ☐ sack/bag
b, manner of handling is there any pouring? ☐ yes ☐ no
c, concerned persons: ☐ delivery, ☐ handling, ☐ clearance, ☐ packing
else: ☐
d, number of concerned persons: How many people are present during normal operating process? ☐

3b. Are there any protection measures?

Filter Is there some sort of filter used? And how?
☐ Replacement of filters is performed by staff
☐ Replacement of filters is outsourced. Name of company? ☐
☐ No filter is used. If there is an extractor hood (air flow) where does the air go? ☐

Powder What kind of air-protection measurements are used?
☐ organisation, separation etc..
☐ pressure, air draught, fume cupboard etc.
☐ filter, etc.
(personal protective equipment)
☐ mask, ☐ gloves, ☐ safety glasses, else: ☐?

Liquids What kind of protective equipment is used?
(personal protective equipment)
☐ mask, ☐ gloves, ☐ safety glasses, else: ☐?

Institut universitaire romand de Santé au Travail

4. safety policy... is the problem of nanoparticles discussed?

How often does the safety officer (person in charge of safety) treat the problem of nanoparticles? ☐

☐ **routine information**: employees are informed in a regularly manner.
how often? ☐ per year
☐ **rare information**: employees are informed exceptionally
☐ **no information**: only the safety officer is involved in questions about security of nanoparticles

level: Who is the highest superior who is involved in questions about safety of nanoparticles? ☐

5. Is there an occupational doctor or occupational hygienist at the institute or at the university?

☐ **yes** / ☐ **no** occupational doctor
☐ **yes** / ☐ **no** occupational hygienist

commentaries: ☐

thank you for sending back this survey

8.2 Types of application identified in literature

Table 9: All types of application that were identified in the literature search. VDI = Technologiezentrum, Düsseldorf - Germany[9], Uni Ulm = University of Ulm[10] - Germany, INM = Institut für neue Materialien of Saarbrücken – Germany[11].

Applications	*Source*	*Expected sector*	*Identified in pilot study*
Batteries / fuel cells / condensers	Uni Ulm	Else	No
Composites and „Gradientenwerkstoffe“	Uni Ulm	Else	No
Supramolecular units	Uni Ulm	Else	No
Automotive manufacturers and their subcontractors, ceramic components of motors	Uni Ulm	Else	No
Materials lightweight construction	Uni Ulm	Else	No
Gasholder	Uni Ulm	Else	No
Absorbability elements	Uni Ulm	Else	No
Catalysers with heightened surface	Uni Ulm	Else	No
High-speed embossing (flexible CD for Bertelsmann/Topac), Holography, light steering	INM	Else	No
New biotechnological and biomedical applications (affinity chromatography, immobilisation of enzymes and cells), waste water treatment, decontamination of harmful substances.	INM	Else	No
Optical fibres	VDI	Else	No
Bio detection and labelling	VDI	Else	No
Bio magnetic separations	VDI	Else	No
Thermals spray coatings	VDI	Else	No
Automotive catalyst	VDI	Else	No
Membranes	VDI	Else	No
Propellants	VDI	Else (Army?)	No
Systems of compact nano materials (membranes, strengthened plastics, light absorber, aero gels, light emitter)	Uni Ulm	Else, plastics	No
Antimicrobials	VDI	Food/ -packing	No
MRI contrast agents	VDI	Medicine	No
Polymer composites or organical-anorganical nano composites as plastics for contrasting implants, catheter etc. Nanoparticles as carrier for gene or drug targeting, super paramagnetic nanoparticles for cancer therapy.	INM	Medicine, Surface coating	No
Orthopaedics/implants	VDI	Medicine/Surface coating	No
Extra hard alloys	Uni Ulm	Metal treatment	No
Photovoltaic solar power plant	Uni Ulm	Microelectronics	No
Quantum components	Uni Ulm	Microelectronics	No
Metal pigments for data drives	Uni Ulm	Microelectronics	No
Background lights	Uni Ulm	Microelectronics	No
Magnetic fluid seals and recording media	VDI	Microelectronics	No
Quantum optical devices	VDI	Microelectronics	No
Photo catalysts	VDI	Microelectronics	No
Solar cells	VDI	Microelectronics	No
Rotary movements	Uni Ulm	N/A	No
Pastes	Uni Ulm	N/A	No
Resistes	Uni Ulm	N/A	No
Inductive components	Uni Ulm	N/A	No
Packaging of integrated circuits	Uni Ulm	N/A	No
Zeolithe reaktors	Uni Ulm	N/A	No
Molecular chemionics	Uni Ulm	N/A	No
Multi layer capacitors	VDI	N/A	No
Phosphors	VDI	N/A	No
Components for non linear optics	Uni Ulm	Optics	No
Hybrid pigments, effects pigments	Uni Ulm	Paintings	No
Drug targeting (homing of pharmaceuticals)	Uni Ulm, VDI	Pharma	No
Key-target – material systems	Uni Ulm	Pharma	No
Nanoemulsions	Uni Ulm	Pharma/Cosmetics	No
Crystallites, emulsions, clusters, fullerenes, nanotubes	Uni Ulm	Powder production	No
Soft magnets, ferrofluids, magnetic particles	Uni Ulm	Powder production	No
Polymers / nano composites, micro system techniques (micro injection die moulding), sensors, membranes	INM	Sensors	No
Nano composites with biocompatible surfaces, microbiocidic surfaces	INM	Surface coating	No
Alternative for enamel, super scratch-resistant polycarbonate eyeglasses with additional functions (UV-, IR-absorption, microbiocidic effects, antistatic effects), self structuring systems for transparent blinds on all plastics and metals.	INM	Surface coating	No
Antigraffiti	INM	Surface coating	No
Electro conductive coatings	VDI	Surface coating	No
Sunscreen	VDI	Cosmetics	Yes

