

Nanotechnology in the Danish Industry

– Survey on production and application

Cand.arch. Kathe Tønning and MSc, PhD Mikael Poulsen
Danish Technological Institute

Environmental Project No. 1206 2007
Miljøprojekt

The Danish Environmental Protection Agency will, when opportunity offers, publish reports and contributions relating to environmental research and development projects financed via the Danish EPA.

Please note that publication does not signify that the contents of the reports necessarily reflect the views of the Danish EPA.

The reports are, however, published because the Danish EPA finds that the studies represent a valuable contribution to the debate on environmental policy in Denmark.

Content

PREFACE	7
SUMMARY AND CONCLUSIONS	9
NANOMATERIALS	9
LEGISLATIVE OVERVIEW	9
QUESTIONNAIRE AND INTERVIEWS	9
CONCLUSIONS	11
RESUME IN DANISH (DANSK RESUMÉ)	13
SPØRGESKEMAUNDERSØGELSE	13
INTERVIEWS	14
RESULTATER	14
KONKLUSIONER	15
1 NANOMATERIALS	17
1.1 BACKGROUND	17
1.2 REFERENCES	17
1.3 DEFINITIONS	18
1.4 HEALTH EFFECTS	19
1.4.1 <i>Inhalable nanomaterials</i>	19
1.4.2 <i>Skin penetration of nanomaterials</i>	20
1.4.3 <i>Ingestion of nanomaterials</i>	21
1.5 ENVIRONMENTAL EFFECTS	21
1.5.1 <i>Airborne nanomaterials</i>	21
1.5.2 <i>Suspended nanomaterials</i>	21
1.6 HANDLING OF NANOMATERIALS	22
1.7 SUMMARY	22
2 LEGISLATIVE OVERVIEW	23
2.1 ENVIRONMENT	23
2.2 WORKING ENVIRONMENT	24
2.2.1 <i>The Danish Working Environment Act</i>	24
2.2.2 <i>Specific legislative areas</i>	24
3 QUESTIONNAIRE	26
3.1 SCOPE	26
3.2 STRUCTURE OF THE QUESTIONNAIRE	26
3.3 RECIPIENTS OF THE QUESTIONNAIRE	26
3.4 EXECUTION OF THE QUESTIONNAIRE	27
3.5 NUMBER OF RESPONSES	27
3.6 RESULTS	28
4 INTERVIEWS WITH NANOTECHNOLOGICAL COMPANIES	30
4.1 DANISH TECHNOLOGICAL INSTITUTE	31
4.1.1 <i>Tribology Centre</i>	31
4.1.2 <i>Sol-gel group at Centre for Materials Testing</i>	32
4.1.3 <i>Centre for Plastics Technology</i>	33
4.1.4 <i>Centre for Microtechnology and Surface Analysis</i>	34
4.1.5 <i>Centre for Chemistry and Water Technology</i>	34

4.2	DYRUP A/S	34
4.2.1	<i>Company description</i>	34
4.2.2	<i>Customers</i>	34
4.2.3	<i>Nanomaterials</i>	34
4.2.4	<i>Handling of nanomaterials</i>	35
4.2.5	<i>Product life cycle</i>	36
4.2.6	<i>Possibilities of nanomaterial exposure</i>	36
4.2.7	<i>View on guidelines and regulation</i>	37
4.3	HALDOR TOPSØE A/S	37
4.3.1	<i>Company description</i>	37
4.3.2	<i>Customers</i>	37
4.3.3	<i>Nanomaterials</i>	37
4.3.4	<i>Handling of nanomaterials</i>	37
4.3.5	<i>View on guidelines and regulations</i>	38
4.4	AALBORG PORTLAND A/S	38
4.4.1	<i>Company description</i>	38
4.4.2	<i>Customers</i>	39
4.4.3	<i>Nanomaterials</i>	39
4.4.4	<i>Handling of nanomaterials</i>	39
4.4.5	<i>Possibilities for nanomaterial exposure</i>	39
4.4.6	<i>View on guidelines and regulation</i>	40
4.5	COMPANY A	40
4.5.1	<i>Company description</i>	40
4.5.2	<i>Customers</i>	40
4.5.3	<i>Nanomaterials</i>	40
4.5.4	<i>Handling of nanomaterials</i>	40
4.5.5	<i>Product life cycle</i>	41
4.5.6	<i>Possibilities of nanomaterial exposure</i>	41
4.5.7	<i>View on guidelines and regulation</i>	42
4.6	PERSANO GROUP A/S	42
4.6.1	<i>Company description</i>	42
4.6.2	<i>Customers</i>	42
4.6.3	<i>Nanomaterials</i>	42
4.6.4	<i>Handling of nanomaterials</i>	42
4.6.5	<i>Product life cycle</i>	43
4.6.6	<i>Possibilities of nanomaterial exposure</i>	43
4.6.7	<i>Toxicology</i>	43
4.6.8	<i>View on guidelines and regulation</i>	44
4.7	UNISENSE	44
4.7.1	<i>Company description</i>	44
4.7.2	<i>Customers</i>	44
4.7.3	<i>Nanomaterials</i>	44
4.7.4	<i>Handling of nanomaterials</i>	45
4.7.5	<i>Possibilities of nanomaterial exposure</i>	45
4.7.6	<i>View on guidelines and regulation</i>	45
5	RESULTS	46
5.1	NANOTECHNOLOGICAL COMPANIES	46
5.1.1	<i>Size of companies</i>	46
5.1.2	<i>Activities</i>	46
5.2	NANOTECHNOLOGICAL MATERIALS	48
5.2.1	<i>Nanoparticles</i>	48
5.2.2	<i>Other types of nanomaterials</i>	49
5.3	HANDLING OF NANOMATERIALS	50
5.3.1	<i>Instructions for use</i>	50
5.3.2	<i>Employee uncertainty</i>	50

5.3.3	<i>Knowledge level</i>	50
5.3.4	<i>Processes</i>	51
5.3.5	<i>Safety measures</i>	51
5.3.6	<i>Exposure measurements</i>	52
5.3.7	<i>Waste handling</i>	52
5.3.8	<i>Possibilities of release of nanomaterials to the surrounding environment</i>	53
5.4	NANOTECHNOLOGICAL PRODUCTS	54
5.4.1	<i>Content of nanomaterials</i>	54
5.4.2	<i>Information to customers</i>	54
5.4.3	<i>Certification</i>	54
5.4.4	<i>Possibilities for user exposure</i>	54
5.4.5	<i>Possibilities for nanomaterial release during or at the end of product lifetime</i>	55
5.4.6	<i>Consumer health risk in relation to nanomaterials and nanotechnological products</i>	55
5.4.7	<i>Environmental effects of nanomaterials and nanotechnological products</i>	55
5.5	OPINIONS ON GUIDELINES AND REGULATION	55
5.5.1	<i>Definition of nanotechnology – distinguishing between different types of nanomaterials</i>	55
5.5.2	<i>Nanomaterials and the current legislation</i>	56
5.5.3	<i>Access to information</i>	56
6	BIBLIOGRAPHY	58
6.1	COMPREHENSIVE REPORTS ON THE INDUSTRIAL APPLICATIONS AND POSSIBLE RISKS OF NANOTECHNOLOGIES	58
6.2	REPORTS ON RISK ASSESSMENT OF NANOMATERIALS	58
6.3	RECOMMENDATIONS FOR GOVERNMENT	58
6.4	SAFE AND GOOD PRACTICES IN THE NANOTECHNOLOGY WORKPLACE	59
6.5	INTERNAL GUIDELINES FOR NANOTECHNOLOGY WORKPLACES	59
6.6	SURVEYS ON INDUSTRIAL ACTIVITIES ON NANOMATERIALS	59
6.7	OTHER REFERENCES	59

Annex A Questionnaire

Preface

Due to the massive national and international focus on nanotechnology, the industrial application of nanoparticles and other nanomaterials is expected to increase significantly in the years to come.

Although nanoparticles have been used in certain industrial processes for quite many years, it is foreseen that the use of nanomaterials in many new contexts may result in uncertainties with regard to handling during production, use and disposal of such materials.

This project seeks to make a survey of the nanomaterials being applied and produced within Danish industry, how these materials are handled in processes and how the waste from these processes and products is disposed.

The project includes a short resume on international reports on environmental and occupational exposure and health aspects of nanotechnology.

In the survey companies who have shown interest in nanotechnology were contacted. The work is based on the experiences made by the four partners involved in the project and on information received through questionnaires sent to companies expressing an interest in nanotechnology and additional interviews with selected companies with nanotechnological production.

The purpose was to identify and characterise the companies that are producing and/or using nanotechnological materials. Further, information was gathered about their experiences with products, application and disposal of nanomaterials and their source of information concerning health and environmental effects. In this context the companies have been asked to state any uncertainties or wishes to a potential official regulation or guideline within the area.

The project was carried out by Danish Technological Institute by cand.arch. Kathe Tønning and MSc, PhD Mikael Poulsen.

The project was followed by a steering committee with the following members:

Dorte Lerche	Danish Environmental Protection Agency (Chairman of the steering committee)
Poul Bo Larsen	Danish Environmental Protection Agency
Flemming Ingerslev	Danish Environmental Protection Agency
Keld Alstrup Jensen	National Research Centre for the Working Environment
Steen Piil	Danish Working Environment Authority
Poul Andersen	Danish Working Environment Authority
Ebrahim Moradjow-Namin	Danish Working Environment Authority

The project has been implemented in the period December 2006 to November 2007 and is financed by the Danish Environmental Protection Agency

Summary and conclusions

Nanomaterials

Based on the approach of international reports on the environmental and working environmental aspects of nanotechnology, nanomaterials were divided in six material types: nanoparticles, nanofibres (nanotubes), nanoflakes, nanostructured surfaces, nanofilm (nanolayers) and nanoporous structures.

Nanoparticles, nanofibres or nanoflakes may pose a possibility for exposure within the working environment, especially exposure to the materials in the form of powders appear to pose a greater challenge. Liquid suspensions of these nanomaterials may also pose a risk of exposure to nanomaterials. However, this exposure appears to be more easily controlled and thus often associated with lower risk. The environmental risks of nanomaterials are largely unknown.

Nanostructured surfaces, nanofilm (nanolayers) and nanoporous structures do not present immediate chance for exposure. However, if nanoparticles, nanofibre or nanoflakes are used in the production, produced as a byproduct or released during wear, use or destruction, these materials also present nano-related concerns. Thus, in this study the main focus is on nanoparticles, nanofibres or nanoflake.

Legislative overview

Although nanomaterials are not specifically mentioned in the legislation regarding protection of the environment and regulation of chemicals, nanomaterials are covered by the existing legislation. However, it is still not clear if some technical adjustments may be needed.

Overall, the general provisions in the Working Environment Act cover nanomaterials. If specific safety and health problems are identified at a workplace, the existing legislation requires that specific demands are made to the handling of the material, e.g. work with carcinogenic materials is subjected to special legal requirements such as preliminary approvals of working with the materials and demands for special training of the workers. As it is today suppliers of nanomaterials are to submit a materials safety data sheet with information about any hazardous effects so that the employers can take measures accordingly.

Questionnaire and interviews

A questionnaire covering various aspects regarding production and use of nanomaterials was sent to 165 Danish companies, which in different contexts had expressed an interest in nanotechnology. 75 responses were received. Of the 75 responses, 24 companies worked with nanomaterials.

Of the 24 companies working with nanomaterials, 16 companies worked with nanoparticles, nanofibres or nanoflakes. The majority of these 16 companies were interviewed, either directly or by telephone. The following conclusions of the survey are based both on the received questionnaires and the interviews.

1) Danish nanotechnological companies

- a) The companies responding that they work with nanomaterials are broadly distributed in size and work within nine different industrial areas: Paints & inks, coatings, cosmetics, pharma & biotech, optics, sensors, catalysts, concrete and textile
- b) More than half of the companies working with nanoparticles, nanofibres and nanoflakes work on R&D level or very small scale (<1 kg per year). Companies working with nanomaterials on larger scale (>100 kg per year) work with nanoparticles within the paint & ink, concrete, textile or cosmetics industries.
- c) Nanomaterials are most often used in products, in which they are suspended in liquid or embedded in a solid matrix. The endproducts are rarely nanomaterials themselves.

2) Nanomaterials

- a) The nanomaterials which are used in large scale (>100 kg per year) in the Danish industry are metal oxide, polymer, silica and carbon black nanoparticles.
- b) Nanoparticles are for large scale use obtained from foreign suppliers in powder or suspended form.

3) Handling of nanomaterials

- a) The handling of nanomaterials depends on the material. In general nanomaterials are handled according to the same procedures as other chemicals or fine powders. Companies handling nanoparticulate powders are aware of precautions needed for handling fine powders.
- b) The companies' knowledge on physical characteristics of their nanomaterials mainly stem from their supplier (four companies occasionally measure particle size, no companies measure specific surface area).
- c) With one exception the companies' knowledge on toxicology and ecotoxicology of their nanomaterials only stem from data given by the supplier
- d) Only one company has reported to have knowledge of or an impression that employees are uncertain or insecure about the handling of nanomaterials.
- e) Measurements or other estimations of exposure levels of airborne nanomaterials in the working environment are rare.
- f) The handling of nanomaterial waste varies. The majority of companies dispose nanomaterials as regular waste or in waste water when they consider the nanomaterial harmless or embedded in macroscopic structures.
- g) No companies perceived any environmental risks due to nanomaterials in their regular waste or waste water, since according to their knowledge current legislation was complied.

4) Products containing nanomaterials

- a) With the exception of textiles, all products (made in Denmark) on the market containing nanomaterials have a content of nanomaterials above 0.1%
 - b) None of the companies 'nano' branded their products or took part in nano-certification systems.
 - c) No companies perceived any risks to users of their products related to nanomaterial content, since according to their knowledge current legislation was complied.
 - d) Most often customers (consumers and industrial) were not informed about nanomaterial content in products.
 - e) No companies perceived environmental risks due to nanomaterials in their products, since according to their knowledge current legislation was complied.
 - f) The extent to which nanomaterials can be released during use, wear or destruction of products containing nanomaterials is unknown.
- 5) View on official guidelines or regulation on nanomaterials
- a) The majority of companies perceived no need for new specific legislation regarding nanomaterials. Companies preferred regulation of nanomaterials to be carried out in the existing regulatory framework on chemicals rather than as a separate issue.
 - b) A very prominent view among the companies regarding regulation of nanomaterials was the need to distinguish between different types and forms of nanomaterials.
 - c) Several companies expressed the opinion that the Material Safety Data Sheet (MSDS) should include 'nano-specific' information such as particle size, surface area etc.
 - d) Some companies expressed an interest in an easier access to knowledge on nanomaterial hazards and how to handle nanomaterials.

Conclusions

The knowledge of the effects of nanomaterials on health and environment is increasing but still limited. Therefore little is known about the possible exposure and effects to workers, consumers and the environment due to use, wear and disposal of nanotechnological products.

There is a strong focus on nanotechnology in both research and industry. However, the interest in new technologies has for many companies not yet manifested in use or production of nanomaterials even on R&D scale. Large scale use of nanomaterials is still restricted to industries, which have used these materials for decades, such as paint and concrete industries.

Regulatory efforts on nanomaterials thus face two different scenarios: Small scale use of nanomaterials in new contexts and large scale use of nanomaterials in traditional industries.

When nanomaterials are used on small scale or for R&D purpose, the companies apply the same precautions that are applied within the synthesis of other new chemicals with unknown properties. In this case the materials are handled in fume cupboards and nanomaterial waste is handled as hazardous waste.

Nanomaterials used in large scale in traditional industries are handled according to the information provided on the safety data sheets, which often

imply; in the same way the companies handle other chemicals, without special focus on nano-related risks except for a pronounced focus on the precautions needed for handling fine powders. Current products resulting from large scale production including nanomaterials are products, which have been on the market for many years. Since the products have been on the market for years without apparent nano-related effects, the producers do not perceive any nano-related risks to users or the environment. Assessments of exposure to nanomaterials in the working environment, from nanomaterial containing products or unintentionally produced nanomaterials are rare.

Furthermore, the companies would like regulation to address the diversity of types and forms of nanomaterials (particles, fibres, tubes, flakes etc.). The industry prefers the regulation of nanomaterials to be carried out in the existing regulatory framework rather than as a separate issue.

Resume in Danish (Dansk resumé)

Som følge af den massive nationale og internationale satsning på nanoteknologi forventes den industrielle anvendelse af nanopartikler og andre nanomaterialer at forøges markant de kommende år. Selvom nanopartikler har været anvendt i visse industrielle processer i mange år, må det forventes, at anvendelsen af nanomaterialer i mange nye sammenhænge kan give anledning til en del usikkerhed omkring håndtering og bortskaffelse af disse materialer. På den baggrund blev nærværende projekt igangsat for at kortlægge hvilke nanomaterialer, der anvendes og produceres i Danmark, hvordan de håndteres i processer, og hvordan affaldsprodukter bortskaffes.

Kortlægningen er blevet gennemført dels gennem en spørgeskemaundersøgelse og dels gennem dyberegående interviews med udvalgte virksomheder med nanoteknologisk produktion.

Spørgeskemaundersøgelse

Som basis for udarbejdelsen af spørgeskemaerne og som grundlag for interviewene blev en række internationale rapporter [ref. 1-16] om nanomaterialer og håndteringen af disse studeret. På baggrund af de internationale rapporter blev nanomaterialer i dette projekt inddelt i seks kategorier: Nanopartikler, nanofibre (eller -rør), nanoflager, nanofilm, nanostrukturerede overflader og nanoporøse strukturer. Af disse kategorier er det de første tre, hvor der er den største mulighed for eksponering. De sidste tre materialekategorier forventes ikke at give anledning til eksponering i samme grad, medmindre nanopartikler, nanofibre eller nanoflager anvendes i fremstillingen, produceres som biprodukt eller afgives under brug, slid eller destruktion. Derfor fokuserer denne undersøgelse på de første tre typer af nanomaterialer.

Der blev rettet henvendelse til 165 virksomheder, som i forskellige sammenhænge har tilkendegivet en interesse for nanoteknologi. Disse virksomheder fik tilsendt to spørgeskemaer: Et generelt skema om emnet og et specifikt skema, som skulle udfyldes for hvert nanomateriale (nanopartikler, nanofibre eller nanoflager) som virksomheden arbejdede med. Fokus i undersøgelsen var hovedsagligt virksomheder, der arbejder med nanopartikler, nanofibre (eller -rør) eller nanoflager. Virksomheder, der kun arbejder med nanofilm, nanostrukturerede overflader og nanoporøse strukturer, blev spurgt hvorvidt nanopartikler eller nanofibre indgår i fremstillingsprocesser eller opstår som biprodukt.

75 virksomheder besvarede spørgeskemaundersøgelsen. Af disse anvendte de 51 slet ikke nanomaterialer. Ud af de 24 virksomheder, der arbejdede med nanomaterialer, var der 16, som anvender nanopartikler, nanofibre eller nanoflager.

