Danish Ministry of the Environment
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Exposure assessment of nanomaterials in consumer products

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Exposure assessment of nanomaterials in consumer products

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Preface

Nanomaterials (NM) are applied in a wide range of consumer products and the commercial use of NM in both amounts and diversity is anticipated to increase rapidly in the near future. It is increasingly recognised that NMs can have unique properties as compared to their bulk substances favouring the use of NM in products, articles and technologies. At the same time, concerns in relation to the possible health and environmental properties and impacts of NMs have surfaced.

On this background, the Danish government and the Red-Green Alliance (a.k.a. Enhedslisten) have signed an agreement for four years (2012-2015) that focuses on the use of nanomaterials in products on the Danish market and their consequences on consumers and the environment. The Danish Environmental Protection Agency (EPA) has initiated a series of projects with the aim of further clarifying possible risks to consumers and the environment.

The current project addresses consumer exposure and risk assessment of nanomaterials in products on the Danish market. It runs from third quarter 2013 through second quarter 2015.

The project is foreseen to result in four reports:

- Occurrence and exposure assessment of nanomaterials in consumer products and review of available risk assessment tools (the current report)
- Hazard assessment of nanomaterials in consumer products
- Human exposure to nanomaterials in the environment – as a reference to nanomaterials exposure from consumer products
- Consumer risk assessment and overall conclusions (final report)

The first three reports will be finalised during 2014, whereas the final report with the consumer risk assessment and overall conclusions will be finalised during the second quarter of 2015.

This report covers the first work package concerning *occurrence and exposure assessment of nanomaterials in consumer products and review of available risk assessment tools*.

The project has been implemented with support from a reference group:

- Susan Dekker, National Institute for Public Health and the Environment (RIVM), The Netherlands
- Andrea Haase, Bundesinstitut für Risikobewertung (BfR), Germany
- Gregory Moore, Swedish Chemicals Agency (KEMI), Sweden
- Derk Brouwer, Netherlands Organisation for Applied Scientific Research (TNO), The Netherlands

The reference group has assisted with comments and ideas, but are not responsible for the content of the project reports.

Summary and conclusions

Under the Agreement "Better Control of Nanomaterials" (“Bedre styr på nanomaterialer”), the Danish EPA has commissioned a number of projects aiming to investigate and generate new knowledge on the presence of nanomaterials in products on the Danish market and assess the possible associated risks to consumers and the environment.
This report is part of a series of four from a project, which addresses consumer exposure and risk assessment of nanomaterials in products on the Danish market.

The following summarises the findings in the seven chapters of this report focusing on the findings and conclusions made.

Chapter 1: Introduction
Nanomaterials are found in a wide range of consumer products and the commercial use of nanomaterials is anticipated to increase rapidly in the future both in quantity and diversity. It is increasingly recognised that materials in the nanoform can have unique properties as compared to the microforms and macroforms of the same material. This favours the use of nanomaterials in products, articles and technologies. At the same time concerns in relation to the possible health and environmental properties and impacts of nanomaterials have surfaced.

The current report addresses presence and exposure of nanomaterials in consumer products, as well as an analysis of available methodologies and tools, which could be used to assess exposure and risk from use of nanomaterials in consumer products.

The overall objectives with the current report have been to:

- Evaluate existing methods/approaches/tools for assessing consumer exposure and risks associated with consumer nanoproducts.
- Identify representative consumer nanoproducts from which to select and describe a total of 20 exposure scenarios for further risk assessment.

Chapter 2: Nanoproducts and consumer scenarios to look for
To kick-off the product activities, relevant data sources describing nanomaterial exposure to consumers were identified. A very relevant starting point for our project was found to be the RIVM (2009) report “Exposure to nanomaterials in consumer products” which identified important factors/ parameters for assessing the consumer exposure to nanomaterials and made rough overall evaluation of the exposure potential for several consumer product categories. Further important sources for our projects, when looking on specific products and product categories on the market, were databases/inventories containing information of products containing (- or claimed to contain) nanomaterials. These were:

-the Nanodatabase from DTU Environment, The Danish Ecological Council and Danish Consumer Council;
-the BUND database;
-the ANEC/BEUC database; and
-the US Nanotechproject database.