[9] http://www.zukuenftigetechnologien.de/11.pdf, last access: 24.05.06
[10] http://wwwex.physik.uni-ulm.de/vortraege/StudiumGenerale/Nanot_20.htm, last access: 24.05.06
[11] http://www.inm-gmbh.de/htdocs/technologien/schwerpunkte/schwerpunkte_de.htm, last access: 28.02.06

Ceramic process techniques	Uni Ulm	Else	Yes
Chemical-mechanical polishing	VDI	Else	Yes
Production of food (milk, juices, brewery)	INM	Food	Yes
Lubricants	Uni Ulm	Optics	Yes
Colour effects and colour layers	Uni Ulm	Paintings	Yes
Chemistry / material science, nanoparticle production (colloids, pigments, dispersions, powders)	Uni Ulm	Powder production	Yes
Research in active agent (pharmacology)	Uni Ulm	Research	Yes
Fine mechanics, optics, analytics: low abrasion bearing	Uni Ulm	Surface coating	Yes
Corrosion inhibitors	Uni Ulm	Surface coating	Yes
Functional layers (anti undercoating, climatisation coating, antifilm coating)	Uni Ulm	Surface coating	Yes
Scratch-resistant lacquers as topcoat (automotives etc.)	INM	Surface coating	Yes
Scratch-resistant coatings	VDI	Surface coating	Yes
Fuel cells	VDI	Else	Yes (Empa?)
Structural ceramics	VDI	Else	Yes (Empa?)

8.3 Syndicate with member addresses on their web page

Industry sector	*Syndicate's homepage*
Printing production	www.druckindustrie.ch
Paint production	www.vslf.ch
Cosmetics production	www.skw-cds.ch
Varnish production	www.flh.ch
Paper production	www.zpk.ch
Chemical production	www.sgci.ch
Plastic production	www.kvs.ch
Cleaning agent production	www.skw-cds.ch
Animal feed production	www.vsf-mills.ch
Food science[12]	www.sglwt.ch
Microelectronic production	www.swico.ch
Sensors	www.sensors.ch
Clock production	www.fhs.ch
Construction materials	www.vsbh.ch

[12] A questionnaire was sent to over 200 members of this syndicate. The return was very little with less than 4% responses.

8.4 Types of protection measures for the different applications

Table 10: Types of protection measures used in the individual companies for the different application types (liquid, powder, solid, else). The compared types of applications are liquid; powder; both (powder an liquid), solid (matrix like); else like coating by sputtering in vacuum etc. The protection types are separation (the application of closed environments like closed machines or separated rooms); airflow (the use of a fume cupboard or a suction device); filter (the use of some air filtering system) and personal protective equipment (the use of masks, gloves, eyeglasses etc.). Some other forms protection types were identified. The re-selling companies mostly did not provide the information about their protection measures (marked as N/A), four of the interviewed companies could not tell what type of application they use with their nanoparticles.