Interviews

Fra projektets start var der truffet aftale med tre partnervirksomheder (Dyrup A/S, Haldor Topsøe A/S og Aalborg Portland A/S) om deltagelse i dyberegående interviews omkring deres anvendelse af nanomaterialer. Foruden de tre partnervirksomheder blev fem relevante centre på Teknologisk Institut interviewet omkring deres anvendelse af nanomaterialer.

Da antallet af svar på spørgeskemaundersøgelsen var begrænset blev yderligere tre virksomheder interviewet: Persano, Unisense og et anonymt firma, der arbejder med maling og trykfarver. Derudover blev der foretaget fem telefoninterviews.

Interviewene havde til formål at indsamle mere dybdegående information omkring virksomhedernes erfaringer med produktion, anvendelse og bortskaffelse af nanomaterialer, og om der i den forbindelse er områder hvor virksomhederne er usikre eller om der er ønsker til hvad en evt. fremtidig officiel guide inden for området kunne indeholde.

Resultater

Følgende resultater er baseret både på spørgeskemaundersøgelsen og interviewene:

- 1) Nanoteknologiske virksomheder I Danmark
 - a) Virksomheder i Danmark, der arbejder med nanomaterialer er bredt fordelt i størrelse og arbejder indenfor ni forskellige industrielle områder: Maling & trykfarver, coatins, kosmetik, farma & biotech, optik, sensorer, katalysatorer, cement og tekstil.
 - b) Over halvdelen af virksomhederne, som arbejder med nanopartikler, nanofibre eller nanoflager arbejder på F&U skala eller meget lille skala (<1 kg pr. år). Virksomheder, som arbejder med nanomaterialer på større skala (>100 kg pr. år) arbejder indenfor maling & trykfarver, cement, tekstil eller kosmetik.
 - c) Nanomaterialer er oftest anvendt i produkter, hvor de er suspenderet i væske eller indlejret i en fast matrice.
- 2) Nanomaterialer
 - a) De nanomaterialer, som anvendes i større skala (>100 kg pr. år) i den danske industri er metal oxid, polymer, silika og carbon black nanopartikler.
 - b) Nanopartikler anvendt i større skala indkøbes fra udenlandske leverandører i pulver eller suspenderet form.
- 3) Håndtering af nanomaterialer
 - a) Håndteringen af nanomaterialer er materialeafhængig. Generelt håndteres nanomaterialer efter de samme producerer, som andre kemikalier eller pulvere. Virksomheder, der håndterer pulvere af nanopartikler er bevidste om de nødvendige forholdsregler for håndtering af fine pulvere.
 - b) Virksomhedernes viden om fysiske karakteristika for deres nanomaterialer stammer hovedsagligt fra leverandørerne (fire virksomheder måler til tider partikel størrelse, ingen virksomheder måler specifikt overfladeareal).

- c) Med en enkelt undtagelse stammer virksomhedernes viden om toksikologiske og økotoksikologiske egenskaber for deres nanomaterialer udelukkende fra leverandørerne.
 - d) Kun en virksomhed har kendskab til ansatte, som er usikre eller utrygge ved håndtering af nanomaterialer.
 - e) Måling eller anden bestemmelse af eksponeringsniveauet af luftbårne nanomaterialer i arbejdsmiljøet sker sjældent.
 - f) Håndteringen af affald, der indeholder nanomaterialer, varierer. Hovedparten af virksomhederne bortskaffer nanomaterialer som almindeligt affald eller i spildevand, når nanomaterialet vurderes at være uskadeligt eller indlejret i makroskopiske strukturer.
 - g) Ingen virksomheder forudser miljømæssige ricisi som følge af deres bortskaffelse af nanomaterialer som almindeligt affald eller i spildevand, da de anser den nuværende lovgivning for overholdt.
- 4) Produkter, der indeholder nanomaterialer
- a) Med undtagelse af tekstiler har alle danskproducerede produkter, som indeholder nanomaterialer, et indhold af nanomaterialer over 0,1%.
 - b) Ingen danske virksomheder 'nano' brandede deres produkter eller deltog i nano-certificerings ordninger.
 - c) Ingen virksomheder forudså ricisi for brugere af deres produkter relateret til indholdet af nanomaterialer, da de anså den nuværende lovgivning for overholdt.
 - d) Oftest informeres kunder (forbrugere og industrielle) ikke om indhold af nanomaterialer i produkter.
 - e) Ingen virksomheder forudså miljømæssige ricisi forbundet med deres produkters indhold af nanomaterialer, da de anså den nuværende lovgivning for overholdt.
 - f) Det vides ikke i hvilken grad nanomaterialer kan afgives ved brug, slid eller destruktion af produkter, som indeholder nanomaterialer.
- 5) Virksomhedernes syn på officielle guidelines eller regulering af nanomaterialer
- a) De fleste virksomheder så intet behov for ny specifik lovgivning om nanomaterialer. Virksomhederne foretrækker at regulering foretages indenfor de eksisterende rammer på kemikalieområdet fremfor som et ny separat emne.
 - b) Et meget udbredt synspunkt blandt virksomhederne er at det i forbindelse med regulering er meget vigtigt at skelne mellem forskellige typer og former af nanomaterialer, og ikke skære al nanoteknologi over en kam.
 - c) Adskillige virksomheder efterspurgte at kemikaliesikkerhedsdatablade indeholdt 'nano-specifik' information så som partikel størrelse, overfladeareal etc.
 - d) Nogle virksomheder udtrykte interesse i en simplere adgang til viden om risici ved og håndtering af nanomaterialer.

Konklusioner

Viden om nanomaterialers effekter på sundhed og miljø er stigende, men stadig begrænset. Derfor vides kun lidt om mulighederne for eksponering og effekter for ansatte, forbrugere og miljø som følge af brug, slid og bortskaffelse af nanoteknologiske produkter.

Der er stærkt fokus på nanoteknologi indefor både dansk forskning og dansk industri; men interessen for nye teknologier har for mange virksomheder endnu ikke udmøntet sig i egentlig anvendelse af nanomaterialer. Anvendelse af nanomaterialer i større skala er stadig forbeholdt industrier, der har anvendt disse materialer i årtier, såsom farve/lak og cement industrierne.

Regulering af nanomaterialer står over for to forskellige scenarier: Anvendelse af nanomaterialer i lille skala i nye sammenhænge og anvendelse af nanomaterialer i større skala i traditionelle industrier.

Når nanomaterialer anvendes i lille skala eller til F&U formål tager virksomhederne de samme forholdsregler som når de syntetiserer andre nye kemikalier med ukendte egenskaber. I de tilfælde håndteres nanomaterialer i stinkskab og affald, der indeholder nanomaterialer håndteres som farligt affald.

Nanomaterialer som i mange år har været anvendt i større skala håndteres ifølge de informationer der angives på sikkerhedsdatabladene, dvs. i mange tilfælde på samme måde som virksomhederne håndterer andre kemikalier uden specielt fokus på nano-relaterede risici bortset fra en udtalt fokus på de nødvendige forholdsregler for håndtering af fine pulvere.

Nuværende danskproducerede produkter på markedet, som indeholder nanomaterialer, er velkendte produkter, der har været tilgængelige i mange år. Da produkterne har været på markedet i mange år tilsyneladende uden nano-relaterede effekter, ser producenterne ingen nano-relaterede risici for brugere eller miljø. Virksomhederne foretager sjældent bestemmelser af eksponering for nanomaterialer; hvad enten det er i arbejdsmiljøet; fra produkter, der indeholder nanomaterialer eller fra nanomaterialer, der opstår som biprodukt

Det er virksomhedernes holdning at regulering af nanomaterialer bør tage højde for de mange forskellige typer og former af nanomaterialer (partikler, fibre, rør, flager etc.). Industrien foretrækker at ny regulering sker indenfor de eksisterende rammer for kemikaliereregulering fremfor som et selvstændigt område.

1 Nanomaterials

1.1 Background

To identify the most relevant questions to ask companies regarding their use and concerns in handling nanomaterials a selection of national and international reports on nanotechnology applications was reviewed. Focus was on the state of knowledge on health and environmental effects of nanomaterials used by the industry and recommendations for safe use of nanomaterials.

The text below is thus by no means an extensive scientific review of the issues covered in the cited literature, but is meant as a summary of the key learnings, which have formed the basis of the questionnaire used in this study.

1.2 References

A complete list of the used literature can be found in the bibliography. The literature falls into the following categories:

- *Comprehensive reports on the industrial applications and possible risks of nanotechnologies [ref. 1-3]*
These reports from international projects on nanotechnology define the basic terms of nanotechnology and cover the different types of nanomaterials used, their applications and possible environmental and health risks.
- *Reports on risk assessment of nanomaterials [ref. 4-5]*
These more technical reports describe how risk assessment of nanomaterials could be done.
- *Recommendations for government [ref. 6-7]*
Recommendations for government action on nanotechnology have been made both on national level (*ref 6.*) and on EU level (*ref 7*)
- *Recommendations on safe and good practice in the nanotechnology workplace [ref. 8-11]*
Some organisations have published interim recommendations, which will probably form the basis of finalized versions [8-9]. Other organizations have recently finalized their recommendations [10-11].
- *Internal guidelines for nanotechnology workplaces [ref 12-13]*
Some companies and institutions have prepared their own internal guidelines for handling of nanomaterials. They are based on the recommendations by *ref. 9* and others.
- *Surveys on industrial applications and handling of nanomaterials [ref. 14-16]*
At present the an international survey on nanomaterials have been completed [14]. In both Germany [15] and the UK [16], national survey initiatives have been started. The questionnaires of these surveys have been used as inspiration for the questionnaire used in the present study.

In addition to the reports above a nordic report on evaluation and control of occupational health risks from nanoparticles [17] has very recently been published.

1.3 Definitions

Nanomaterials are usually defined as materials, which have structure in the 1-100 nm range in at least one dimension. Nanomaterials are normally categorised by their structure and by their chemical composition. Unlike bulk chemicals, nanomaterials may have physical, chemical and toxicological properties, which besides the chemical composition depend on the nanostructure [1-3].

Table 1.1 Definitions of the different types of nanomaterials usefc in this report

Type of nanomaterial	Definition	Example
Nanoparticle	Particle with all 3 dimensions in the range of 1-100 nm or aggregate hereof.	TiO ₂ nanoparticles used as UV-absorber in e.g. sunscreens.
Nanofibre, nanotube	Object with at least 2 dimensions in the range of 1-100 nm and an aspect ratio of more than 3.	Carbon nanotubes used in e.g. electronics or composite materials.
Nanoflake	Flake, where at least one dimension is less than 100 nm.	Nanoclay used e.g. to give strength in nanocomposite plastic materials.
Nanofilm or nanocoating	Coatings with layers thinner than 100 nm.	Ultrathin coatings.
Nanostructured surface	Surface with structure (protrusions or grooves) in the 1-100 nm range.	Nanostructured superhydrophobic easy-to-clean surfaces
Nanoporous structure	Porous structure with pore sizes in the 1-100 nm range.	Biocompatible 3D porous implantable structures (artificial bone material)

The categorisation of the different types of nanotechnological materials summarized in table 1.1 will be used throughout this report. There are no standardized definitions of the terms and some references use slightly different definitions e.g.:

- The term “nanoparticle” in some cases (e.g. ref. 5) refers to both nanoparticles and nanofibres (nanotubes)
- The term “nanoparticle” is in some cases (e.g. ref. 9) exclusively used for engineered materials, whereas the term “ultrafine particle” is used for natural or unintentionally produced nanoparticles.

Another categorisation of nanomaterials, which is based on how nanoscale structure is placed in the surrounding medium, has also been suggested¹. This categorisation does not discriminate between different shapes of nanomaterial (e.g. nanoparticles, nanofibres or nanoflakes).

¹ Britt Hvolbæk Larsen, Nano-DTU (Danish Technical University)

1.4 Health effects

Nanomaterials are different chemical substances with the added phenomena that can be linked to the role of size, composition or reactive surface area. Therefore, the toxicity of nanomaterials can not be described in general terms covering all nanomaterials and evaluation on specific nanomaterials should therefore at present rely on case specific evaluations. With the current state of knowledge we can only make crude categorisations of nanomaterials and describe their potential health effects within these categories.

The toxicity of a nanomaterial is thus related to chemical composition as well as size and shape of the nanomaterial. For many chemicals, there is substantial knowledge about the health effects of the chemical substance but due to the specific properties of nanomaterials, this information can not be directly applied for assessment of the same substance in a nanoformulation. Therefore, precise knowledge of possible health effects of nanomaterials is sparse. However, based on the limited research in the field of nanotoxicology some general remarks can be made on the health effects specific to nanomaterials.

Most health effects require substances to enter the body². To induce health effects, a material must therefore either

- be inhaled
- penetrate the skin
- be ingested
- be injected into the body

The injection exposure route is only relevant for medical uses and thus outside the scope of this report.

As a consequence three of the six classes of nanomaterials: nanofilms, nanostructured surfaces and nanoporous structures are not expected to cause nano-specific health effects unless nanoparticles, nanofibres or nanoflakes are used or produced as by-product when the product is produced, used or disposed. Like any other material the materials might also cause non-nano-related health effects (e.g. through release of volatile organic compounds), these effects are, however, outside the scope of this report.

Since nanofilms, nanostructured surfaces and nanoporous structures do not *directly* give rise to nano-related health effects; the main focus of the present study has been industrial use and produce of nanoparticles, nanofibres and nanoflakes. Companies using the former three types of nanomaterials have been included only to a lesser extend (see section 3.2).

1.4.1 Inhalable nanomaterials

1.4.1.1 Nanoparticles

It has been known for years that ultrafine aerosols (airborne nanoparticles) from e.g. diesel engines can have adverse respiratory, systemic, neural and reproductive health effects [2,3].

² In principle materials can induce health effects such as skin sensitization without entering the body. For example skin irritation might be caused by close fitting material blocking natural outlet of sweat.

Studies on engineered nanoparticles have shown that the toxicity of low-soluble airborne nanomaterials depends on the size, or more specifically, the specific surface area of the materials; the smaller particles, having larger specific surface area, are generally more toxic [1,9]. The apparent strong relationship between particle size and toxicity means that a tiny mass fraction of small nanoparticles might pose a larger risk than a much larger mass fraction of microparticulate dust of the same chemical substance.

Nanoparticles are normally present in both outside and indoor air at a natural concentration of 10^4 - 10^6 particles/cm³ [2,3]. This particle concentration can be exceeded in many contexts. As an example, the extremely small size of nanoparticles means, that the distribution of 1g of monodisperse 10 nm particles in a 20m³ room results in an average particle concentration of approximately 10^{14} particles/cm³.

The presently used standards for measuring airborne dust levels are usually gravimetric (mg/m³). In occupational hygiene the standards are based on the mass concentration of either total suspended dust (TSP) or the biologically relevant inhalable, thoracic, respirable dust. Special sampling techniques are also employed to measure fibrous materials, such as asbestos. In Denmark, environmental monitoring of particulate air-pollution has until recently been measured as PM₁₀ alone (the mass concentration of particles ≤ 10 μ m in size). Now, the regulation has moved toward monitoring of PM_{2.5}, which correspond to the mass of particles small enough to reach the alveolar region [4,20]. Since the gravimetric measurements of especially TSP and single PM-size fractions does not take particle size-distribution into account, the result from such data should be used with caution when nanoparticulate dust is expected.

1.4.1.2 Nanofibres

Like ultrafine aerosols, inhalation of microscopic fibres has been known for years to cause respiratory health problems (such as asbestosis) [2,3]. Some airborne nanofibres and nanotubes may cause the same type of health problems. This assumption has been confirmed by research on the toxicology of carbon nanotubes [1].

1.4.1.3 Nanoflakes

The toxicity of airborne nanoflakes has not been addressed in the cited reports. However, since the typical size of nanoflakes is usually less than 1 μ m they can be assumed to pose the same hazards as fine dust. Furthermore, if the flakes are fragile, they might be divided into nanoparticles.

1.4.2 Skin penetration of nanomaterials

It has been shown that nanoparticles in some cases may penetrate the skin to a much larger extent than microparticles [1]. Particles larger than 1 μ m can only penetrate the outer layer (dermis) of undamaged skin, whereas small nanoparticles (5-20 nm) can penetrate into the skin and interact with the immune system [1]. Whether toxic effects can occur due to nanoparticles penetrating through skin remain unknown [1,3]. Sunscreens containing nanoparticulate titaniumdioxide have been widely used in recent years without reported toxic effects.

Since the toxicological knowledge of the subject is very sparse no definite conclusions can be made on possible toxic effects of suspended nanoparticles penetrating through the skin.

No reports on the penetration of nanofibres or nanoflakes through skin have been found. However, MSDS's for e.g. carbon nanotubes sometimes advise to use dermal protection, because skin irritation may occur at dermal exposure³.

1.4.3 Ingestion of nanomaterials

Ingestion of nanomaterials can happen either intentionally (when nanomaterials are used in medicaments or as food ingredients) or unintentionally, when free or suspended nanomaterials are handled without gloves and subsequently transferred to the mouth or when airborne nanomaterials are inhaled. Unless diseased, the epithelium of the gut is impermeable to larger molecules (including nanoparticles) and environmental and occupational causes of diseases of the gut are uncommon [1]. Biological effects such as gastro-intestinal cancer, however, has been linked to a number of occupational exposures, including exposures to particulate matter³. It has been shown that some ingested nanoparticles may be taken up by the lymphatic vessels; however little information is available regarding behaviour and translocation [1].

1.5 Environmental effects

The knowledge of environmental effects of nanomaterials is even sparser than the toxicological knowledge on the health effects. In general the risk of negative environmental effects of nanomaterials depends strongly on the chemical composition of the materials [2].

1.5.1 Airborne nanomaterials

At the current production levels of engineered nanomaterials, the emission of airborne engineered nanoparticles is low compared to the concentration of particles produced unintentionally from conventional sources: diesel engines, wood fired stoves and others [3]. As a consequence it can be assumed that negative environmental effects of nanoparticles are due to nanoparticles produced by conventional sources, unless engineered nanoparticles are more toxic or have a specific toxicity profile (e.g. prolonged biopersistence) than nanoparticles produced by conventional sources.

Regarding nanofibres and nanoflakes the current scale of production is very low. As a consequence the release of engineered nanofibres and nanoflakes to the environment is currently low.

1.5.2 Suspended nanomaterials

Knowledge on environmental effects of suspended nanomaterials is very scarce. One small and disputed study has shown negative effects on fish subject to fullerenes (C_{60} , diameter: ~1 nm) in concentrations of 0.5-1 ppm [2,3,6]. Other recent scientific studies have also indicated negative environmental effects of suspended nanoparticles³.

³ Keld Alstrup Jensen, National Research Centre for the Working Environment

1.6 Handling of nanomaterials

Since knowledge on the toxicological properties of nanomaterials is sparse, recommendations for safe handling of nanomaterials are mainly concerned with limiting exposure to avoid negative health effects. Precautions are thus to work in closed systems, to wear breath protective equipment and similar approaches to limit exposure [9]. A problem is however, that only little specific information is available about the suitability of this type of equipment with respect to nanomaterials.