Data from these databases were supplemented with data from a recent Danish EPA 2014 report "Supplementary survey of products on the Danish market containing nanomaterials" (REF).

Together with the Danish EPA, it was decided to collect data from products within the following product categories:

Food and beverages; Cosmetics; Cleaning agents; Coatings/ impregnation; Maintenance products (car, boats); Textiles; Construction materials; Medical devices; Air-cleaners; Fuel and lubrication oil additives; Electronic devices; Appliances (e.g. refrigerators).

Data on more than 120 nanoproducts was extracted from these data sources and the data was entered into a template inspired by RIVM (2009) in order to give information on the parameters that were considered especially relevant for the assessment of the exposure potential.

The following strategy was as far as possible used when identifying the products for which to extract data to enter into our template:

- the nanomaterial had been identified (i.e. chemistry known);
- the product should be of relevance for the Danish and European market (this was often based on assumptions. It was generally assumed that products on the European market could also be on the Danish marked);
- for each product category the products should cover as many different i) formulations, ii) types of uses and iii') and ways of handling as possible.

As an overall observation it became clear that for many products the specific nanomaterials were often vaguely or not reported and also it was difficult to assess in which state or concentration the nanomaterial was present in the product. Furthermore, it was difficult to assess to which extent the nanomaterial was fully matrix bound, occurred in layers and/or could be released during use. Thus, often the content of a nanomaterial was claimed without any further specification or documentation of the nano-content.

It was noticed that dead links to manufacturers and vendors as well as wrong data base information was sometimes encountered. Thus, care has to be taken when using information from the databases/inventories. Also it was noted that there are several overlaps between the databases as they often feed into each other.

Sometimes it was difficult to categorise a product into one of our chosen product categories. A cleaning agent may as an example also be grouped as a coating/impregnation agent, and a paint product can be considered relevant both for the coating/impregnation category as well as for the construction materials category.

Especially with respect to data on food and beverages, it is important to note that the databases only present nanomaterials in food supplements and do not cover the content of nanomaterial in food products as such, which might e.g. originate from the use of additives in nanoform.

Overall, available information on nanomaterials in consumer products in available databases/inventories is largely biased towards products for which the manufacturer/provider claims the presence of nanomaterials. Throughout the project activities, the knowledge on nanomaterials in consumer products was supplemented with information in the open literature; as described in Chapter 5 of the report. Also, input from the work-package addressing hazards of nanomaterials in consumer products was received.

(The Appendices 1, 2, 3 and 4 in the appendix report contain additional information regarding the activities conducted in relation to Chapter 2).

Chapter 3: Review of available risk assessment tools
This chapter reviewed a selected suite of relevant exposure and risk assessment tools and addressed whether the tools include exposure assessment, hazard characterisation and/or risks characterisation modules.

The overall aim of the activity was to identify a tool, which in itself or adapted could be used for making risk assessment of the 20 exposure scenarios to be identified in the project.

The reviewed exposure and risk assessment tools were identified in cooperation with the Danish EPA. The tools were selected based on their specificity for assessing nanomaterials or for their general applicability for assessing conventional chemicals and possible relevance for assessment of nanomaterials. The tools reviewed included:

- *NanoRiskCat (DTU and NRCWE)*
- *NanoSafer (NRCWE, DTI)*
- *Stoffenmanager Nano (TNO)*
- *Stoffenmanager (TNO)*
- *The ANSES tool*
- *Swiss Precautionary Matrix (Swiss consortium)*
- *ECETOC TRA*
- *ConsExpo (RIVM)*
- *DREAM (TNO and IOM)*
- *Margin of Exposure (MOE) concept (The US Soap and Detergent Industries)*

It should be noted that we have not only addressed tools intended for assessment of consumer exposure.

Occupational exposure/risk assessment tools were also included, as their approaches or the tools themselves might be applicable for some consumer exposure scenarios.

The reviews of the tools were conducted following an assessment template with relevant questions in relation to the approach/performance of the models/tools. A completed assessment template can be found for each tool in Appendix 5 in the appendix report**.**

The overall learning from this activity was that the assessed tools vary considerably in terms of coverage, scope/approach, level of quantification, target groups in the population and exposure routes addressed, etc. The nano-specific tools were generally rather qualitative and not specifically designed to assess whether there necessarily was a concrete risk. The tools rather indicated where there could be a risk potential and how strong indications there was for implementing (precautionary) risk management/mitigation. Furthermore, none of the nanomaterial exposure assessment tools specifically addressed exposure routes in relation to oral, dermal and eye exposure.