Company no.	*Application type*	*Separation*	*Airflow*	*Filter*	*Personal protection*	*Other protection*	*No protection*
1	Liquid 1				1		
2	Liquid 2	N/A	N/A	N/A	N/A	N/A	N/A
3	Liquid 3				1		
4	Liquid 4				1		
5	Liquid 5	N/A	N/A	N/A	N/A	N/A	N/A
6	Liquid 6						1
7	Liquid 7	N/A	N/A	N/A	N/A	N/A	N/A
8	Liquid 8	1	1	1	1		
9	Liquid 9		1	1	1		
10	Liquid 10				1		
11	Liquid 11	1	1	1	1		
12	Liquid 12	1	1	1	1		
13	Liquid 13				1		
14	Liquid 14						1
15	Liquid 15				1		
16	Liquid 16	N/A	N/A	N/A	N/A	N/A	N/A
17	Liquid 17				1		
18	Liquid 18	1					
19	Liquid 19	N/A	N/A	N/A	N/A	N/A	N/A
20	Liquid 20	N/A	N/A	N/A	N/A	N/A	N/A
21	Liquid 21				1		
22	Liquid 22					1	
23	Liquid 23				1		
24	Liquid 24	N/A	N/A	N/A	N/A	N/A	N/A
25	Liquid 25	N/A	N/A	N/A	N/A	N/A	N/A
26	Liquid 26	N/A	N/A	N/A	N/A	N/A	N/A
27	Liquid 27				1		
Subtotal “Liquid”		4	4	4	14	1	2
28	Liquid & Powder 1	1	1	1	1		
29	Liquid & Powder 2	1	1	1			
Subtotal "Liq. & Pow."		1	2	2	2	0	0
30	Powder 1	1	1	1	1	1	
31	Powder 2	N/A	N/A	N/A	N/A	N/A	N/A
32	Powder 3		1	1	1		
33	Powder 4				1		
34	Powder 5	1					
35	Powder 6	1	1	1	1		
36	Powder 7		1	1	1		
37	Powder 8	N/A	N/A	N/A	N/A	N/A	N/A
38	Powder 9	1	1	1	1	1	
39	Powder 10		1		1		
40	Powder 11	1	1	1	1		
41	Powder 12	1	1	1	1		
42	Powder 13	1	1		1		
43	Powder 14	1					
44	Powder 15	1					
45	Powder 16	1	1	1	1		
46	Powder 17		1				
Subtotal "Powder"		10	11	8	11	2	0
47	Solid 1	1			1		
48	Solid 2						1
Subtotal "Solid"		1	0	0	1	0	1

Company no.	*Application type*	*Separation*	*Airflow*	*Filter*	*Personal protection*	*Other protection*	*No protection*
49	Else 1	1					
50	Else 2	N/A	N/A	N/A	N/A	N/A	N/A
51	Else 3	N/A	N/A	N/A	N/A	N/A	N/A
Subtotal "Else"		1	0	0	0	0	0
52	N/A	N/A	N/A	N/A	N/A	N/A	N/A
53	N/A	N/A	N/A	N/A	N/A	N/A	N/A
54	N/A	N/A	N/A	N/A	N/A	N/A	N/A
55	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Grand Total		17	17	14	28	3	3

8.5 Company size distribution

Table 11: Distribution of the size of companies that stated in the telephone interview to use nanoparticles.

Numbers of employees in the companies	*Classes*
1, 1, 3, 6, 6, 6	<10 employees (small)
10, 25, 25, 30, 35, 35	<50 employees (middle)
50, 60, 85, 85, 100, 115, 115, 130, 150, 150, 180, 180, 230	<250 employees (big)
350	<500 employees (very big)
750, 800, 1500, 1700	>500 employees (biggest)

8.6 Distribution of the quantities of used nanoparticles

Table 12: Quantities distribution of used nanoparticles per year in the Swiss industry identified by the targeted telephone interview. The mean of the used nanoparticles is 41700 kg, the median 100 kg.

Kilograms of nanoparticles used per year in the interviewed companies	*Classes*
1, 1, 1, 1, 1, 1, 5, 10, 25	<100 kg
100, 100, 100, 300, 365, 500, 500	100-1000 kg
1000, 1000, 1000, 1000, 2000, 2000	1000-5000 kg
70’000, 100’000	5000-25'000 kg
365’000	25’000-100'000 kg
1’000’000	1'000'000 kg and more