There are at present no finalized standards for appropriate ways of measuring exposure levels of nanomaterials. Some of the present standards for measuring workplace exposure are not suitable for nanomaterials. For example, gravimetric dust measurements are not suitable for nanoparticulate dust and phase contrast microscopy used for measuring airborne fibre concentrations can not detect individual nanofibres [9].

1.7 Summary

The specific properties of nanomaterials may imply that nanomaterials possess other health and environmental effects than those of the chemical substances that the nanomaterials are made of. There are at present no finalized standards for assessing this issue, and toxicological data addressing the specific properties of nanomaterials are sparse. Recommendations for handling of nanomaterials focus on limiting exposure; however, there are currently no standardized methods for exposure measurements of nanomaterials.

At present the major concern is the negative health effects due to inhalation of airborne nanoparticles or nanofibres. However, possible negative health and environmental effects from suspended nanomaterials cannot be dismissed.

2 Legislative overview

The text below is based on information from the Danish Environmental Protection Agency and the Danish Working Environment Authority.

2.1 Environment

The objective of the Danish Environment Protection Act is to protect and preserve nature and environment and covers regulations regarding protection of air, earth, and groundwater and protection of surface water as well as regulations concerning polluting industries and activities, waste and recycling and cleaner technology. The environmental legislation does in some areas follow the common EU rules and in other areas it is drawn up as special national rules.

The chemicals directive covers regulations for classification, packaging, labelling, sales and storage of chemical substances and products as well as special requirements in a number of areas such as toys, cosmetics, pesticides and biocides. Further, it comprises a number of executive orders about application restrictions for a number of substances. The chemicals directive is to a great extent a result of the EU harmonisation. Currently REACH the new chemical legislation in EU is implemented and a new global harmonized classification system, GHS is under preparation for implementation in the legislation. In REACH there is further requirements for the manufactures and importers in order to provide hazard data and to document safe use of their chemicals when compared to the existing regulation.

The aim of both the environmental and the chemicals directives is to protect against environmental and health dangers in connection with production, discharge, application and disposal of chemical waste regardless of state and size of the substances. So even though nanomaterials are not specifically mentioned in the environment and chemicals directives, chemical substances in nanosize (and other chemical states) are covered by the rules.

In connection with the Environment Protection Act the emissions of chemicals to the environment is regulated by means of environmental and health quality standards. It is possible to state specific values for specific substances , eg specific nanomaterials, if necessary.

It is currently discussed, nationally as well as internationally, to which extent technical adjustments to the existing chemicals directive are needed.

It is important to emphasize that if risk towards environment or health can be shown in connection with a specific use of a specific nanomaterial the existing legislation today cover such an situation and the authorities can act on this knowledge.

2.2 Working Environment

2.2.1 The Danish Working Environment Act

According to the Working Environment Act (Executive Order No. 268 of 18 March 2005 with amendments) it is the employer's responsibility to ensure that the working conditions are safe and sound in any way. Further, the employer shall ensure that a Workplace Assessment of the health and safety activities is worked out, with consideration to the nature of the work, the work methods and processes applied and to the size and organisation of the enterprise.

Substances and materials with properties which can be hazardous to, or in any other way adversely affect, safety or health, may only be produced and used in working processes and methods which effectively protect the employees against accidents and diseases. As it is today, there are no provisions which specifically concern nanomaterials. If specific circumstances in connection with nanomaterials are identified indicating possible consequences for the health and safety at the enterprise, it is within the frames of the existing working environment legislation allowed to make specific requirements for the handling of the materials.

2.2.2 Specific legislative areas

Within the legislative areas mentioned here nanomaterials are included on the same conditions as substances and materials.

2.2.2.1 *Workplace Assessment*

According to § 6a and § 6b in executive order no. 559 of 17 June 2004 on the performance of work, the employer is obliged to identify and describe the scope of any working environmental problem caused by application of a nanomaterial and further to describe the necessary actions to be taken to secure that the working conditions are safe and sound in any way.

2.2.2.2 *Dangerous substances and materials*

Executive order on work with substances and materials describes the overall demands to the employer in connection with work with hazardous substances and materials. In this Executive Order, dangerous substances and materials mean substances and materials which are classified as dangerous according to Council Directives 67/548/EØF² and 1999/45/EF of 31 May 1994. It is further supplemented with a broader definition for "substances and materials that owing to their physico-chemical, chemical or toxicological properties and the way in which they are used or occur at work, may involve a risk of exposure to substances and materials" as well as substances listed on the Working Environment Service's GV list, see § 1, clause. 2 in executive order no. 559 of 4 July 2002 Special Duties of Manufacturers, Suppliers and Importers, etc. of Substances and Materials pursuant to the Danish Working Environment Act with amendments. According to this, substances need not be classified and marked according to the mentioned directives in order to be treated as dangerous. If nanoparticles covered by the "danger concept" constitute any risk for the employees due to their physical properties and the way in which they are used, the employer can be obliged to work out a special workplace assessment with substitution consideration.

² Directive on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on classification, packing, and labelling of dangerous products

2.2.2.3 Unnecessary effects

According to § 16 in Executive order no. 559 of 17 June 2004 on Performance of work any unnecessary effect of substances and materials shall be avoided. Therefore, the effect of substances and materials during work shall be reduced to the lowest level reasonably practicable taking account of technical progress, and any limit values fixed shall be complied with. Limit values for pollution by substance and materials at working place are published in AT- guideline C.01 Limit Values for substances and Materials. If a fraction of a substance turns out to have special toxic properties, limit values can be set for this substance. In some cases different limit values have been set for the respirable fraction and for the total dust fraction.

2.2.2.4 Material Safety Data Sheets

The supplier's Material Safety Data Sheets (MSDS) must be worked out according to Article 31 in REACH regulation no 1907/2006 of 18 December 2006. The MSDS must be worked out for the substances and materials which are covered by Article 31 and further for the substances and materials which are covered by the "danger concept" in executive order no. 559 of 4 July 2002 about Special Duties of Manufacturers, Suppliers and Importers, etc. of Substances and Materials. This involves information about hazards identification, first aid measures, handling and storage, toxicological information, disposal considerations, physical, chemical properties, etc. in order for the user to take the necessary safety measures in connection with handling and working with the substance.

2.2.2.5 Carcinogenic substances

Executive Order no. 908 of 27 September 2005 on Measures to Protect Workers from the Risks related to Exposure to Carcinogenic Substances and Materials at Work deals with protection of the workers and is based on employers risk assessment of work with such substances materials with regard to e.g. choice of precautionary measures.

A number of the substances are subject to requirements in connection with the work, e.g. requirements to preliminary approval, special training and to work in closed systems.

2.2.2.6 Code numbered products

Work with paint articles, glue, filling materials, ink and other products used for preparation/finishing is subjected to Executive order no. 301 (Determination of code numbers) and no. 302 (Work with code-numbered products) of 13 May 1993. The code number (MAL-factor) for a product indicates the security measures to be taken in certain work situations. The code number for a product is determined with due consideration to all the constituents in the products. Thus nanomaterials are already governed by the existing code number system.

3 Questionnaire

3.1 Scope

The focus of the questionnaire was to map the industrial use and production of nanomaterials and to gain insight into the industrial need for guidelines and regulation on nanotechnology. Specifically, the questionnaire covered:

- Size of companies and line of business
- Types and quantities of nanomaterials used
- End-products, their use and disposal
- Methods and processes for handling nanomaterials (routines, guidelines and precautions used)
- Information on health and environmental risks
- Waste management
- Perceived need for guidelines and recommendations for aspects that might need regulation.

3.2 Structure of the questionnaire

The questionnaire was structured to make it as quick and easy as possible to answer. Therefore, the questions were mainly given with checkboxes for answers and the number of questions was limited. The structure of the questionnaire allowed companies without relevant activities on nanotechnology to finish the questionnaire very fast.

The focus of the study was mainly usage or production of nanoparticles, nanofibres or nanoflakes. Companies using nanostructured surfaces, nanofilm or nanoporous structures were asked whether nanoparticles, nanofibres or nanoflakes were used or produced in their processes; when that was not the case the main part of the questionnaire was not completed.

The questionnaires of the surveys in England [16] and Germany [15] as well as the international ICON survey [14] have been used as inspiration for the questionnaire in this study. Like the German survey, the questionnaire was split in two sections: a general part and a material-specific part. This split allowed the companies to fill out the specific questionnaire for each nanomaterial, the company worked with. The questionnaires are attached in appendix A.

3.3 Recipients of the questionnaire

The questionnaire was sent to companies which in some way have expressed an interest in nanotechnology as well as to companies in other ways known to work with nanomaterials. In total 165 companies received the questionnaire.

The recipients were:

- Members of NaNet, the Danish Nanotechnological Network
- Members of Danish Standard's Forum for Nanotechnology (S-418)

- Member companies using nanoparticles selected by SPT, the Association of Danish Cosmetics, Toiletries, Soap and Detergent Industries
- Companies cooperating with iNANO, the Interdisciplinary Nanoscience Center
- Nanotechnological companies reported in “Technology Foresight on Danish Nanoscience and Nanotechnology, action plan” (ref. 18).
- Companies involved in nanotechnological projects supported by Højteknologifonden, the Danish National Advanced Technology Foundation
- Companies selected by Dansk Industri, the Confederation of Danish Industries, subgroup for production
- Nanotechnological companies selected by specialist at the interviewed centres at Danish Technological Institute
- Companies selected by Keld Alstrup Jensen, Forskningscenter for Arbejdsmiljø, National Research Centre for the Working Environment

3.4 Execution of the questionnaire

The companies received the questionnaire by mail and were given a deadline for response of four weeks. Companies that did not respond within four weeks received a reminder by mail. Companies that still had not responded were then contacted by telephone ones and kindly asked for their cooperation.

3.5 Number of responses

165 Companies received the questionnaire.

75 Companies (45%) responded.

24 Companies (15%) responded that they use or produce nanotechnological materials. 8 of these companies only work with nanostructured materials, nanoporous structures or nanofilm, thus

16 Companies (9%) responded that they use or produce nanoparticles, nanofibres or nanoflakes.

The distribution of responses is illustrated in figure 3.1. 90 companies have not responded to the questionnaire. The large majority of the late responding companies (companies responding after written reminders and telephone inquiry) reported that they do not use or produce nanotechnological materials. Based on this observation we assume that the large majority of the non-responding companies do not use or produce nanotechnological materials.

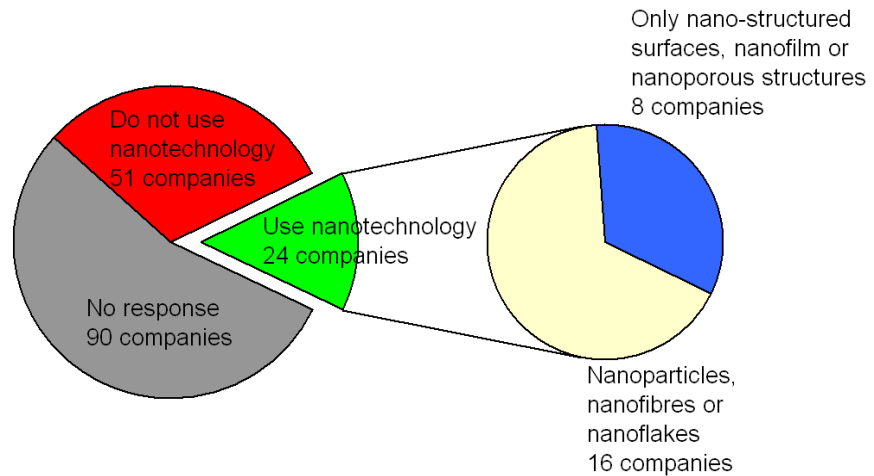


Figure 3.1. Number of responses to the questionnaire

Of the 24 companies responding that they work with nanotechnological materials, 8 companies stated that they only work with nanostructured materials, nanoporous structures or nanofilms and that no nanoparticles, nanofibres or nanoflakes are used or produced when working with these materials.

The high fraction of companies responding that they do not use or produce nanomaterials may seem surprising, since only companies expressing an interest in nanotechnology received the questionnaire. However, for many companies the interest in new technologies has not yet manifested in use or production of nanomaterials even on R&D scale. The response of only 16 companies using or producing nanoparticles, nanofibres or nanoflakes is in accordance with other surveys on industrial use of nanotechnology:

- The UK Voluntary Reporting Scheme for Engineered Nanomaterials [16] has during the first nine months received 7 responses from companies based in Great Britain.
- The ICON international survey of current practices in the nanotechnology workplace [14] received a total of 15 responses from companies with nanotechnological activities in Europe.

3.6 Results

The 24 companies that have responded that they use nanotechnological materials have completed at least the first six questions of the general questionnaire.

12 of the 16 companies working with nanoparticles, nanofibres or nanoflakes were interviewed, either directly (see section 4) or by telephone. The results of the study, which are based both on the received questionnaires and the interviews, are presented in section 5.

4 Interviews with nanotechnological companies

To get more detailed information about the handling of nanomaterials and the need for guidelines and regulations within the Danish industry, a number of nanotechnological companies were interviewed.

Initially, the centres at Danish Technological Institute working with nanomaterials (our “internal partners”) and three partner companies working with nanomaterials in different industries (Dyrup, Haldor Topsøe and Aalborg Portland) were interviewed. Since the number of positive responses on the questionnaire was limited, it was decided to extend the number of companies interviewed to include a company in the paints & inks industry (called “company A”, since the company prefers to be anonymous), a cosmetics company (Persano) and a producer of microsensors (Unisense). Summarized information about the interviewed companies, their products as well as type and scale of the used nanomaterials is listed in table 4.1.

Besides the interviews reported below the majority of the remaining companies working with nanoparticles, nanofibres or nanoflakes were interviewed by telephone. The telephone interviews are not reported separately below but were used to clarify the answers on the questionnaire and to get a general feel of how the companies feel about nanotechnology and nanomaterials.

Table 4.1. List of interviewed companies

Company	Nanotechnological products	Nanomaterials (nanoparticles, nanofibres or nanoflakes)	Scale of use (nanomaterial per year)
Danish Technological Institute:			
Tribology Centre	Tribological coatings, mainly for metal tools	Primarily metal nitride nanoparticles produced as by-product.	100-1000 kg
Sol-gel group	Coatings and lacquers	Silane and metal nanoparticles	Small scale production < 1 kg
Plastic Centre	Polymeric materials	Photoactive TiO ₂ Nanoclays	< 1 kg (R&D level) 1-10 kg (experimental production)
Microtechnology and Surface Analysis	Nanostructured surfaces	None	-
Chemistry and Water Technology	Nanoparticulate DNA-probes. Analysis of nanoparticles	Synthesis of metal nanoparticles (Ag or Au). Analysis of customer materials	< 1 kg (R&D level)
Dyrup A/S	Paints	Polymer nanoparticles Metal oxide nanoparticles Silicate nanoparticles	> 100 tons 1-10 tons app. 1 ton
Haldor Topsøe	Catalysts	Suspended nanoparticles	< 1 kg (R&D level)

Aalborg Portland	Cement	Silicates (microsilica) Nanoclays	tons not reported
Company A	Inks	TiO ₂ nanoparticles, silicate nanoparticles, carbon black	not reported
Persano	Sunscreen	TiO ₂ nanoparticles	1-10 tons
Unisense	Sensors	Nanoparticulate fluorophores	< 1 kg (R&D level)

4.1 Danish Technological Institute

Danish Technological Institute provides analyses, consultancy and development in a very broad range of areas. The company employs approximately 800 people in Denmark distributed on 30 specialist centres. Five centres, with a total of approximately 100 employees, have activities related to nanomaterials. Each of the five relevant centres was interviewed.

4.1.1 Tribology Centre

4.1.1.1 Description

The Tribology Centre produces functional thin films for corrosion and wear protection (e.g. CrN, TiAlN, TiN, TiCN), as well as Diamond Like Carbon (DLC) for low friction purposes. The thin films are made by vacuum based techniques such as Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD) or ion implanting. Typical objects for coating are tools for drilling and milling of metal, plastic moulds, knives, cutting/forming/stamping tools.

4.1.1.2 Customers

Typical customers are users and producers of tools for metal working and plastic moulding. However, the centre has customers from many other industries as well.

4.1.1.3 Nanomaterials

The centre has development projects that involve coatings and embedded crystals with layers in the nanometer range. However, for the present study it is nanoparticles produced as a by-product in the processes that is of most relevance. These nanoparticles are primarily metalnitrides which may be converted into oxides through interaction with air. In some coatings nanoparticles are incorporated into the coating. In all cases nanoparticulated dust is produced as a by-product. The particle size and aggregative state of the nanoparticles is unknown. The centre estimates that they produce 10-1000 kg nanoparticles as by-product each year including metal containings and from sand blowing

4.1.1.4 Handling of nanomaterials

The coating processes are performed under high temperature in closed systems. After the coating process is finished, the coating chambers are opened to remove the coated products and clean the chambers. At that time the workers are exposed to nanoparticulate dust. Thus, in connection with cleaning situations dust masks are worn.

4.1.1.5 Product life cycle

No specific information on nanoparticle content of coatings is given to customers.

Since the coated products are often tools for drilling or milling, the coatings are often subject to substantial wear. The extent to which nanomaterials are released during wear is unknown. Measurements have shown that nanoparticles are released during an artificial wear test on one of the centres coatings, which does not incorporate nanoparticles. It is however not known whether the measured level of nanoparticle release during wear is high or low compared to other coatings and surfaces.

4.1.1.6 Waste handling

Dust masks are worn when nanoparticulate waste products are handled. The waste is handled as hazardous chemical waste.

4.1.1.7 View on guidelines and regulations

The centre would like to help to assess the potential dangers of nanomaterials, to know whether materials are safe or not. The centre would also like guidelines on the handling of nanomaterials, which protective equipment should be used? What type of dust mask etc?

4.1.2 Sol-gel group at Centre for Materials Testing

4.1.2.1 Description

The sol-gel group at the Centre for Materials Testing develops and produces silane based sol-gel coatings for e.g. scratch resistance and biological activity. The sol-gel group consists of five people.

4.1.2.2 Customers

The coatings are used for a broad range of purposes. The application of the coatings is either done by the sol-gel group itself or by professional coating companies.

4.1.2.3 Nanomaterials

In some of the coatings nanoparticles are added to provide functional property to the coating. The sol-gel group uses silane, titanium, silver and copper nanoparticles. The particle size depends on the material and varies from 10-100 nm. The quantities of the coating production in the centre are in all cases small (<1 ton per year) and the used quantities of nanoparticles are less than 1 kg for all types.

4.1.2.4 Handling of nanomaterials

The nanoparticles are usually purchased as dry powder and subsequently dispersed in solution. When an applied coating dries, incorporated nanoparticles are embedded in a solid matrix.