In contrast to this, the general (non nano-specific tools) were generally rather quantitative with a wider coverage, e.g. in terms of exposure routes addressed. Noteworthy, the exposure assessment algorithms in most of the non nano-specific tools were simpler and more conservative than the algorithms in the most advanced nano-specific tools.

The tools generally applied the mass metric (e.g. mg/m^3) which may not always be the most relevant, as a metric related to particle number or total particle surface area might be more relevant for assessing nanomaterials exposure and risks, in particular for inhalation.

Overall, no single tool (or combinations of tools) was identified that might enable an adequate and harmonised exposure/risk assessment for all types of consumer nanoproducts. Thus, significant work would be required to further develop the tools with modifications for incorporating nanospecific properties, harmonizing the output and validation of the tool.

For the exposure assessments to be completed in this project, the following was considered:

1) To assess some of the selected scenarios with all the tools (to the extent possible, e.g. considering data availability and tool coverage) and based on this make an expert based qualitative assessment;
2) To apply (components of) several tools as appropriate;
3) Not to apply the assessed tools, but rather perform a case-by-case expert assessment of each of the selected scenarios.

Based on discussions with the external expert panel, it was suggested to follow a combination of the second and third option depending on the data availability and the scenarios identified. The exact procedures for assessment of the consumer exposure and risk in the next phases of the project would then depend on the specific scenarios to be addressed, as well as the specific exposure and hazard data that might be available (hazard data are identified in another part of this project).

(Appendix 5 in the appendix report contain additional details regarding the activities conducted in relation to Chapter3).

Chapter 4: Exposure assessment and key factors affecting exposure
The objective of this chapter was to provide an overview of the knowledge needed to conduct a reliable conservative exposure assessment for a nanomaterial used in a consumer product. The most important factors/parameters determining the consumer exposure were identified and described in more detail in relation to the different exposure routes and use scenarios for the various product categories and formulations.

To achieve this goal, the first part of this chapter describes the learnings that could be obtained from relevant guidance documents and tools for exposure assessment to *chemicals*, in consumer products and articles, as well as from guidance documents and tools specifically addressing exposure to *nanomaterials*.

The following guidance documents and tools were evaluated for identifying the most important factors/ parameters determining consumer exposure:

- *RIVM (2009)* Exposure to nanomaterials in consumer products
- *REACH guidance documents on exposure assessment from chemical products and articles*
- *SCCS guidance on nanomaterials in cosmetics*
- *EFSA guidance on nanomaterials in food*
- *Environmental Defense – DuPont approach*
- *ECETOC TRA*
- *ConsExpo*
- *NanoSafer*
- *NanoRiskCat*
- *Stoffenmanager*

- *Stoffenmanager Nano*
- *ANSES*
- *Swiss Precautionary matrix*
- *Dream*
- *Margin of exposure concept*

As mentioned, RIVM (2009) had already performed an analysis of consumer exposure to nanomaterials. Key parameters were identified in the RIVM (2009) study and these key parameters formed a benchmark in the current analysis of the other guidance documents and tools. On this basis, descriptions and evaluations of the other guidance documents and tools were made (details in appendix 6) and it was evaluated whether additional important exposure parameters could be identified.

Having performed this stepwise analysis of the various tools and guidance documents, the following parameters, as indicated below, could be identified as relevant for exposure assessment of consumer products:

IDENTIFIED IMPORTANT QUALITATIVE AND QUANTITATIVE EXPOSURE PARAMETERS

Qualitative exposure parameters
• ID of nanomaterial • Product category • Type of product • Volume/package design of the product • Matrix for the nanomaterial (nanomaterial location in the product free/matrix bound) • Product use/ handling of the product during use/application method or processes involved (various life-cycle steps may be covered by different exposure scenarios/ assessments) • Considerations regarding foreseeable misuse • Site of body area exposed • Identification of specific exposure routes (primary and secondary exposure routes) • Direct/ indirect use (intended for human exposure/or not intended but a follow by normal use) • Indoor/ outdoor use (inhalation exposure) • Generation of nanomaterial during use (especially inhalation exposure) • Specific target groups (children, teenagers, adult men, adult women, etc.)
Quantitative exposure parameters
• Size distribution of particles and fraction in nano-size • Concentration of nanomaterial in the product • Volume used per use event • Retention rate of product (e.g. dermal exposure or fraction ingested) • Degree of liberation/ migration of nanomaterial from a matrix (dermal exposure, oral exposure) • Body surface area exposed (dermal exposure) • Article surface area in contact (dermal exposure, oral exposure) • Volume released to air (inhalation) • Concentration in air (inhalation) • Duration of exposure • Frequency of exposure