Since the produced quantities are small, all production takes place in fume cupboards, which is necessitated by the use of epoxy-based resins.

The liquid coatings are usually applied by roll or spray. In both cases protective gloves (4H) are worn. Filter masks and protective clothing are used during spraying application.

All waste is disposed as hazardous chemical waste (epoxy waste).

4.1.2.5 Product life cycle

When liquid coatings are sold to customers, the customers are informed about nanoparticulate content. Based on their knowledge on particle chemistry the centre believes that nanoparticles are not released during application of the

coating, however, this has not been confirmed by measurements. The centre does not know whether nanoparticles are released when coated end-products are destroyed and has not investigated the issue.

4.1.2.6 View on guidelines and regulation

The sol-gel group believes it has a good understanding of the nanomaterials, which are used by a well-educated group. According to the sol-gel group, nanomaterials should be regulated by the same set of legislation and guidelines that are used for chemicals in general.

4.1.3 Centre for Plastics Technology

4.1.3.1 Description

The Centre for Plastics Technology provides counselling, development and analysis of plastics and other materials. Nanomaterials are used in three different contexts in the Centre for Plastics Technology. The PEC group, which develops dye-sensitized solar cells and the photocatalytic group that works with dirt and bacteria repellent surfaces both use photoactive titaniumdioxide nanoparticles. Another group at the centre uses nanoclays for improving the properties of polymer materials.

4.1.3.2 Customers

Since the materials are only used in R&D projects, no products are sold to customers.

4.1.3.3 Nanomaterials

4.1.3.3.1 TiO₂ Nanoparticles

Both the PEC group and the photocatalytic group work with nanoparticulate photoactive crystalline TiO₂, anatase (CAS no. 1317-70-0⁵). Three different commercially available types are used. The particle sizes of the used products are 9nm, 13nm and <25nm respectively. The specific surface area is in the range 100-250 m²/g. The used quantities are in all cases very small (< 1 kg).

4.1.3.3.2 Nanoclay

The nanoclays are silicate nanoflakes thinner than 10 nm. The flakes are usually approximately 1 nm thick and 100-1000 nm wide. The nanoclays are used in concentrations up to 5% in polymer materials. The centre uses 1-10 kg nanoclays per year.

4.1.3.4 Handling of nanomaterials and waste

4.1.3.4.1 TiO₂ Nanoparticles

TiO₂ nanoparticles are handled in lab scale wet processes in fume cupboards. In the endproducts the nanoparticles are embedded in porous matrices. There was some uncertainty about the waste handling of the nanomaterials. While one supplier clearly stated that waste should be disposed as hazardous waste, another supplier gave no clear recommendations.

4.1.3.4.2 Nanoclay

Nanoclays are purchased as a powder. They are compounded with polymers in a wet process. The end product is a solid polymer in which the nanoclays are

⁵ The CAS number identifies the chemical composition of the material (in this case TiO₂ in the anatase crystalline phase) but does not contain information on the particle size.

incorporated. The materials are handled in closed air circulated systems. The materials are considered non-toxic and waste is handled as regular waste.

At present nanoclay is only handled in R&D contexts and not incorporated in commercial products.

4.1.3.5 View on guidelines and regulation

The centre would like to have clear guidelines on how to handle nanoparticulate waste and on which protective equipment should be used.

4.1.4 Centre for Microtechnology and Surface Analysis

Centre for Microtechnology and Surface Analysis manufacture nanofilm and nano/micro-structured surfaces by top-down methods such as molecular vapour deposition (MVD) and laser ablation. No nanoparticulate material is believed to be produced as by-products of these processes. The centre does not use or produce nanoparticles, nanofibres or nanoflakes in other ways either. The centre does not know whether nanoparticles, nanofibres or nanoflakes can be produced during use, wear or destruction of the materials.

4.1.5 Centre for Chemistry and Water Technology

The particle lab at Centre for Chemistry and Water Technology does physical and chemical characterization of various types of nanomaterials. The Centre also synthesizes nanoparticles for R&D projects, mainly silver, gold or silicates. The amount of material handled is in both cases very small (grams). All materials are treated as hazardous chemicals in regard to both handling and disposal.

4.2 Dyrup A/S

4.2.1 Company description

Dyrup A/S is a major Danish producer of exterior and interior paints, stains and impregnations for wood surfaces. The company employs approximately 500 people in Denmark and has production facilities in Søborg and Kolding. Most of the employees handle nanomaterials.

4.2.2 Customers

Dyrup's paints are sold to both industrial users (e.g. windows producers), professional users (professional house painters) and DIY (do it yourself) consumers.

4.2.3 Nanomaterials

The company uses three different types of nanoparticles:

4.2.3.1 Polymeric particles

Acrylic polymeric nanoparticles are the basic binder in conventional paints. Upon curing the particles bind together to form the polymeric network that constitutes a dry paint.

Acrylic polymeric particles are thus a major component (>10%) in all paints. The particles are non-aggregated and app. 50 nm - 200 nm in size.

Dyrup handles more than 100 tons of this material per year.

4.2.3.2 Inorganic pigments

Metaloxide nano- and microparticles are widely used as pigments in conventional paints. Dyrup's most commonly used pigments are TiO₂ (white) and Fe₂O₃ (red). Besides giving colour the inorganic pigments also acts as UV absorbers.

Pigments are usually present in paints in concentrations about 1 percent (0.1-10%). The particles are often aggregated and the primary particle size usually 100 nm – 1 µm. The trend in the paint industry is to use smaller particles (nanoparticles), which can give the same effect (colour and UV absorption) in smaller (weight) concentrations.

Dyrup handles 10-100 tons of inorganic pigments per year.

4.2.3.3 Silicates

Amorphous silica (SiO₂) nanoparticles are used to improve the stability and rheological properties (viscosity) of paints.

Silicate is used as an additive in concentrations less than 0.1%. The particles are non-aggregated and 10-20 nm in size (specific surface area 50-200 m²/g). Dyrup handles 1-10 ton silica per year.

Apart from these three types of nanomaterials, Dyrup also to a minor degree uses carbon black as a paint pigment.

4.2.4 Handling of nanomaterials

4.2.4.1 Procedures

Dyrup receives material safety data sheets (MSDS) for all ingredients they purchase. The MSDS are used to define the procedures for safe handling of the chemicals at Dyrup's facilities. The MSDS contain information on the chemicals in general but no information specific to materials as nanoparticles. Dyrup has no specific guidelines for handling nanomaterials compared to chemicals in other forms.

4.2.4.2 Processes

The ingredients for Dyrup's paint formulations are purchased from different vendors and mixed by Dyrup's facilities. Dyrup mainly uses wet processes. The polymeric binder particles can only be handled in suspension. Inorganic pigments are usually purchased as pastes (suspensions with a very high concentration of solids). Silicates are also purchased as suspended particles. In the past Dyrup has obtained many of their pigments as dry powders. However, the company has phased out most of the dry powder processes to improve product quality and working environment. The only remaining dry powder material is carbon black which is handled on a minor scale. The handling of dry pigments is undertaken in closed containers and closed production units.

4.2.4.3 Safety measures

Mechanical ventilation is used throughout the production, due to the presence of organic solvents. Gloves and breath masks are used when indicated in the MSDS.

4.2.4.4 Waste handling

At Dyrup waste is handled according to these regulations:

- Dry paint as regular waste.

- Liquid material (waste paint and suspensions) is classified as hazardous waste and sent to Kommunekemi for destruction.
- Water used to wash containers is handled as common waste water

4.2.5 Product life cycle

Dyrup's products are distributed with information about contents and instructions for use. These instructions do not contain information about content of nanoparticles. The application of the products depends on the customer group:

- Industrial customers usually spray paint their products in closed automated systems.
- Professional and DIY users usually use brushes for application. Some users may use spray.

Ultimately, Dyrup's products end as dry paint on wood. In the case of exterior paint it will gradually break down and some of the constituent be released to the environment. Painted furniture and interior paint is likely to end as regular waste.

4.2.6 Possibilities of nanomaterial exposure

4.2.6.1 Possibilities of worker exposure

Since Dyrup mainly uses wet processes there is probably no exposure to airborne nanoparticles. In the dry powder handling (carbon black) the process is done in a closed system to avoid worker exposure. When nanoparticle suspensions dry a solid matrix (dry paint) is formed. In that case the nanoparticles are assumed to be embedded in the dry matrix

4.2.6.2 Possibilities of user exposure

Industrial users normally use spray paints in closed systems minimizing worker exposure. Professional and DIY users most often use brushes and paint rolls. For these "wet" applications the company assumes the exposure to airborne nanoparticles to be minimal, based on general particle chemistry considerations. In some cases professional and DIY users may use spray application. In this case there may be a risk for exposure to aerosols containing nanoparticles.

4.2.6.3 Possibilities of environmental exposure

Waste water used to clean empty paint containers is classified as common waste water. Waste water from Dyrup's production thus contains suspended nanoparticles. Waste water from paint users will most likely also contain nanoparticles originating from paints.

In principle airborne nanoparticles originating from paint may be produced whenever painted products are burned. The company has no knowledge of the extent to which this occurs.

When exterior paints are degraded through environmental exposure (rain, sun and microbiology) there is in principle a possibility for leaching of nanoparticles. Based on general particle chemistry considerations it is believed that in this case the nanoparticles will stay bound in micrometer-sized aggregates.

4.2.7 View on guidelines and regulation

Dyrup is aware of the risks related to the handling of fine powders. It is one of the reasons the company prefers to use wet processes, which they believe are safe. However, the company would welcome clear information on any potential hazards in the present handling procedures for fine particles. The company prefers regulation and legislation to follow a precautionary approach. Dyrup wants to use new nanomaterials for improving their products and nanotechnology to avoid having an ill reputation in the public, such as the biotechnological use of gene modified organisms (GMO) has. Therefore, the company prefers an early regulatory, so that regulations are rather too strict than too lax.

4.3 Haldor Topsøe A/S

4.3.1 Company description

Haldor Topsøe produces solid phase catalysts primarily for use in the chemical industry, cleaning of exhaust gasses, and cleaning and upgrading of petroleum products in the petrochemical industry. The company employs 1350 people in Denmark. The company has production facilities in Frederikssund. R&D and administration is located at the Lyngby headquarter.

4.3.2 Customers

The company's products are sold to industrial customers (business to business).

4.3.3 Nanomaterials

The catalysts produced by Haldor Topsøe falls in the category of nanoporous structures. The catalysts consist of pellets/extrudates of a support material (e.g. Al_2O_3) with an active phase. The pellets are made from microparticulate powder (particle size $\sim 1 \mu\text{m}$). The active (nanoparticulate) phase is formed *in-situ* inside the porous structure and is so strongly bound to the support material that it is incorporated in the structure.

As a consequence nanoparticles, nanofibres or nanoflakes are not used or produced in Haldor Topsøes production of nanoporous structures.

However, the R&D departments occasionally handle small quantities of suspended nanoparticles for research purposes.

4.3.4 Handling of nanomaterials

The R&D departments handle small quantities of suspended nanoparticles for research purposes.

4.3.4.1 Instructions for use

When chemicals are introduced in the Haldor Topsøe R&D departments, instructions for use are adapted to local conditions in Safety Data Sheets (SDS) for the working place. The instructions are based on the distributor's SDS cross checked with relevant knowledge from literature sources.

4.3.4.2 Risk assessment of nanomaterials

Haldor Topsøe closely follows the development of standard methods for risk assessment of nanomaterials. For example:

- ISO Technical Committee in Nanotechnologies (TC229)
- American National Standards Institute - The Nanotechnology Standards Panel (ANSI-NSP)
- American Society for Testing and Materials (ASTM). E56: standards and guidance materials for nanotechnology & nanomaterials
- OECD development of test guideline
- CEN
- Nanosafe projects.

The company is aware of recent research on the health and environmental effects of nanomaterials, from which it is concluded that airborne nanoparticles and fibres pose the most prominent health hazards.

4.3.5 View on guidelines and regulations

4.3.5.1 General view on regulations

The present legislation requires suppliers of chemicals to provide all relevant information needed for user to be able to assess the hazards for working with a specific chemical. Therefore, if there is any risks specially related to the nano-form of the chemical these should be stated in the MSDS.

Since the health and environmental risks of nanomaterials depend strongly on their form (e.g. airborne nanoparticles pose a much greater potential risk than nanoparticles embedded in a solid matrix) regulatory efforts on nanomaterials should therefore address only the material forms that pose risks.

4.3.5.2 Access to information

Haldor Topsøe is a member of Danish Standard's Forum on Nanotechnology. Through the forum, the company is updated on the various international efforts on assessing the risks of nanomaterials and suggestions for working practices.

To ease the accessibility of relevant information, the company recommends that the homepage of the Danish Working Environment Authority (Arbejdstilsynet, www.at.dk) link to:

- International guidelines for work involving nanomaterials
- International suggestions on exposure limits
- Guidelines on exposure control (e.g. ISO)
- Relevant reports on nanotechnology in the working environment

4.4 Aalborg Portland A/S

4.4.1 Company description

The Aalborg Portland Group develops and produces cement and concrete. The company employs more than 1100 people in Denmark within research, production, administration, sales and marketing.

4.4.2 Customers

The company's products are sold in a large range of countries and used in most Danish buildings and constructions.

4.4.3 Nanomaterials

The main properties of cement and concrete are governed by phenomena and structures on the nanoscale. For instance, the finalized concrete is a nanoporous structure.

Commercially available silica nanoparticles (Microsilica) with a grain size of 100-200 nm are used in the production of concrete. In dry form the used silica nanoparticles are aggregated with an aggregate size above 100 nm. When dispersed in water the aggregates break up into primary particles smaller than 100 nm. The specific surface area of the particles is in the range 200-1000 m²/g.

Furthermore, the company is involved in significant research activities (e.g. project FUTURECEM in cooperation with iNANO and GEUS) to use nanoscience to improve the properties of cement and concrete and to develop entirely new materials. The research activities include the use of nanoclay (nanoflakes). It is the intention, to incorporate the nanoparticles in commercial products.

4.4.4 Handling of nanomaterials

The silica nanoparticles used in production are handled as dry powders. In the dry form the particles are aggregated as larger particles. The clay nanoparticles are used in aqueous suspension. The company is aware of the risks concerned with airborne nano- and microparticles. The production is ISO certified on environmental and working environmental safety. As part of the certification gravimetric measurements of airborne dust concentration have been made.

4.4.5 Possibilities for nanomaterial exposure

The health risks of exposure to airborne particles (section 1.4.1) are well known in the industry.

4.4.5.1 Possibilities for worker exposure

Since the particulate materials are handled as dry powders there is a risk for worker exposure to airborne particles (aggregates of silica particles). This is similar to the other materials used (cement, fly ash).

4.4.5.2 Possibilities for user exposure

The risk for exposure to fine dust also applies to both industrial and consumer use of cement.

4.4.5.3 Possibilities for environmental exposure

During production and use of the products nanoparticulate dust can escape either as airborne particles or suspended in waste water. In both cases the levels are believed to be so low that effects are negligible.

4.4.6 View on guidelines and regulation

The opinion of the company is that the present legislation sufficiently covers nanomaterials. In regard to guidelines, the company wants information on how to handle nanomaterials, to be as easily accessible as information on handling other materials. They do therefore not want nano-specific guidelines, but nano-related information incorporated into general material handling information, e.g. MSDS.

4.5 Company A

4.5.1 Company description

Company A is a Danish production company in the paints & ink industry. The company employs between 50-100 people and mainly produces ink for printing purposes.

4.5.2 Customers

The company's customers are printing companies, for e.g. printing on food packaging.

4.5.3 Nanomaterials

The company uses three different types of nanoparticulate material:

4.5.3.1 *TiO₂ nanoparticles*

Titanium dioxide (CAS no. 13463-67-7⁶) microparticles are used as white pigment. The particles are believed to have a broad size distribution around 0.5–1 µm. The fraction of particles, which can be classified as nanoparticles (<100 nm) is thus believed to be small. The company handles in total approximately 300 tons of TiO₂ per year, however only a small fraction of this falls within the usual definition of nanoparticles.

4.5.3.2 *Amorphous silicate nanoparticles*

Amorphous silicate particles are used to control the gloss of the ink. The size distribution of the particles is unknown. The company handles 6 tons of silicate per year; it is unknown how large a fraction of this is nanoparticles.

4.5.3.3 *Carbon black*

Carbon black is used as black pigment. The company handles carbon black in the form of nitrocellulose coated carbon nanoparticles. The purpose of the coating is to improve the dispersive properties of the dye. The company handles 100-1000 kg carbon black per year.

4.5.4 Handling of nanomaterials

4.5.4.1 *Processes*

All the company's nanomaterials are purchased as powders and subsequently dispersed in solvent. The powders are handled either in 25 kg bags which are cut open manually, whereupon the content is dispersed in solvent or as big-

⁶ This CAS no refers to a mixture of two crystalline phases of TiO₂, rutil and anatase.

bags which have a semi-closed system for transferring the powder into the dispersing solvent.

4.5.4.2 Safety measures

The company's main focus areas regarding safety are volatile organic compounds (VOC) and fine dust. As a consequence mechanical ventilation is employed at all stages in production. Gloves and breath masks are worn when handling the powders.

4.5.4.3 Waste handling

Empty bags containing small amounts of material are disposed as regular waste. Whole bags and misproductions are disposed as hazardous waste.

4.5.5 Product life cycle

The company's products are not sold to consumers. Most are used by professional printing companies. These companies use the inks in automatic printing systems. In the printing process the inks dry. Based on general particle chemistry considerations, the company does not believe any nanomaterials are released in this process.

Since much of the printing is done on packaging material, the printed material (containing company A's products) end relatively fast as regular waste. The company has no knowledge whether nanoparticles are released from the ink when printed products are destroyed.

4.5.6 Possibilities of nanomaterial exposure

4.5.6.1 Possibilities of worker exposure

Workers at company A are exposed to airborne nanoparticles when handling dry powder raw material, especially when handling 25 kg bags rather than big-bags. This exposure is limited by ventilation and by dust masks worn by the workers.

Workers at company A are also exposed to suspended nanoparticles, which are contained in the company's products. This exposure is limited by gloves worn by the workers.

4.5.6.2 Possibilities of user exposure

The users of the company's products are exposed to suspended nanoparticles in the products and airborne nanoparticles when the products are used in spraying processes.

Only professional companies use the company's products.

4.5.6.3 Possibilities of environmental exposure

Water used to clean empty containers is classified as hazardous waste (due to content of VOC). Nanomaterials thus normally do not come into company A's waste water except in situations where e.g. employees get some material on their hands and subsequently wash them.

Ceramic dust filters are mounted in the exhaust from rooms where fine dust is handled. The supplier states that these filters stop all particles, so that no particles are emitted to the environment.

The possibility for environmental exposure from company A's customers, depend on their exposure control measures.

In principle airborne nanoparticles originating from ink might be produced whenever printed materials are burned as waste. The extent to which this occurs is unknown.

4.5.7 View on guidelines and regulation

Company A lacks knowledge on nanomaterials in order to express a view on the need for guidelines or regulation. The company looks forward to the outcome of the Nanokem project on nanoparticles in the paint & lacquer industry [21] which will be completed in 2010. The main research partner in the project is the Danish National Research Centre for the Working Environment (Forskningscenter for Arbejdsmiljø).

4.6 Persano Group A/S

4.6.1 Company description

Persano is a cosmetic and healthcare company which develops and produces a wide range of products for international companies. The company has approximately 200 employees and production facilities situated at two different sites. In Stenløse west of Copenhagen the company has placed the tablet production of pharmaceuticals and food supplements. All liquid and cosmetic production is situated in Blistrup in northern Sealand.

4.6.2 Customers

Persano does not market or sell own products, but only act as a contractor for international cosmetics and pharmaceutical companies for whom the company performs development, production and filling. The company's products are thus ready-made consumer products sold under the contractor's name.

4.6.3 Nanomaterials

The company only uses one type of nanomaterial: Nanoparticulate TiO_2 used as UV absorber in sunscreen. TiO_2 nanoparticles (CAS no. 13463-67-7) are present in sunscreen with "physical filter" in concentrations of 0.1-10%. The particles are aggregated and the primary particle size is 10-20 nm. The specific surface area is 50-200 m^2/g . Persano handles 1-10 tons of TiO_2 nanoparticles per year.

4.6.4 Handling of nanomaterials

4.6.4.1 Processes

TiO_2 nanoparticles are purchased as a powder. The powders are handled in 25 kg bags which are cut open, hereafter the content is dispersed in the lotion that constitutes the sunscreen base.

4.6.4.2 Safety measures

Handling of powders takes place in a closed ventilated section. Workers wear gloves and dust masks when handling nanopowder.

4.6.4.3 Waste handling

Water used to wash containers is handled as common waste water. Empty bags containing small amounts of material are disposed as regular waste. Whole bags and miss productions are disposed as hazardous waste.

4.6.5 Product life cycle

Persano's sunscreen products are ready-made consumer products. The products are not declared as 'nano-products'. The labelling states that the sunscreen contains 'physical filter'.

When consumers use sunscreen containing nanoparticulate TiO₂ some nanomaterial is released to the environment when bathing. Remaining nanomaterial is washed off and released to waste water during showering. Unused sunscreen is normally disposed of by consumers as regular waste.

4.6.6 Possibilities of nanomaterial exposure

4.6.6.1 Possibilities of worker exposure

Workers at Persano are exposed to airborne nanoparticles when handling dry powder raw material. This exposure is limited by handling powders in closed ventilated room and by dust masks worn by the workers.

Workers at Persano are also exposed to suspended nanoparticles, which are contained in the company's products. This exposure is limited by using gloves.

4.6.6.2 Possibilities of user exposure

Use of sunscreen implies that the skin of the user is directly exposed to suspended TiO₂ nanoparticles. If nanoparticles are used in products with spray application, the user might be exposed to airborne nanoparticles (Persano no longer produces sunscreen spray products containing nanoparticles).

4.6.6.3 Possibilities of environmental exposure

TiO₂ nanoparticles are released directly to the aqueous environment when sunscreen users bathe in sea or lakes. Nanoparticles are also released to waste water when sunscreen users shower.

In principle airborne nanoparticles originating from sunscreen might be produced whenever unused sunscreen is burned as waste. The company has no knowledge of the extent to which this occurs.

4.6.7 Toxicology

Nanoparticulate TiO₂ is one of the best described nanomaterials in the scientific literature. The availability of literature has allowed Persano to assess the toxicology of the material when used in sunscreen. The toxicological assessment is based on international reports and scientific literature on TiO₂ in its nanoparticulate form.

In a scenario where a sunscreen user uses 36 g sun lotion per day, Persano has calculated a Margin of Safety⁷ (MoS) for negative health effects of nanoparticulate TiO₂ of 6250. Since no scientific reports have shown penetration of TiO₂ nanoparticles through undamaged skin, the calculated MoS is based on an assumption that the skin is damaged. From this very high MoS for damaged skin Persano concludes that nanoparticulate TiO₂ contained in their sunscreen products is harmless. Furthermore, Persano quote research showing that subcutane injected TiO₂ nanoparticles are eliminated in the phagocytic barrier and thus not systemic available⁸.

Persano has previously produced a pump-spray sunscreen product containing a low concentration of TiO₂ nanoparticles. In a scenario where this product is sprayed once towards the face of the user, Persano calculated a MoS of 388000. From this very high MoS Persano concludes that nanoparticulate TiO₂ contained in their pump-spray sunscreen products is harmless. However, to avoid any negative publicity due to public focus on the potential hazards of airborne nanoparticles, the Persano's contractor decided to remove nanoparticulate TiO₂ from the spray products.

4.6.8 View on guidelines and regulation

The company believes they have gained sufficient knowledge on the nanomaterial, they work with from international reports and scientific literature. As a consequence the company sees no need for new guidelines on nanomaterials.

The company is of the opinion that the present legislation on perfume and cosmetics sufficiently covers their use of nanomaterials in products.

4.7 Unisense

4.7.1 Company description

Unisense produces microsensors and measurement systems for a range of applications, primarily for scientific and/or medical use. The company is located in Århus and has approximately 20 employees.

4.7.2 Customers

The company's customers are professional users primarily in research institutions, health services or companies in the medical industry.

4.7.3 Nanomaterials

Parts of the company's microsensor products are nanoporous structures or nanostructured surfaces. No nanoparticles, nanofibres or nanoflakes are used or produced in the manufacture of these nanostructures. The company does therefore not have industrial scale use or production of nanomaterials.

However, the company has R&D activities on nanoparticles, and is currently involved in a project together with the University of Copenhagen on

⁷ The margin of safety expresses the distance from harmful dose. Normally a MoS > 100 is preferred.

⁸ T. J. Miller *et al.*, The FASEB Journal 21:730.10 (2007)

development of a sensor, which incorporates fluorescent nanoparticles. The fluorescent nanoparticles are used in very small quantities, less than 1 mg per sensor.

4.7.4 Handling of nanomaterials

4.7.4.1 Processes

The fluorescent nanoparticles are acquired from the university suspended in organic solvent. The nanoparticles are then deposited on the sensor and subsequently embedded in a solid matrix.

The nanoparticle based sensor is tested for leaching of nanoparticles, which would detriment the function of the sensor. This test is relatively simple since the nanoparticles fluoresce.

4.7.4.2 Safety measures

Since the nanoparticles are suspended in organic solvent they are handled in fume cupboards. The finalized sensor, in which the nanoparticles are embedded in a solid matrix, is to be used under ambient conditions.

4.7.4.3 Waste handling

All nanoparticles containing waste is handled as hazardous waste.

4.7.5 Possibilities of nanomaterial exposure

4.7.5.1 Possibilities of worker exposure

Workers at Unisense are exposed to suspended nanoparticles. The suspended nanoparticles are handled in fume cupboards and workers would normally wear protective gloves.

4.7.5.2 Possibilities of user exposure

Unisense has no nanoparticle containing products at the moment. For the future nanoparticle based sensor, the user exposure will be limited since the nanoparticles are embedded in a solid matrix from which they can not leach. Users would thus not be exposed to nanoparticles except in extreme situations where the sensor is opened or broken by accident – and even in that case the nanoparticles would most probably still be embedded in fragments of the surrounding material.

4.7.5.3 Possibilities of environmental exposure

No nanoparticles are released to ordinary waste or wastewater from Unisense. No nanoparticles are expected to be released from future users of the company's nanoparticle based sensors since the particles are embedded in a solid matrix.

4.7.6 View on guidelines and regulation

The company perceives no need for new guidelines or regulations on nanomaterials.

5 Results

The results presented in this section are based both on the received questionnaires, the interviews presented in the previous section, and additional interviews conducted by telephone. In some cases the conclusions are illustrated by citations from the interviews, the citations are put in quotation marks and written in *italics*.

As presented in section 3.5 responses were received from 24 companies using nanotechnological materials. Of the 24 companies 16 companies work with nanoparticles, nanofibres or nanoflakes.

5.1 Nanotechnological companies

5.1.1 Size of companies

The distribution in size of the 24 nanotechnological companies is shown in figure 5.1. As it can be seen from the figure the companies have a large variation in size.

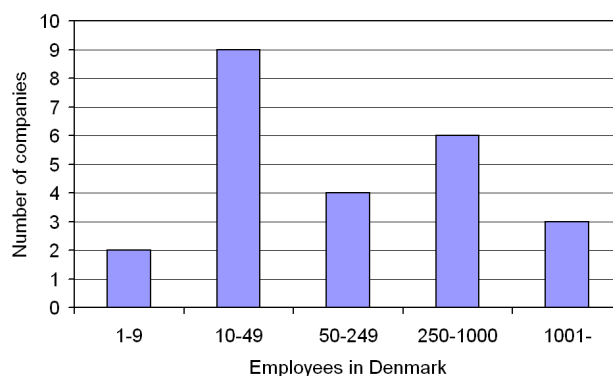


Figure 5.1. Number of employees in responding companies working with nanomaterials.

5.1.2 Activities

The companies are broadly distributed over many different industrial areas, see table 5.1.

Industry	Number of responding companies ⁹	End products	Nanomaterials
Paints & inks	3	Paint, wood protection systems, inks	Metal oxide pigments (nano and microparticles, >100 tons per year) Carbon black nanoparticles (tons per year) Polymeric nanoparticles (>100 tons per year) Silicate nanoparticles (kg - tons per year)
Coatings	6	Coatings	Nanofilm Nanoparticles (metaloxides, metal nitrides, silicates) (kg per year)

⁹ Some of the responding companies are active in more than one industry.

Cosmetics	3	Sunscreen, zinc balm	Nanoparticulate TiO ₂ (kg – tons per year) Nano- and microparticulate ZnO
Pharma & biotech	2	-	Nanoparticles: R&D level (<1 kg per year)
Optics	3	Optical fibres, nanoimprint stamps, nanolabels	Nanoporous structures, Polymeric nanofibres (<1 kg per year)
Sensors	5	Nano and microprobes	Nanostructured materials Nanofilm Nanoparticles (<1 kg per year)
Catalysts	1	Catalysts	Nanoporous structures Nanoparticles (R&D level, <1 kg per year)
Concrete	1	Cement, concrete	Nano and microparticulate silicates, nanoclay nanoflakes (R&D level)
Textile	2	Textile and nonwovens	Carbon black nanoparticles (>10 tons per year) Nanofibres (R&D level) Silver nanoparticles (R&D level)

Table 5.1. Industries or companies responding that they use or produce nanomaterials.

For 9 of the 16 companies that use nanoparticles, nanofibres or nanoflakes the extent of the use is low or at R&D level (<10 kg per year). Large scale use of nanomaterials (>100 kg per year) is restricted to 7 companies using nanoparticulate powders and suspensions in the paint & ink, concrete, textile and cosmetics industries. The nanomaterial containing products of these 7 companies are traditional products that have been on the market for many years (for example cement, paint or sunscreen) The companies were not asked about the production volume of nanostructured surfaces, nanofilm or nanoporous structures.

The 16 companies working with nanoparticles, nanofibres or nanoflakes were asked in which context the materials were used. The distribution of answers is illustrated in figure 5.2. As seen from figure 5.2 the companies mainly use nanomaterials in their processes (e.g. when nanoparticles are used in paint or sunscreen) or have R&D activities on nanomaterials. Only one company reported the nanomaterial to be the endproduct, this product was produced on a very small scale (<1 kg per year).

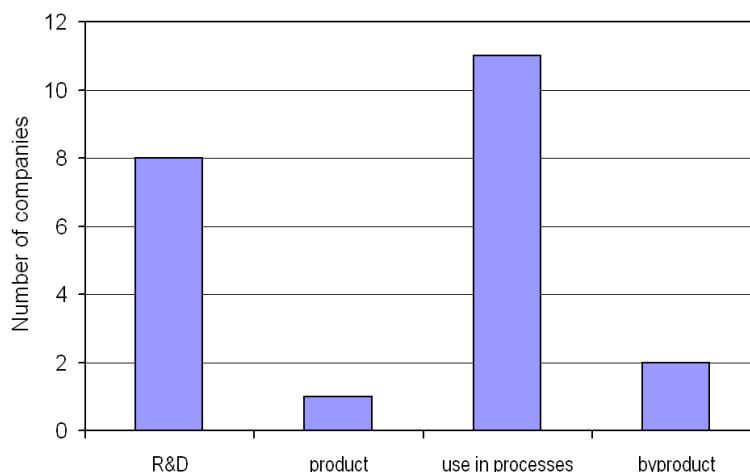


Figure 5.2. Context in which companies handle nanomaterials (nanoparticles, nanofibres or nanoflakes).

The Technology Foresight on Danish Nanoscience and Nanotechnology in 2004 [18] predicted a steep rise in industrial activities on new applications of nanomaterials in Denmark. Judging from the responses of the present survey the pace for new industrial applications of nanomaterials within the last three

years seems less rapid than predicted. New applications of nanomaterials are restricted to small scale or R&D use and have not yet reached a scale of production requiring the use of more than 1 kg of nanomaterial per year. However, no conclusions on future usage and applications of nanomaterials in Denmark can be made on the basis of the present study.

5.2 Nanotechnological materials

The number of companies working with the different types of nanotechnological materials is illustrated in figure 5.3 (some companies work with more than one type).

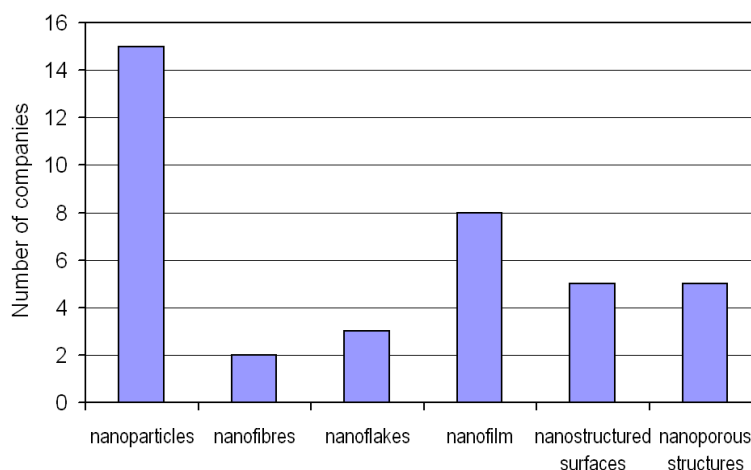


Figure 5.3. Number of companies working with different types of nanomaterials (some companies work with more than one type).

The nanomaterials used within different industrial areas are summarized in table 5.1.

5.2.1 Nanoparticles

As seen from figure 5.3 nanoparticles is the most widely used type of nanotechnological material. The nanoparticulate materials used in largest quantities are polymer particles, metal oxides, silica and carbon black. Metal oxide, silica and carbon black nanoparticles are handled both as powder and suspended in liquid. Polymer nanoparticles are only handled in suspension.

All other nanoparticulate materials are only used in small quantities or in R&D context (<1 kg per year). The composition of the nanoparticles used in R&D context is reported as metal oxides, metals or polymers (if not kept secret).

Table 5.2 summarizes the nanoparticulate materials for which the specific chemistry was identified. Except for the polymer nanoparticles, which are the main constituent of paints, all materials used on large scale (>100 kg per year) is included in table 5.2.

Nanoparticulate material	CAS No	Industrial area (sizes)	Scale
TiO ₂ (rutil+anatase)	13463-67-7	Cosmetics (10-20 nm) paints & inks (nano/microparticles)	>1 ton per year >100 tons per year
TiO ₂ (anatase)	1317-70-0	Coatings (9-25 nm)	<1 kg per year
Fe ₂ O ₃	1309-37-1	Paints & inks (nano/microparticles)	>100 tons per year

Carbon black	7440-44-0	Paints & inks (nanoparticles) Textile (nanoparticles)	>1 ton per year >10 tons per year
Silica (amorphous)	7631-86-9	Paints & inks (10-20 nm) Coatings (10-25 nm) Concrete (100-200 nm)	> 1 ton per year kg per year not reported
ZnO	1314-13-2	Cosmetics (nano/microparticles)	not reported
Ag	7440-22-4	Coatings (nanoparticles) Textile (nanoparticles)	< 1 kg per year < 1 kg per year
Cu	7440-50-8	Coatings (nanoparticles)	< 1 kg per year

Table 5.2. Specifically identified nanoparticulate materials.

The particle size of the used materials varies from approximately 10 nm and up. In the case of metaloxide pigments in the paints & ink industry, silica in the concrete industry and zinc oxide in the cosmetics industry the medium particle size of the particulate materials used is far above the upper size limit (100 nm) of the usual definition of nanomaterials. However, the particle size distribution of the used materials is by the companies estimated to be so broad that an unknown fraction of the particles falls within the usual definition of nanoparticles.

The specific surface area was unknown for all other nanomaterials than silica nanoparticles. For the used silica nanoparticles the surface area stated by the supplier depends on application and varies from 50-300 m²/g.

When nanoparticles are obtained from a supplier (which is the case for all materials used outside R&D context) the particle size, particle size distribution and specific surface area is either given by the supplier or unknown. In the case of materials with a medium particle size above 100 nm, the content fraction of particles <100 nm is in all cases unknown. Four companies have stated in interviews that they occasionally measure particle size by various methods. No companies routinely measure particle size of all their materials

5.2.2 Other types of nanomaterials

Very few companies reported that they work with nanofibres or nanoflakes. The nanofibres used are polymeric or glass fibres. No companies work with nanotubes. The used nanoflakes are all nanoclays. No physical characteristics (size, shape, surface area etc.) of these materials were reported.

13 companies report that they work with nanofilm, nanostructured surfaces or nanoporous structures. These companies were asked whether nanoparticles, nanofibres or nanoflakes were *used* to make the materials or *released* in the process of making the materials.

- 4 companies *use* nanoparticles to produce nanofilm, nanostructured surfaces or nanoporous structures.
- 2 companies report that nanoparticles are *released* in the process of making nanofilm, nanostructured surfaces or nanoporous structures.
- None of the 13 companies reported that they used or released nanofibres or nanoflakes.

5.3 Handling of nanomaterials

5.3.1 Instructions for use

All companies report that nanomaterials are handled according to the legislation on substances and materials in the working environment. No companies report that they use a special set of written guidelines when handling nanomaterial as opposed to handling of other chemicals.

All companies obtaining their nanomaterials from a supplier use the MSDS from the supplier to define how the material should be handled. Five of the interviewed companies state that they seek further information from technical datasheets or open literature to define more accurate instructions for use of the material.

5.3.2 Employee uncertainty

Only one company has reported to have knowledge of or an impression that employees are uncertain or insecure about the handling of nanomaterials.