The ***qualitative parameters*** are mainly for characterising the exposure scenario for a product, but they may contain some quantitative elements e.g. the packaging volume in which the product is sold. The **quantitative parameters** are parameters, which can be used in an algorithm to obtain a quantitative estimate of the exposure.

Some of the above parameters are primarily important in connection with specific exposure routes, which are indicated in brackets.

It should be stressed that some parameters and type of information are considered especially relevant for nanoproducts and nanomaterials. These are nanomaterial identification, surface coating of the nanomaterial, particle size distribution, details on the matrix, attachment to matrix (e.g. embedded or surface attached), and product formulation (e.g. pump spray vs propellant spray etc.).

Whereas semi-quantitative *oral and dermal exposure* assessment may be addressed in a rather simplistic and transparent way using rather few assumptions concerning e.g. the amount ingested or the amount applied on skin, it may be more difficult or complex to obtain semi-quantitative estimates on *inhalational exposure*. This is because multiple factors in addition to the volume used may affect the exposure. A key parameter is the concentration of the air in a person's breathing zone, which depends on various factors such as: emission rate of droplets/solid particles into air from the product, the air exchange rate in the room, particle size distribution, sedimentation rate of the different particle sizes, the persons distance to the emission source (e.g. spray or air cleaner), and the breathing rate and breathing volume of the person.

(Appendix 6 in the appendix report gives further details regarding the activities conducted in relation to the Chapter 4 activities).

Chapter 5: Specific nanomaterial exposure assessment
In addition to the collection of data on specific nanoproducts (Chapter 2) and descriptions of the relevant assessment tools (Chapter 3 and 4), a literature search was conducted in order to gain knowledge from the scientific literature and reports on *concrete examples of exposure assessment* to nanomaterials from consumer products within the product categories defined in Chapter 2. These exposure assessments may either have been carried out by use of some of the tools described above or have been based on measurements of the amount of liberated nanomaterial during product use. Thus, these examples for several of the products in the product categories defined in Chapter 2 provided additional information regarding the exposure potential. In addition, some new products and nanomaterials in certain products were identified during this exercise. Thus, the specific information gained from this chapter further fed into the next phase of the project, where representative and specific consumer exposure scenarios were selected (Chapter 6) and the exposure assessed (Chapter 7).

(The reader is referred to Section 5.12 for summaries on the various findings for the various product categories).

Chapter 6: Selection of exposure scenarios for further exposure and risk assessment
Based on the knowledge gained in Chapter 2 and from Appendix 4 (data on specific nanoproducts on the market); Chapters 3 and 4 (knowledge from tools, models and guidance) and Chapter 5 (specific exposure assessment from literature on products from the selected product categories) and a working table overview (Appendix 7 in appendix report), the project team made a draft table with 20 representative consumer exposure scenarios representing various nanoproducts.

The selection of the scenarios/products was made using the following criteria agreed with the Danish EPA:

-Coverage of the various product categories and type of use
-Coverage of various formulations and matrices of the products/articles
-Coverage of various type of use/application methods
-Coverage of low as well as high quantitative use of the product
-Coverage of high/ low/ uncertain exposure potential
-Coverage of specific user or target group populations
-Coverage of all relevant exposure routes (dermal, oral, inhalation and eye)
-Coverage of uses of nanomaterials that may be of toxicological concern
-Coverage of most used nanomaterials

The draft table was discussed during a workshop with the external expert panel in order to include comments and ideas from the panel members. The resulting choice of the 20 exposure scenarios *(see Table 6-1)* was the outcome of this process. It was during the workshop emphasized by the external experts that although each of the 20 scenarios may be representative for similar products/scenarios, the total of the 20 scenarios was far from being representative for the overall consumer exposure to nanomaterials. On the other hand, the scenarios chosen could be seen as representing possible high exposure/risk scenarios (and some possible low exposure/risk scenarios) given the current knowledge about nanomaterials in consumer products.