5.3.3 Knowledge level

5.3.3.1 Knowledge on physical characteristics

The level of knowledge on the physical characteristics of the nanomaterials, the companies are working with, is often limited. Most companies rely solely on the information provided by the supplier with regard to particle size, surface area, etc. The supplier information about physical characteristics is often placed outside the MSDS in technical datasheets, only available upon special request or unavailable. Very few companies analyse these parameters themselves. Four companies state in interview that they occasionally analyse particle size. The methods used vary but includes: Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), SMPS (Scanning Mobility Particle Sizer), Laser Diffraction (LD) and Dynamic Light Scattering (DLS). No companies measure particle surface area.

Several companies are handling materials, not knowing whether they should be classified as nanomaterials. This is for example often the case for metal oxide pigments, which are usually micro and/or submicroparticles with broad particle size distributions – *“We don’t know the particle size distribution. Based on the dispersive properties, we expect the distribution to centre about 1 µm with a very broad distribution, so there is probably a fraction of nanoparticles in the material”*.

Approximately half the interviewed companies expressed an interest in having “nano-related” information on physical characteristics (particle size, surface area etc.) included in the MSDS.

5.3.3.2 Knowledge on health & environmental effects

Knowledge on health and environmental effects of nanomaterials stems almost exclusively from supplier statements on MSDS, *“We expect our supplier to provide this type of information”*. When the companies seek additional information the focus is mainly on the practical side of handling the materials (cf. section 5.3.1). With the exception of Persano, the companies do not make toxicological assessments of their materials.

The basis for determining the toxicology and ecotoxicology of the used nanomaterials is thus (with one exception) the supplier's statements on the MSDS. In this study we could only get access to a few of the MSDS, which the companies' referred to. In these MSDS the information on on toxicology and ecotoxicology are very sparse: *"No data available on ecotoxicological effects"*, *"the chemical, physical and toxicological properties of this material have not been sufficiently investigated"*.

With two exceptions, all the interviewed companies believed they had sufficient information on health and environmental effects of their nanomaterials in the MSDS. Assuming that the level of information of the few MSDS on nanomaterials accessed in this study is representative of the level of information generally in the MSDS, it might seem quite surprising that the companies believe they have sufficient information on the subject. However, the companies generally appears to be more interested in practical information on how to handle the material in order to avoid exposure than information on the possible effects of exposure.

Furthermore, a recent study has shown that the information in the MSDS is often based on the material in bulk rather than nano form [17]. This might be noteworthy since the MSDS as stated above form the basis of knowledge in the companies on the properties of the materials.

5.3.4 Processes

The type of process used for working nanotechnological materials depends on the type of nanotechnological material. The distribution of process types is illustrated in figure 5.4.

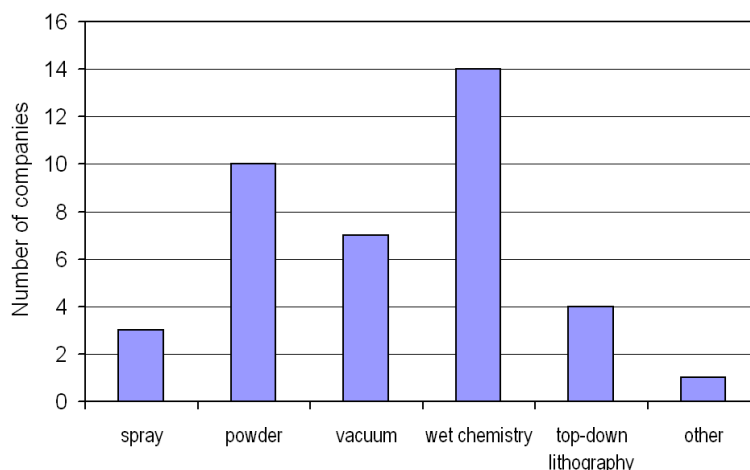


Figure 5.1. Type of process used with nanotechnological materials.

Vacuum and top-down lithography are used for nanostructures, i.e. nanofilm or nanostructured surfaces. When working with nanoparticles, nanofibres or Nanoflakes, spray, powder and wet chemistry processes are used.

5.3.5 Safety measures

When nanomaterials are used in R&D context, the materials are normally handled in fume cupboards.

No companies have reported large scale use of nanofibres or nanoflakes. Apart from nanostructured surfaces, nanofilms and nanoporous structures, nanoparticulate powder and suspended nanoparticles are thus the types of nanomaterials handled on larger (>1 kg per year) scale.

The safety focus of the industry is mainly on nanoparticulate powders. These powders are being handled on large scale in the paint & ink, concrete, textile and cosmetics industries. These industries have handled fine and ultrafine (nanoparticulate) powders for decades – *“long before anyone started calling it nanotechnology”*. All companies, handling nanoparticulate powders on large scale, install ventilation and often use breath protection, where the powders are not handled in closed systems.

With regard to suspended nanoparticles the general perception based on particle chemistry considerations is that once nanoparticles are suspended they can no longer escape to the surrounding air. Therefore, the safety focus with regard to suspended nanoparticles is most often on the solvent. However, gloves and protective clothing are normally worn when handling suspended nanoparticles.

5.3.6 Exposure measurements

Measurements of exposure levels of airborne nanoparticles are not common. Only one company (Aalborg Portland) reports that they have measured the exposure level of airborne nanoparticles.

The paint & ink industry has recently started the “Nanokem” project [21] together with the Danish National Research Centre for the Working Environment (Forskningscenter for Arbejdsmiljø). The focus of that project is to measure the release of airborne nanoparticles, when dry paints are subject to wear and when paint is applied by spray. A similar project involving the plastics industry has recently been launched as well.

5.3.7 Waste handling

Waste containing high concentrations of nanomaterials (e.g. misproductions) or nanomaterial waste containing hazardous chemicals is treated as hazardous waste. In many situations nanomaterial waste is disposed of as regular waste or in waste water. Usually this is the case when:

- The concentration of nanomaterial is low (e.g. water used to wash empty paint containers)
- The nanomaterial is embedded in a solid matrix
- The nanomaterial is aggregated to larger particles

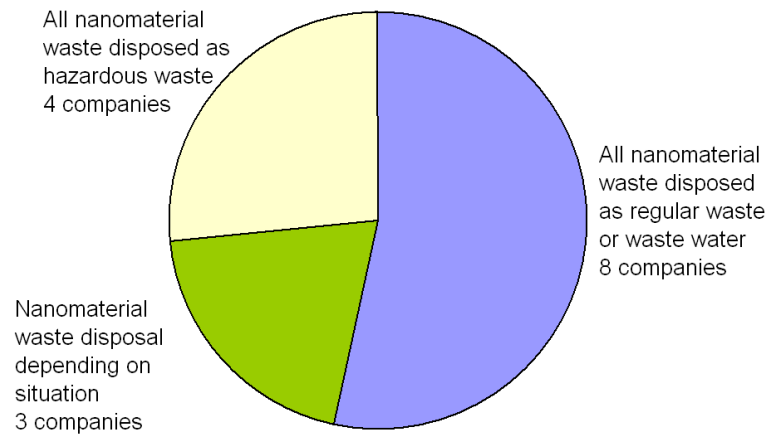


Figure 5.2. Disposal of nanomaterial waste (nanoparticles, nanofibres or nanoflakes).

Most of the interviewed companies state that the amounts of nanomaterial waste are small – “*These materials are expensive, we don’t discard much*”. The handling of nanomaterial waste in the responding companies is illustrated in figure 5.5.

No companies have focus on or knowledge of release of nanomaterials during use, wear or destruction of their products.

5.3.8 Possibilities of release of nanomaterials to the surrounding environment

Approximately half the responding companies report that nanomaterials can be released to the surrounding environment in their processes (figure 5.6), mainly through waste water. Since the nanomaterials are handled according to the rules and legislation on chemicals, the released quantities of material are considered low and harmless and no companies could foresee any environmental consequences of the release.

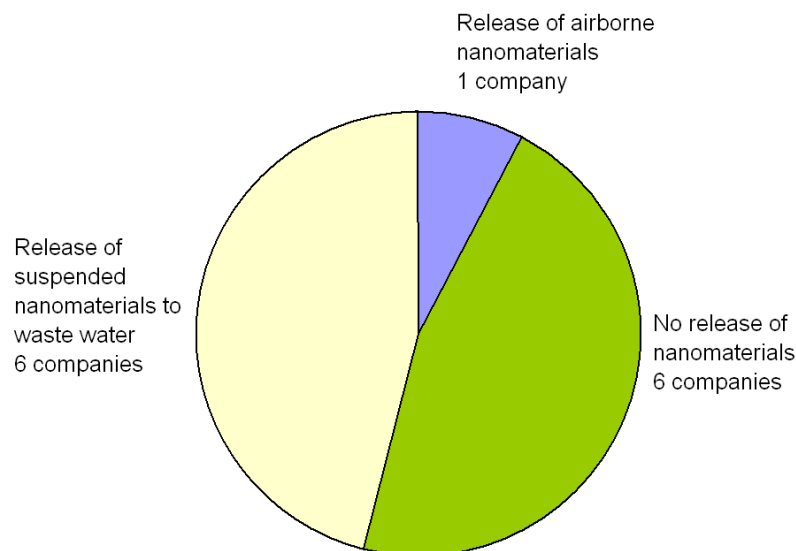


Figure 5.3. Possibility of release of nanomaterials to the surrounding environment during the companies' processes.

5.4 Nanotechnological products

All of the responding companies using nanomaterials outside an R&D context, had products containing nanomaterials. None of the responding companies perceived any nano-related risks to users of their products. With one exception (section 4.1.1.5) no companies had made experiments or measurements to confirm this or evaluated nano-related risks in other ways.

It can be noted that a recent report on consumer products containing nanoparticles or based on nanotechnology [19] names only one Danish producer of such products (sunscreen)¹⁰. Two of the responding companies in the paint & ink industry and three companies in the cosmetics industry report that they produce consumer products containing nanoparticles. All other companies using or producing nanomaterials market their products business to business.

5.4.1 Content of nanomaterials

The content of nanomaterials in nanotechnological products varies and depends on the application. In the paint and concrete industries nanoparticles are major constituents (>1%). In sunscreen nanoparticle content is in the interval 0.1-10%. In coatings the reported contents was in the interval 0.1-10%. In textile the content (when reported) was below 0.1%.

5.4.2 Information to customers

With two exceptions all of the responding companies' nanomaterial containing products was not branded as "nano" products and no information regarding nanomaterial content was given to customers. In the few cases where nanomaterial content was declared only the name of the nanomaterial was given.

5.4.3 Certification

Recently several international nano-certification initiatives have been launched. For example:

- "Nano safe" certification by the Glycemic Research Institute (www.nanocertification.com)
- TÜV CENARIOS® nano-certification system (www.tuev-sued.de)
- "Nano Mark System" certification system initiated by the Taiwanese government (www.taiwan.com.au/Scitech/RandD/Public/20060217.html)

The aim of these certification systems is to certify that the "nano" products are really nanotechnological products, work as claimed, and are safe to use.

None of the responding companies participated in nano-certification.

5.4.4 Possibilities for user exposure

Companies, whose products contain nanomaterials embedded in a solid matrix, see no risk of user exposure to nanomaterials.

¹⁰ The report names two companies: Blumøller and Persano. However, Blumøller's sunscreens containing nanoparticles are produced by a subcontractor.

For products, which contain nanoparticles in liquid suspension, there is a possibility for user exposure. These products are mainly sunscreen, paints, inks and coatings. As to sunscreens, users are in skin contact with suspended nanoparticles. In the case of paints, inks and coatings users may accidentally get in skin contact with the products or be exposed to airborne nanoparticles, if the products are used in a spray application.

No companies have measured exposure levels of nanomaterials during use of their products. With one exception (Persano) no companies have in other ways estimated exposure levels or possible health risks. The paint & lacquer industry as well as the plastics industry have recently initiated research projects together with the National Research Centre for the Working Environment and other partners [21-22] to address the issue.

5.4.5 Possibilities for nanomaterial release during or at the end of product lifetime

In principle, there is a possibility that nanomaterials can be released from products during wear (mechanical wear or outdoor weathering depending on application). The extent to which this occurs is largely unknown.

With one exception (section 4.1.1.5) no companies have measured or in other ways estimated release of nanomaterial from their products during wear or end destruction. The aforementioned research projects initiated by the paint & lacquer industry and the plastics industry [21-22] will also address these issues.

5.4.6 Consumer health risk in relation to nanomaterials and nanotechnological products

Since both the knowledge of possible health risks in relation to exposure to nanomaterials (section 1.4) and knowledge of the possibilities of release of nanomaterials from products (cf. section 5.4.3) are scarce, nothing definitive can be said about health risks to consumers in relation to nanomaterials.

5.4.7 Environmental effects of nanomaterials and nanotechnological products

Very little is known about the environmental effects of release of nanomaterials (cf. section 1.5). Furthermore, very little is known about the release of nanomaterials from products (cf. section 5.4.4).

In general the concentration of airborne engineered nanoparticles is low compared to the concentration of particles produced unintentionally from conventional sources: diesel engines, wood fired stoves and others [3].

5.5 Opinions on guidelines and regulation

The opinions on the need for guidelines and regulation expressed in both the direct and telephone interviews are summarized below.

5.5.1 Definition of nanotechnology – distinguishing between different types of nanomaterials

A very prominent view among the interviewed companies was the need to define nanotechnology more accurately and to distinguish between different

types - “*It seems that for politicians all ‘nano’ is the same thing. It is not.*” A general view was that discussion of guidelines and regulation of nanomaterials requires a more precise definition of nanotechnology and nanomaterials – “*If you look closely enough you will find that everything is ‘nano’, for example this table we are sitting at has plenty of nanostructure*”

Several companies expressed concern that regulation of nanomaterials would not distinguish between type and form of nanomaterial. The general opinion was that:

- Nanostructured surfaces, nanofilm and nanoporous structures do not present any concerns and thus needs no regulation unless “free” nanomaterial is used to make the materials or is produced as byproduct.
- It is very important to distinguish between nanoparticles (nanofibres or nanoflakes) in liquid suspension, embedded in a solid matrix or in powder form, since the properties of nanomaterials depend on the surrounding material (air, liquid or solid)
- Besides material type, it is very important to take chemical composition and modification in to account; for example to distinguish between raw carbon black and carbon black with a protective coating, since the properties of the material depend on these factors.

5.5.2 Nanomaterials and the current legislation

Most companies are of the opinion that the current legislation sufficiently covers nanomaterials since it requires suppliers to provide all relevant information needed for the user to be able to assess the hazards for working with a specific material.

All companies preferred that any regulation of nanomaterials was incorporated in the current regulation of chemicals rather than a separate set of regulations.

Some expressed the view that an early regulatory effort using a precautionary approach, resulting in stricter than necessary regulation, was preferable to a public ‘nano-scare’, an ill reputation of nanotechnology in the public, such as the biotechnological use of gene modified organisms (GMO) has.

5.5.3 Access to information

5.5.3.1 Material Safety Data Sheets (MSDS)

Several companies expressed the view that their suppliers’ MSDS did not always contain all the needed information regarding nanomaterials. Most often MSDS for nanomaterials does not contain ‘nano-specific’ information such as particle size, surface area, tendency for aggregation etc. Often suppliers provide this type of information outside the MSDS in technical data sheets or other documents. Since this type of information is sometimes necessary to assess the hazards for working with a specific material, many companies would prefer ‘nano-specific’ information when available is included in the MSDS – “*We prefer that all relevant information is in the MSDS*”.

No companies had specific requests for how the MSDS format should be changed to include 'nano-specific' information.

5.5.3.2 Guidelines for handling nanomaterials

The interviewed companies' responses to the need for guidelines on the handling of nanomaterials were diverse. Many reported that they felt confident in their procedures and did not need advice or guidelines. Several others would like information and guidelines on:

- assessment of nanomaterial hazard
 - types and forms of nanomaterial posing special nano-related hazard
 - processes posing special hazards
- handling nanomaterials, specifically on
 - safety measures (ventilation, masks, gloves etc.) "*What type of dust mask should we use?*"
 - waste handling

In principle this information is available (e.g. ref. 8-11). However, companies would prefer the information in a simpler format and in the context of general information of handling chemicals in the workplace. Handling of nanomaterials is thus not seen as a separate issue but rather as an integral part of handling chemicals.

6 Bibliography

6.1 Comprehensive reports on the industrial applications and possible risks of nanotechnologies

- [1] “Industrial application of nanomaterials – chances and risks” (Nanosafe project report), Wolfgang Luther (ed.), Future Technologies Division, VDI, Düsseldorf, Germany, 2004
http://www.vditz.de/no_cache/home/publikationen/publikationen_detail/index.html?tx_vdiinfo_pi1%5BshowUid%5D=145
- [2] “Nanoscience and nanotechnologies: opportunities and uncertainties”, The Royal Society & The Royal Academy of Engineering, Great Britain, 2004
<http://www.nanotec.org.uk/finalReport.htm>
- [3] “Opportunities and risks of nanotechnologies”, Christoph Lauterwasser (ed.), Allianz Center for Technology, Munich, Germany, 2004
<http://www.oecd.org/dataoecd/4/38/35081968.pdf>

6.2 Reports on risk assessment of nanomaterials

- [4] ISO/TC 146/SC 2 N 399: Workplace Atmospheres – Ultrafine, nanoparticle and nano-structured aerosols – Exposure characterization and assessment, 2006
<http://www.iso.org/iso/en/CatalogueListPage.CatalogueList?COMMID=3617&scopelist=PROGRAMME>
- [5] “Characterising the potential risks posed by engineered nanoparticles”, Department for Environment, Food and Rural Affairs (DEFRA), London, Great Britain, 2005
http://www.nanoforum.org/nf06~modul~showmore~folder~99999~scid~352~.html?action=longview_publication&

6.3 Recommendations for government

- [6] “Regulering af miljø- og sundhedsaspekter ved nanoteknologiske produkter og processer”, Teknologirådet, 2006
http://www.tekno.dk/pdf/projekter/p06_nanotechnology_rapport.pdf
- [7] “The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies”, Scientific committee on emerging and newly identified health risks (SCENIHR), EU, 2005
http://ec.europa.eu/health/ph_risk/committees/04_scenihhr/docs/scenihhr_o_003b.pdf

6.4 Safe and good practices in the nanotechnology workplace

- [8] ISO/TC 229 N 085: Proposal for a technical report on Occupational Safe Practices Regarding Nanotechnologies, ISO proposal for TR, 2006
<http://engineers.ihs.com/news/iso-nanotechnologies-tc.htm>
- [9] "Approaches to Safe Nanotechnologies", Department of Health and Human services, National Institute for Occupational Safety and Health (NIOSH), USA, 2006
<http://www.cdc.gov/niosh/topics/nanotech/safenano/>
- [10] "Guidance for handling and use of nanomaterials at the workplace", VCI and BAuA, Germany, 2007
<http://www.vci.de/default~cmd~shd~docnr~121215.htm>
- [11] "Nanopartikel an Arbeitsplätzen", Schweizerische Unfallversicherungsanstalt (SUVA), Switzerland, 2006
http://www.suva.ch/home/suvapro/branchenfachthemen/nanopartikel_an_arbeitsplaetzen.htm