Chapter 7: Consumer exposure to nanomaterials - exposure assessment of selected scenarios
Based on the findings from evaluating existing methods and tools (Chapter 3) and discussions with the Danish EPA and the external expert group, it was decided to perform a *case-by-case assessment* for each scenario based on existing information and expert knowledge, including a careful description of uncertainties.

Based on the conclusions in Chapter 4, an overall template for collection and presentation of relevant exposure parameters, and for performing the exposure assessment for the various scenarios, was made. Based on this template exposure assessment and exposure, estimates were made for the 20 scenarios (see Appendix 8 in the appendix report) and the results from this were compiled into Table 7-1. In this table the exposure estimations were given for the target groups considered most relevant (or for which most specific data have been found) and for each exposure route. The results were given in *mg NM/cm²* (dermal load); *mg NM/*m³ (inhalation); *mg NM/person/ day* (dermal, oral, inhalation exposure) and *mg NM/ kg bw/day* (dermal, oral, inhalation exposure). In specific cases where data was available, also exposure estimates in particle number concentrations were given.

The reader is referred to Section 7.2 discussing the outcome of the exposure estimates regarding:
- the potential for nanomaterial exposure for the various exposure routes (oral, dermal, inhalational and eye exposure);
- the potential for exposure of the 7 specific nanomaterials covered by the scenarios;
- the potential of nanomaterial exposure for the different target groups (children, teenagers and adults).

Moreover, Chapter 7 identified main uncertainties to be considered.

Main uncertainties to consider in the further project activities
Based on the findings in this report, the following key uncertainties related to assessment of consumer exposure to nanoproducts were identified to be considered in the further activities in this project:

-Generally, the chemical identify and/or properties of nanomaterials applied in consumer products is not very well described. Several entries in available inventories/databases give no (indicated as "Unknown") or very generic information about the contained nanomaterial and seldom any details about their characteristics. Also in some cases, the claim of a nanoproduct is not due to actual nano-content but due to reactive chemistry and formation of nano-scale particles or surface structures during/after application of the products as in the case of some "nanosprays".

-Related to this, the nanomaterial concentration in a consumer product is often not (precisely) indicated and therefore the exposure estimate becomes associated with high uncertainty.

- In many cases the exposure to nanoparticles will be in association with a matrix or liberated from a matrix where the transfer out of a droplet or a surface layer (e.g. the matrix of a sanding fragment) is less understood as compared to exposure from soluble chemicals. Thus, it may be very uncertain to which extent the nanomaterial can be liberated (or can migrate) from the product matrix, and this very much influences the actual oral or dermal exposure to the nanomaterial.

-With a few exceptions, available data and models, only allow exposure estimation in the mass metric. In particular for inhalation, the particle number concentration or the total surface area might for some specific cases be more relevant for further risk assessment.

-In general, current exposure estimation models are not designed for estimating nanomaterial exposure.

-Currently, it appears more reliable to estimate (conservatively) oral and dermal exposures to nanomaterials (mass based exposure) compared to inhalational exposure.

- Inhalation exposure is more difficult to assess and from the literature review, it appears particularly difficult to assess exposures following pump and propellant spray applications. Although the amount of scientific publications presenting spray measurement data are growing, a closer look at these publications reveal that exposure concentration are highly dependent on a significant number of experimental parameters (pressure, nozzle size, ventilation, size of experimental chamber, viscosity of sample, analytical measurement techniques, etc.). Thus, in general, representative data for inhalation exposure following spray applications are lacking.

-To some extent, the same applies for data on releases following mechanical reworking (sanding, grinding) as well as wear and tear of nanomaterials containing consumer products.

Thus, when making risk assessment of the 20 scenarios in the next phase of the project especially the following should be noted and taken into account:

- The 20 scenarios identified might be good examples of high (and low) exposures associated with consumer products, but given the current knowledge about nanomaterials in consumer products, they cannot be used to generalise to consumer products in general.