6.5 Internal guidelines for nanotechnology workplaces

- [12] "Guide to safe manufacture and for activities involving nanoparticles at workplaces in BASF AG", BASF AG, Germany, 2006
http://www.corporate.basf.com/en/sustainability/dialog/nanotechnologie/mitarbeiter.htm?id=*PRNCA.*bbcp3tb
- [13] "Interim Guideline for Working Safely with Nanotechnology", Texas A&M Engineering, USA, 2005
http://engineering.tamu.edu/safety/guidelines/nanotechnology/NANO_SafeGuideline.pdf

6.6 Surveys on industrial activities on nanomaterials

- [14] "Survey of current practices in the nanotechnology workplace", international survey conducted by the International Council on Nanotechnology, ICON (USA) in 2006
http://icon.rice.edu/projects.cfm?doc_id=4388
- [15] "Aspekten des Arbeitsschutzes bei der Herstellung und im Umgang mit synthetischen Nano-Materialien", German survey by VCI and BAuA, to be completed in 2007
http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/Nanotechnologie/Aktivitaeten.html__nnn=true
- [16] "Voluntary Reporting Scheme for engineered nanoscale materials", UK survey by Department for Environment, Food and Rural Affairs, DEFRA, to be completed in 2007-2008
<http://www.defra.gov.uk/environment/nanotech/policy/pdf/vrs-nanoscale.pdf>

6.7 Other references

- [17] "Evaluation and control of occupational health risks from nanoparticles", Thomas Schneider et al., TemaNord 2007:581
<http://norden.org/pub/velfaerd/arbetsmiljo/uk/TN2007581.pdf>

- [18] " Technology Foresight on Danish Nanoscience and Nanotechnology, action plan, December 2004", Danish Ministry for Science, Technology and Development
<http://teknologiskfremsyn.dk/download/108.ano>
- [19] "Kortlægning af produkter der indeholder nanopartikler eller er baseret på nanoteknologi", Kortlægning af kemiske stoffer i forbrugerprodukter, Nr. 81 2007, Miljøstyrelsen (Danish Environmental Protection Agency)
<http://www.mst.dk/Udgivelser/Publikationer/2007/05/978-87-7052-468-1.htm>
- [20] Staub info, Berufgenossenschaft der keramischen und Glas-Industrie
www.bggglaskeramik.de/d/staub-info/definition/
- [21] "Nanopartikler i farve- og lakindustrien. Eksposering og toksiske egenskaber – NANOKEM"
Danish National Research Centre for the Working Environment
<http://www.arbejdsmiljoforskning.dk/Aktuel%20forskning/Nanopartikler%20i%20farve-%20og%20lakindustrien%20-%20NANOKEM%20hovedprojekt.aspx>
- [22] "Sikker brug af nanoteknologi i plastindustrien - NanoPlast"
Danish National Research Centre for the Working Environment
<http://www.arbejdsmiljoforskning.dk/Nyheder/Nyhedsarkiv/2007/Sikker%20brug%20af%20nanoteknologi%20i%20plastindustrien.aspx>
- [23] "Kortlægning og sundhedsmæssig vurdering af mulige sundhedsskadelige komponenter i spraymidler til tekstilimpregnering", Kortlægning af kemiske stoffer i forbrugerprodukter Miljøstyrelsen (Danish Environmental Protection Agency), to be published in 2007

Industrial use and production of nanomaterials

Questionnaire – general part

The questionnaire consists of two parts; the present general part and a material-specific questionnaire for each nanomaterial.

1	Which industry does the company belong to?	
	Food, drink and tobacco industry	<input type="checkbox"/>
	Soap, perfume and technical/chemical agents (SPT-industry)	<input type="checkbox"/>
	Textile, leather and clothing industry	<input type="checkbox"/>
	Paper and graphic industry	<input type="checkbox"/>
	Chemical industry	<input type="checkbox"/>
	Rubber and plastic industry	<input type="checkbox"/>
	Stone, clay and glass industry	<input type="checkbox"/>
	Iron and metal industry	<input type="checkbox"/>
	Electronics industry	<input type="checkbox"/>
Other, please specify:		

2	Which nanotechnological products does the company produce?	

3	Total number of employees in Denmark?	
	1-9 employees	<input type="checkbox"/>
	10-49 employees	<input type="checkbox"/>
	50-249 employees	<input type="checkbox"/>
	250-1000 employees	<input type="checkbox"/>
More than 1000 employees	<input type="checkbox"/>	

4	Which type(s) of nanotechnological materials does the company work with? (Mark more than one, if necessary)	
	Nanoparticles <i>Particles, or aggregates hereof, where all three dimensions are less than 100 nm</i>	<input type="checkbox"/>
	Nanofibres <i>Fibres or tubes with diameters less than 100 nm</i>	<input type="checkbox"/>
	Nanoflakes <i>Flakes, where at least one dimension is less than 100 nm</i>	<input type="checkbox"/>
	Nanofilm or nanocoatings <i>Coatings with layers thinner than 100 nm</i>	<input type="checkbox"/>
	Nanostructured surfaces <i>Surfaces with a designed structure finer than 100 nm</i>	<input type="checkbox"/>
	Nanoporous structures <i>Porous materials with pore diameter less than 100 nm</i>	<input type="checkbox"/>
	The company does not work with nanotechnological materials	<input type="checkbox"/>

If the company does *not* work with nanotechnological materials and/or nanoparticles, nanofibres or nanoflakes are not used or produced in the processes, the remaining part of the general questionnaire and the material-specific questionnaire need not be filled out. However, we kindly ask you to return the general part (with questions 1-4) to Danish Technological Institute.

5	Which nanotechnological process(es) does the company work with? (mark more than one, if necessary)	
	Spray	<input type="checkbox"/>
	Powder	<input type="checkbox"/>
	Vacuum-based processes	<input type="checkbox"/>
	Wet chemistry (suspended nanomaterials)	<input type="checkbox"/>
	Top-down lithography (e.g. laser, ion beam, UV lithography)	<input type="checkbox"/>
	Other:	<input type="checkbox"/>

6	Please fill out, if the company work with <i>nanostructured surfaces, nanoporous structures or nanofilm/nanocoatings</i>		
	Are nanoparticles or nanofibres used in processes or production involving nanostructured surfaces, nanoporous structures or nanofilm/nanocoatings?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	Are nanoparticles or nanofibres produced as a by-product in processes or production involving nanostructured surfaces, nanoporous structures or nanofilm/nanocoatings?	Yes <input type="checkbox"/>	No <input type="checkbox"/>

The remaining part of the questionnaire is *exclusively* dealing with nanoparticles, nanofibres and nanoflakes (hereafter called nanomaterials).

If the company does *not* work with nanoparticles, nanofibres or nanoflakes, and/or nanoparticles, nanofibres or nanoflakes are *not* produced as by-product in processes or production involving nanostructured surfaces, nanoporous structures or nanofilm/nanocoatings, the remaining part of the general questionnaire and the material-specific questionnaire need not be filled out. However, we kindly ask you to return the general questionnaire (with questions 1-6) to Danish Technological Institute.

In the remaining part of this questionnaire the term *nanomaterials* is used exclusively for nanoparticles, nanofibres and nanoflakes.

7	How does the company work with nanomaterials?	
	Research and/or development of nanomaterials	<input type="checkbox"/>
	Production of nanomaterials	<input type="checkbox"/>
	Use of nanomaterials in production or processes	<input type="checkbox"/>
	Nanomaterials are produced as a by-product	<input type="checkbox"/>
	Unknown	<input type="checkbox"/>
	Other:	

Working environment

8	How many employees in the company in Denmark <i>work with or have contact with</i> nanomaterials?	
	1-9 employees	<input type="checkbox"/>
	10-49 employees	<input type="checkbox"/>
	50-250 employees	<input type="checkbox"/>
	More than 250 employees	<input type="checkbox"/>

9	Are nanomaterials handled according to the rules and legislation on chemicals and materials in the working environment?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If no, please elaborate:		

10	In addition to normal information in relation to work with chemicals, are there any special instructions on nanomaterials for people working with these materials?
	No special instruction <input type="checkbox"/>
	Written material <input type="checkbox"/>
	Oral instruction <input type="checkbox"/>
	Instruction from colleagues <input type="checkbox"/>
	E-learning <input type="checkbox"/>
	Video <input type="checkbox"/>
	Courses <input type="checkbox"/>
	Other:

11	Does the company use special guidelines for work on nanomaterials?
	No special guidelines <input type="checkbox"/>
	Internally defined guidelines <input type="checkbox"/>
	ISO guidelines <input type="checkbox"/>
	NIOSH guidelines <input type="checkbox"/>
	Guidelines defined by other companies <input type="checkbox"/>
	Other:

12	Does the company have knowledge on possible <i>health</i> risks in relation to the nanomaterials relevant for the company?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, from where does the knowledge come from?		
	Investigations on working environment	<input type="checkbox"/>	
	Epidemic data	<input type="checkbox"/>	
	Distributors	<input type="checkbox"/>	
	Open literature	<input type="checkbox"/>	
Other:			

13	Does the company have knowledge on possible <i>environmental</i> risks in relation to the nanomaterials relevant for the company?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, from where does the knowledge come from?		
	Distributors	<input type="checkbox"/>	
	Open literature	<input type="checkbox"/>	
	Other:		

14	Which safety measures are used in the handling of nanomaterials?	
	<i>Technical</i>	
	None	<input type="checkbox"/>
	Closed system	<input type="checkbox"/>
	Automatic processing	<input type="checkbox"/>
	Wet process (nanomaterials suspended in solvent)	<input type="checkbox"/>
	Other:	
	<i>Ventilation</i>	
	None	<input type="checkbox"/>
	Closed system	<input type="checkbox"/>
	Partly closed system	<input type="checkbox"/>
	Open work area	<input type="checkbox"/>
	Outdoor work	<input type="checkbox"/>
	Mechanical ventilation (suction)	<input type="checkbox"/>
	Other:	
	<i>Other measures</i>	
	None	<input type="checkbox"/>
	Personal protective equipment (please note type)	<input type="checkbox"/>
	Gloves	<input type="checkbox"/>
	Dust filter mask	<input type="checkbox"/>
	Breath protection with fresh air supply	<input type="checkbox"/>
	Other:	
	Other (please elaborate):	

15	Does the company have knowledge of or an impression that employees are uncertain or insecure about the handling of nanomaterials?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please elaborate:		

Waste

16	Does the company process nanomaterial waste prior to disposal?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, in what way?		

17	What is the form of the company's nanomaterial waste?		
	Solid (powder)	<input type="checkbox"/>	
	Liquid (suspended in solvent)	<input type="checkbox"/>	
	Other:		

18	How is nanomaterial containing waste disposed?		
	Together with other regular waste	<input type="checkbox"/>	
	Together with regular waste water	<input type="checkbox"/>	
	As dangerous waste (e.g. chemical waste)	<input type="checkbox"/>	
	Other:		

19	Possibilities of release of nanomaterials to the surrounding environment in the company's processes				
	Possibility of release of airborne nanomaterials (ultrafine aerosols/dust)?	Yes <input type="checkbox"/>	No <input type="checkbox"/>	Unknown <input type="checkbox"/>	
	Possibility of release of nanomaterials to waste water	Yes <input type="checkbox"/>	No <input type="checkbox"/>	Unknown <input type="checkbox"/>	
	Other:				

Product life

20	Do the company's customers receive information about precautions regarding nanomaterials in the products?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please state how:		
	By material safety data sheet (MSDS) (please attach a copy)	<input type="checkbox"/>	
	By enclosure of technical data (please attach a copy)	<input type="checkbox"/>	
	Other information enclosed with the products (please attach a copy)	<input type="checkbox"/>	
	Other:		

21	Are the company's nanotechnological products further processed by the customers?	Yes <input type="checkbox"/>	No <input type="checkbox"/>	
	If yes, is there a possibility of release of nanomaterials in those processes?	Yes <input type="checkbox"/>	No <input type="checkbox"/>	Unknown <input type="checkbox"/>

22	Are the company's nanotechnological products finished goods that do not require any further processing before sale to private consumers?	Yes <input type="checkbox"/>	No <input type="checkbox"/>	
	If yes, is there a possibility of release of nanomaterials when the products are used?	Yes <input type="checkbox"/>	No <input type="checkbox"/>	Unknown <input type="checkbox"/>

23	Is there a possibility of release of nanomaterials when end products, containing the company's nanotechnological products, are destroyed after use by the consumers?	Yes <input type="checkbox"/>	No <input type="checkbox"/>	Unknown <input type="checkbox"/>
-----------	---	---------------------------------	--------------------------------	-------------------------------------

Closing questions

24	Does the company participate in certifications or other regulative measures on nanotechnology beyond legislative obligations?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please elaborate:		

25	Does the company believe there is a need for <i>guidance or advice</i> in relation to work with nanomaterials?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please indicate relevant areas:		
	Working environment	<input type="checkbox"/>	
	Waste management	<input type="checkbox"/>	
	Information to customers of nanotechnological products	<input type="checkbox"/>	
	Other:		
	Please indicate what kind of guidance/advice is needed and if possible to what extent:		

26	Does the company believe there is a need for <i>legislative adjustments</i> in relation to work with nanomaterials?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please indicate relevant areas:		
	Working environment	<input type="checkbox"/>	
	Waste management	<input type="checkbox"/>	
	Information to customers of nanotechnological products	<input type="checkbox"/>	
	Other:		
	Please indicate what kind of legislation is needed and if possible to what extent:		

27	Are there subjects regarding work with nanomaterials which you believe should have been covered by this questionnaire?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please indicate which subjects:		

If we may contact you for further information, please state name and telephone number of a contact person:	
Name:	Telephone no.

Please fill out the material-specific questionnaire for each nanomaterial relevant for the company.

Industrial use and production of nanomaterials

Questionnaire – material-specific part

Please fill out this questionnaire for *each* nanomaterial (or each type or group of nanomaterial, e.g. metaloxides), which the company *produces* or *uses*, as well as for nanomaterials which are produced as *by-product*.

The term *nanomaterials* is in this context used exclusively as a collective term for nanoparticles, nanofibres and nanoflakes (the questionnaire need therefore not be filled out for nanostructured surfaces, nanoporous structures or nanofilm/coatings).

Name (product name or other) of the nanomaterial:

1	Type of nanomaterial	
	Metaloxides (e.g. Fe ₂ O ₃ , TiO ₂ , Al ₂ O ₃)	<input type="checkbox"/>
	Metalnitrides (e.g. TiN, AlN)	<input type="checkbox"/>
	Pure metals (e.g. Ag, Au, Pt)	<input type="checkbox"/>
	Silicates (silicic acid, glass, quartz)	<input type="checkbox"/>
	Carbon nanoparticles (e.g. carbon black)	<input type="checkbox"/>
	Fullerenes	<input type="checkbox"/>
	Polymeric particles	<input type="checkbox"/>
	Dendrimers	<input type="checkbox"/>
	Nanofibres or nanotubes	<input type="checkbox"/>
	Nanoflakes (e.g. nanoclay)	<input type="checkbox"/>
	Other:	
Unknown:	<input type="checkbox"/>	

2	Please state as precisely as possible the constituent chemical substances or elements (CAS-numbers, if possible):

3	How do you work with the nanomaterial?	
	The nanomaterial is a product	<input type="checkbox"/>
	The nanomaterial is used in a process	<input type="checkbox"/>
	The nanomaterial is produced as a by-product	<input type="checkbox"/>
	Other:	

4	What form does the nanomaterial have?	
	<i>In processes:</i>	
	Powder	<input type="checkbox"/>
	Suspended in solvent	<input type="checkbox"/>
	Suspended in solid material	<input type="checkbox"/>
	Other:	
	<i>In products:</i>	
	Powder	<input type="checkbox"/>
	Suspended in solvent	<input type="checkbox"/>
	Suspended in solid material	<input type="checkbox"/>
	Not part of product	<input type="checkbox"/>
	Other:	

5	What is the typical concentration (weight%) of the nanomaterial in the company's products?	
	The nanomaterial is not present in the company's products	<input type="checkbox"/>
	< 1 ppm	<input type="checkbox"/>
	1 ppm-0.1 %	<input type="checkbox"/>
	0.1 %-10 %	<input type="checkbox"/>
	10 %-50 %	<input type="checkbox"/>
	> 50 %	<input type="checkbox"/>
	Unknown	<input type="checkbox"/>

6	What is the particular form of the nanomaterial?	
	Mainly primary particles	<input type="checkbox"/>
	Mainly aggregates of primary particles	<input type="checkbox"/>
	Unknown	<input type="checkbox"/>

7	Is the particle size (of particles or aggregates) of the nanomaterial known?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please indicate particle size (d_{50})		
	< 10 nm	<input type="checkbox"/>	
	10-20 nm	<input type="checkbox"/>	
	20-50 nm	<input type="checkbox"/>	
	50-100 nm	<input type="checkbox"/>	
	> 100 nm	<input type="checkbox"/>	
	Source or measurement principle:		

8	Is the particle size distribution of the nanomaterial known?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please indicate source or measurement principle:		

9	Is the specific surface area of the nanomaterial known?	Yes <input type="checkbox"/>	No <input type="checkbox"/>
	If yes, please indicate the specific surface area		
	< 10 m ² /g	<input type="checkbox"/>	
	10-50 m ² /g	<input type="checkbox"/>	
	50-200 m ² /g	<input type="checkbox"/>	
	200-1.000 m ² /g	<input type="checkbox"/>	
	> 1.000 m ² /g	<input type="checkbox"/>	
	Source or measurement principle:		

10	How much of the nanomaterial does the company handle per year? (as product, raw material or as a by-product)	
	Less than 1 kg per year	<input type="checkbox"/>
	1-10 kg per year	<input type="checkbox"/>
	10-100 kg per year	<input type="checkbox"/>
	100-1.000 kg per year	<input type="checkbox"/>
	1 tons-10 tons per year	<input type="checkbox"/>
	10 tons-100 tons per year	<input type="checkbox"/>
	100 tons-1.000 tons per year	<input type="checkbox"/>
	1.000 tons or more per year	<input type="checkbox"/>
Unknown	<input type="checkbox"/>	

11	How much nanomaterial does an employee typically handle?	
	< 1 mg	<input type="checkbox"/>
	1 mg-1 g	<input type="checkbox"/>
	1 g-1 kg	<input type="checkbox"/>
	1 kg-10 kg	<input type="checkbox"/>
	> 10 kg	<input type="checkbox"/>
Unknown	<input type="checkbox"/>	

12	Have exposure levels of fine/ultrafine airborne particles been measured when handling the nanomaterial?	
	No	<input type="checkbox"/>
	Yes, gravimetric measurements	<input type="checkbox"/>
	Gravimetric concentration: mg/m^3	
	Which type of particles were measured:	
	Yes, measurements of particle concentration	<input type="checkbox"/>
	Particle concentration: particles/cm^3	
	Measurement principle:	
Yes, other types of measurement (please elaborate):	<input type="checkbox"/>	

Industriel produktion og anvendelse af nanomaterialer

Spørgeskema – generel del

Dette spørgeskema består af denne generelle del og et spørgeskema, der bedes udfyldt for hvert nanomateriale

1	Hvilken branche tilhører virksomheden?	
	Føde-, drikke- og tobaksvarerindustri	<input type="checkbox"/>
	Sæbe, parfume og teknisk/kemiske artikler (SPT-industri)	<input type="checkbox"/>
	Tekstil-, læder- og beklædningsindustri	<input type="checkbox"/>
	Papir- og grafisk industri	<input type="checkbox"/>
	Kemisk industri	<input type="checkbox"/>
	Gummi- og plastindustri	<input type="checkbox"/>
	Sten-, ler- og glasindustri	<input type="checkbox"/>
	Jern- og metalindustri	<input type="checkbox"/>
	Elektronikindustri	<input type="checkbox"/>
Andet:		

2	Hvilke nanoteknologiske produkter producerer virksomheden?	

3	Hvor mange ansatte er der totalt i virksomheden i Danmark?	
	1-9 ansatte	<input type="checkbox"/>
	10-49 ansatte	<input type="checkbox"/>
	50-249 ansatte	<input type="checkbox"/>
	250-1000 ansatte	<input type="checkbox"/>
	Flere end 1000 ansatte	<input type="checkbox"/>

4	Hvilke(n) type(r) nanoteknologisk materiale arbejder virksomheden med? (Afkryds evt. flere)	
	Nanopartikler <i>Partikler, hvor alle tre dimensioner er mindre end 100 nm, eller aggregater heraf</i>	<input type="checkbox"/>
	Nanofibre <i>Fibre eller rør, hvor tværsnittet er mindre end 100 nm</i>	<input type="checkbox"/>
	Nanoflager <i>Flager, hvor mindst én dimension er mindre end 100 nm</i>	<input type="checkbox"/>
	Nanofilm eller nanobelægninger <i>Overfladebelægning, hvor hvert lag er tyndere end 100 nm</i>	<input type="checkbox"/>
	Nanostrukturerede overflader <i>Overflader med en designet struktur, der er finere end 100 nm</i>	<input type="checkbox"/>
	Nanoporøse strukturer <i>Porøse materialer, hvor porerne har et tværsnit mindre end 100 nm</i>	<input type="checkbox"/>
	Virksomheden arbejder <i>ikke</i> med nanoteknologiske materialer	<input type="checkbox"/>

Hvis virksomheden *ikke* arbejder med nanoteknologiske materialer, og der *ikke* indgår eller opstår nanopartikler, nanofibre eller nanoflager i fremstilling eller bearbejdning, skal resten af det generelle spørgeskema samt de specifikke spørgeskemaer ikke udfyldes. Dog bedes det generelle spørgeskema (med udfyldt spørgsmål 1-4) returneret til Teknologisk Institut.

5	Hvilke(n) nanoteknologisk(e) procestype(r) arbejder virksomheden med? (Afkryds evt. flere)	
	Spray	<input type="checkbox"/>
	Pulver	<input type="checkbox"/>
	Vakuumbaserede processer	<input type="checkbox"/>
	Våd kemi (suspenderede nanomaterialer)	<input type="checkbox"/>
	Top-down litografi (fx laser, ion beam, UV litografi)	<input type="checkbox"/>
	Andet:	<input type="checkbox"/>

6	Udfyld, hvis virksomheden arbejder med <i>nanostrukturerede overflader, nanoporøse strukturer eller nanofilm/nanobelægninger</i>		
	Indgår nanopartikler eller nanofibre i fremstillingen eller bearbejdningen af nanostrukturerede overflader, nanoporøse strukturer eller nanofilm?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Opstår nanopartikler eller nanofibre som biprodukt i fremstillingen eller bearbejdningen af nanostrukturerede overflader, nanoporøse strukturer eller nanofilm?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>

Den resterende del af spørgeskemaet omhandler *udelukkende* nanopartikler, nanofibre og nanoflager (som samlet betegnes nanomaterialer).

Hvis virksomheden *ikke* arbejder med nanopartikler, nanofibre eller nanoflager, og der *ikke* indgår eller opstår nanopartikler eller nanofibre under fremstilling eller bearbejdning, skal resten af det generelle spørgeskema samt de specifikke spørgeskemaer ikke udfyldes. Dog bedes det generelle spørgeskema (med udfyldt spørgsmål 1-6) returneret til Teknologisk Institut.

I den resterende del af spørgeskemaet bruges betegnelsen *nanomaterialer* udelukkende som samlende betegnelse for nanopartikler, nanofibre og nanoflager

7	I hvilken sammenhæng arbejder virksomheden med nanomaterialer?	
	Virksomheden forsker i og/eller udvikler nanomaterialer	<input type="checkbox"/>
	Virksomheden producerer nanomaterialer	<input type="checkbox"/>
	Nanomaterialer anvendes i processer i virksomheden	<input type="checkbox"/>
	Nanomaterialer opstår som biprodukt i virksomhedens processer	<input type="checkbox"/>
	Ved ikke	<input type="checkbox"/>
Andet:		

Arbejds miljø

8	Hvor mange ansatte i virksomheden i Danmark <i>håndterer/har kontakt med/arbejder med nanomaterialer?</i>	
	1-9 ansatte	<input type="checkbox"/>
	10-49 ansatte	<input type="checkbox"/>
	50-250 ansatte	<input type="checkbox"/>
	Flere end 250 ansatte	<input type="checkbox"/>

9	Håndteres nanomaterialer efter reglerne om stoffer og materialer i arbejdsmiljøet?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis nej, uddyb venligst:		

10	Ud over normal information i forbindelse med arbejde med kemikalier foretages der da en særlig instruktion om nanomaterialer for de medarbejdere, der arbejder med disse materialer?
	Ingen særlig instruktion <input type="checkbox"/>
	Skriftligt materiale <input type="checkbox"/>
	Mundtlig instruktion <input type="checkbox"/>
	Sidemandsoplæring <input type="checkbox"/>
	E-læring <input type="checkbox"/>
	Video <input type="checkbox"/>
	Egentlige kurser <input type="checkbox"/>
	Andet:

11	Har virksomheden særlige retningslinier for arbejdet med nanomaterialer?
	Ingen særlige retningslinier <input type="checkbox"/>
	Internt definerede retningslinier (vedlæg gerne en kopi) <input type="checkbox"/>
	ISO retningslinier <input type="checkbox"/>
	NIOSH retningslinier <input type="checkbox"/>
	Retningslinier udarbejdet af andre virksomheder <input type="checkbox"/>
	Andet:

12	Har virksomheden kendskab til mulige <i>sundhedsrisici</i> i forbindelse med de nanomaterialer, som er aktuelle for virksomheden?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, stammer kendskabet da fra:		
	Arbejdspladsundersøgelser	<input type="checkbox"/>	
	Epidemiske data	<input type="checkbox"/>	
	Leverandører	<input type="checkbox"/>	
	Åben litteratur	<input type="checkbox"/>	
Andet:			

13	Har virksomheden kendskab til mulige <i>miljørisici</i> i forbindelse med de nanomaterialer, som er aktuelle for virksomheden?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, stammer kendskabet da fra:		
	Leverandører	<input type="checkbox"/>	
	Åben litteratur	<input type="checkbox"/>	
Andet:			

14	Hvilke sikkerhedsforanstaltninger anvendes ved håndtering af nanomaterialer?
<i>Tekniske foranstaltninger</i>	
Ingen	<input type="checkbox"/>
Lukket system	<input type="checkbox"/>
Automatisk fremstillingsproces	<input type="checkbox"/>
Våd-proces (nanomaterialer suspenderet i væske)	<input type="checkbox"/>
Andet:	
<i>Ventilation</i>	
Ingen	<input type="checkbox"/>
Lukket arbejdsområde	<input type="checkbox"/>
Delvis lukket arbejdsområde	<input type="checkbox"/>
Åbent arbejdsområde	<input type="checkbox"/>
Fri luft (udendørs)	<input type="checkbox"/>
Mekanisk ventilation (udsugning)	<input type="checkbox"/>
Andet:	
<i>Andre foranstaltninger</i>	
Ingen	<input type="checkbox"/>
Personlige værnemidler (venligst anfør type)	<input type="checkbox"/>
Handsker	<input type="checkbox"/>
Støvmaske	<input type="checkbox"/>
Frisklufforsynet åndedrætsværn	<input type="checkbox"/>
Andet:	
Andet (venligst anfør hvilke):	

15	Har virksomheden kendskab til eller indtryk af, at der er ansatte på virksomheden, som er usikre eller utrygge ved håndtering af eller arbejde med nanomaterialer?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, uddyb venligst:		

Affald

16	Foretages der i virksomheden en bearbejdning af nanomaterialeaffald inden bortskaffelse?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, hvilken?		

17	I hvilken form findes nanomaterialeaffaldet?		
	Fast (pulver)	<input type="checkbox"/>	
	Flydende (suspenderet i væske)	<input type="checkbox"/>	
	Andet:		

18	Hvordan bortskaffes affald fra arbejde med nanomaterialer/affald, der indeholder nanomaterialer?		
	Sammen med andet affald til forbrænding	<input type="checkbox"/>	
	Sammen med spildevand	<input type="checkbox"/>	
	Som miljøfarligt affald (fx kemikalieaffald)	<input type="checkbox"/>	
	Andet:		

19	Mulighed for udslip af nanomaterialer til det omgivende miljø under virksomhedens processer			
	Mulighed for udslip af luftbårne nanomaterialer (aerosoler/støv)?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>	Ved ikke <input type="checkbox"/>
	Mulighed for udslip af suspenderede nanomaterialer i spildevand?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>	Ved ikke <input type="checkbox"/>
	Andet:			

Produkternes videre vej

20	Videregives der oplysninger til virksomhedens kunder om forholdsregler omkring nanomaterialer i produkter?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, sker det da:		
	Ved udlevering/fremsendelse af sikkerhedsdatablade (vedlæg gerne en kopi)	<input type="checkbox"/>	
	Ved udlevering/fremsendelse af tekniske data (vedlæg gerne en kopi)	<input type="checkbox"/>	
	Information, der vedlægges materialerne (vedlæg gerne en kopi)	<input type="checkbox"/>	
	Andet:		

21	Sker der en videre forarbejdning hos aftagerne af virksomhedens nanoteknologiske produkter?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, er der mulighed for, at nanomaterialer frigives under en videre forarbejdning?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
			Ved ikke <input type="checkbox"/>

22	Er virksomhedens nanoteknologiske produkter færdigvarer, der ikke kræver yderligere forarbejdning før afsætning til forbrugerne?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, er der mulighed for, at nanomaterialer frigives under brug af produkterne?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
			Ved ikke <input type="checkbox"/>

23	Er der mulighed for, at nanomaterialer frigives ved affaldsbehandling efter forbrugernes kassering af slutprodukter, hvori virksomhedens nanoteknologiske produkter indgår?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
			Ved ikke <input type="checkbox"/>

Afsluttende spørgsmål

24	Deltager virksomheden i certificeringsordninger eller andre tiltag inden for nanoteknologi ud over de lovmæssige forpligtigelser på området?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, uddyb venligst:		

25	Mener virksomheden, at der er behov for <i>vejledning eller rådgivning</i> i forhold til arbejdet med nanomaterialer?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, angiv venligst område:		
	Arbejds miljøområdet	<input type="checkbox"/>	
	Miljø-/affaldsområdet	<input type="checkbox"/>	
	Information til aftagere af nanoteknologiske produkter	<input type="checkbox"/>	
	Andet:		
	Angiv venligst, <i>hvad</i> der ønskes vejledning/rådgivning om, og evt. i hvilket omfang:		

26	Mener virksomheden, at der er behov for tilpasning af den eksisterende <i>lovgivning</i> i forhold til arbejdet med nanomaterialer?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, angiv venligst område:		
	Arbejds miljøområdet	<input type="checkbox"/>	
	Miljø-/affaldsområdet	<input type="checkbox"/>	
	Information til aftagere af nanoteknologiske produkter	<input type="checkbox"/>	
	Andet:		
	Angiv venligst, <i>hvilke</i> tilpasninger der ønskes af lovgivningen, og evt. i hvilket omfang:		

27	Er der områder eller emner ved arbejdet med nanomaterialer, som ikke er medtaget i dette spørgeskema, og som du vurderer, burde være medtaget?	Ja <input type="checkbox"/>	Nej <input type="checkbox"/>
	Hvis ja, angiv venligst hvilke:		

Såfremt vi må kontakte jer for evt. supplerende spørgsmål, angiv da venligst navn og tlf. nr. på kontaktperson:	
Navn:	Tlf. nr.

Udfyld venligst det specifikke spørgeskema for *hvert* nanomateriale, virksomheden arbejder med

Industriell produktion og anvendelse af nanomaterialer

Spørgeskema – specifik del

Dette spørgeskema bedes udfyldt for *hvert* nanomateriale eller evt. hver type eller gruppe af nanomateriale (fx metaloxider), som virksomheden *producerer* eller *anvender*, samt for nanomaterialer, der *opstår som biprodukt*

Betegnelsen *nanomaterialer* bruges i dette skema udelukkende som samlende betegnelse for nanopartikler, nanofibre og nanoflager (skemaet skal således ikke udfyldes for nanostrukturerede overflader, nanoporøse strukturer eller nanofilm).

Angiv evt. en betegnelse (produkt navn eller andet) for nanomaterialet:

1	Type af nanomateriale	
	Metaloxider (fx Fe ₂ O ₃ , TiO ₂ , Al ₂ O ₃)	<input type="checkbox"/>
	Metalnitrider (fx TiN, AlN)	<input type="checkbox"/>
	Rene metaller (fx Ag, Au, Pt)	<input type="checkbox"/>
	Silikater (kiselsyre, glas, kvarts)	<input type="checkbox"/>
	Kulstofnanopartikler (fx carbon black)	<input type="checkbox"/>
	Fullerener	<input type="checkbox"/>
	Polymerpartikler	<input type="checkbox"/>
	Dendrimerer	<input type="checkbox"/>
	Nanofibre eller -rør	<input type="checkbox"/>
	Nanoflager (fx nanoclay)	<input type="checkbox"/>
	Andet:	
Ved ikke:	<input type="checkbox"/>	

2	Angiv så præcist som muligt, hvilke kemiske forbindelser eller grundstoffer der er tale om (gerne CAS-nr. hvis muligt):

3	Hvordan arbejdes der med nanomaterialet?	
	Nanomaterialet er produktet	<input type="checkbox"/>
	Nanomaterialet anvendes i processen	<input type="checkbox"/>
	Nanomaterialet opstår som biprodukt	<input type="checkbox"/>
	Andet:	

4	I hvilken form findes nanomaterialet?	
	<i>I processer:</i>	
	Som pulver	<input type="checkbox"/>
	Suspenderet i en væske	<input type="checkbox"/>
	Indbygget i fast materiale	<input type="checkbox"/>
	Andet:	
	<i>I produkt:</i>	
	Som pulver	<input type="checkbox"/>
	Suspenderet i en væske	<input type="checkbox"/>
	Indbygget i fast materiale	<input type="checkbox"/>
	Indgår ikke i produktet	<input type="checkbox"/>
	Andet:	

5	Hvad er den typiske koncentration (vægt%) af nanomaterialet i virksomhedens produkter?	
	Nanomaterialet er ikke til stede i virksomhedens produkter	<input type="checkbox"/>
	< 1 ppm	<input type="checkbox"/>
	1 ppm-0,1 %	<input type="checkbox"/>
	0,1 %-10 %	<input type="checkbox"/>
	10 %-50 %	<input type="checkbox"/>
	> 50 %	<input type="checkbox"/>
	Ved ikke	<input type="checkbox"/>

6	I hvilken partikulær form findes nanomaterialet?	
	Hovedsagligt som primærpartikler	<input type="checkbox"/>
	Hovedsagligt som aggregater af primærpartikler	<input type="checkbox"/>
	Ved ikke	<input type="checkbox"/>

7	Kendes partikelstørrelsen (af partikler eller aggregater) på nanomaterialet?	Ja	Nej
		<input type="checkbox"/>	<input type="checkbox"/>
	Hvis ja, angiv venligst størrelse (d_{50})		
	< 10 nm	<input type="checkbox"/>	
	10-20 nm	<input type="checkbox"/>	
	20-50 nm	<input type="checkbox"/>	
	50-100 nm	<input type="checkbox"/>	
	> 100 nm	<input type="checkbox"/>	
Angiv venligst kilde eller målemetode:			

8	Kendes partikelstørrelsesfordelingen af nanomaterialet?	Ja	Nej
		<input type="checkbox"/>	<input type="checkbox"/>
Hvis ja, angiv venligst kilde eller målemetode:			

9	Kendes det specifikke overfladeareal af nanomaterialet?	Ja	Nej
		<input type="checkbox"/>	<input type="checkbox"/>
	Hvis ja, angiv venligst det specifikke overfladeareal		
	< 10 m ² /g	<input type="checkbox"/>	
	10-50 m ² /g	<input type="checkbox"/>	
	50-200 m ² /g	<input type="checkbox"/>	
	200-1.000 m ² /g	<input type="checkbox"/>	
	> 1.000 m ² /g	<input type="checkbox"/>	
Angiv venligst kilde eller målemetode:			

10	Hvor store mængder af nanomaterialet håndterer virksomheden årligt? (som produkt, som råvare eller som biprodukt)	
	Under 1 kg pr. år	<input type="checkbox"/>
	1-10 kg pr. år	<input type="checkbox"/>
	10-100 kg pr. år	<input type="checkbox"/>
	100-1.000 kg pr. år	<input type="checkbox"/>
	1 tons-10 tons pr. år	<input type="checkbox"/>
	10 tons-100 tons pr. år	<input type="checkbox"/>
	100 tons-1.000 tons pr. år	<input type="checkbox"/>
	1.000 tons eller mere pr. år	<input type="checkbox"/>
Vides ikke	<input type="checkbox"/>	

11	Hvor store mængder nanomateriale håndterer den enkelte medarbejder typisk ad gangen?	
	< 1 mg	<input type="checkbox"/>
	1 mg-1 g	<input type="checkbox"/>
	1 g-1 kg	<input type="checkbox"/>
	1 kg-10 kg	<input type="checkbox"/>
	> 10 kg	<input type="checkbox"/>
Vides ikke	<input type="checkbox"/>	

12	Er der blevet udført målinger af eksponeringen for fine/ultrafine luftbårne partikler ved håndtering af nanomaterialet?	
	Nej	<input type="checkbox"/>
	Ja, gravimetrisk målinger	<input type="checkbox"/>
	Gravimetrisk koncentration: mg/m ³	
	Hvilken type partikler blev målt:	
	Ja, målinger af partikelkoncentration	<input type="checkbox"/>
	Partikelkoncentration: partikler/cm ³	
Målemetode:		
Ja, andre typer målinger (angiv venligst):		