-When assessing risks, it should be noted that the characterization of the nanomaterial(s) in the investigated consumer products is generally not very well described, making it challenging to match exposure findings with hazard findings.

-Care should be taken when assessing in particular inhalation risks in the next phases of the project as the mass metric applied is probably not the most appropriate metric for assessing risk. Also, in general, the low tier exposure estimations may be very conservative which of course should be kept in mind and considered when evaluating the outcome of the risk assessment.

Sammenfatning og konklusion

Under overskriften "Bedre styr på nanomaterialer" har den danske Miljøstyrelse iværksat en række projekter, der sigter på at undersøge og generere ny viden om forekomsten af nanomaterialer i produkter på det danske marked og vurdere potentielle risici for forbrugerne og miljøet.

Denne rapport er en del af en serie på fire i et projekt, som omhandler forbrugereksponering og risikovurdering af nanomaterialer i produkter på det danske marked.

Nedenfor opsummeres indholdet fra de syv kapitler i denne rapport med fokus på resultater og konklusioner.

Kapitel 1: Introduktion
Nanomaterialer findes i en lang række forbrugerprodukter, og den kommercielle anvendelse af nanomaterialer forventes at stige hurtigt i fremtiden, både i mængde og i udbredelse. Det erkendes i stigende omfang, at materialer i nanoform kan besidde unikke egenskaber sammenlignet med mikro- og makroformer af det samme materiale. Mens dette på den ene side begunstiger anvendelsen af nanomaterialer i produkter, artikler og teknologier, er der på den anden side opstået betænkeligheder i forhold til de mulige effekter, nanomaterialerne kan have på sundhed og miljø.

Denne rapport har til formål at belyse tilstedeværelsen af og den mulige eksponering for nanomaterialer i forbrugerprodukter samt analysere tilgængelige metoder og værktøjer, som kunne anvendes til at vurdere eksponering og risiko ved anvendelse af nanomaterialer i forbrugerprodukter.

De overordnede mål med denne rapport er at:

- evaluere eksisterende metoder og værktøjer til vurdering af forbrugereksponering og risici forbundet med forbruger-nanoprodukter
- identificere forbruger-nanoprodukter på markedet, hvorfra der derpå udvælges ca. 20 repræsentative produkter til nærmere beskrivelse af eksponeringsscenarier og risikovurdering

Mens eksponeringsscenarier for de 20 produkter beskrives i denne rapport, beskrives resultaterne af risikovurderingen i en efterfølgende rapport i projektet.

Kapitel 2: Nanoprodukter og forbrugerscenarier, udvælgelse
Som den første aktivitet blev relevante datakilder, som beskriver forbrugereksponering for nanomaterialer, identificeret. RIVM (2009) rapporten "Exposure to nanomaterials in consumer products" viste sig i den forbindelse at være et velegnet udgangspunkt. Rapporten udpeger og beskriver således vigtige faktorer/parametre til vurdering af forbrugereksponering for nanomaterialer samt angiver en skønsmæssig vurdering af eksponeringspotentialet for flere kategorier/ typer af forbrugerprodukter. Yderligere blev der udpeget følgende databaser/opgørelser mht. nano-produkter:

- Nanodatabasen fra DTU Miljø, Det Økologiske Råd og Forbrugerrådet;
- BUND databasen;
-ANEC/BEUC databasen;
-US Nanotechproject databasen.

Data fra disse databaser blev suppleret med data fra en netop færdiggjort rapport fra Miljøstyrelsen fra 2014: "Supplementary survey of products on the Danish market containing nanomaterials".

Med viden fra disse kilder og i samråd med Miljøstyrelsen blev det besluttet at koncentrere indsamlingen af produktdata inden for følgende kategorier af nanoprodukter:

Mad og drikkevarer; kosmetik; Rengøringsmidler; overfladehandlings-/imprægneringsmidler; plejeprodukter (biler, både); tekstiler; byggematerialer; medicinsk udstyr; luftrensere; brændstof- og smøreolie-additiver; elektronisk udstyr; andet udstyr (fx sportsudstyr, hvidevarer etc.).

Data for mere end 120 nanoprodukter inden for disse kategorier blev indsamlet fra datakilderne, og oplistet i en tabel inspireret af RIVM (2009) for at give oplysninger om de parametre, der må anses for særligt relevante i forbindelse med en eksponeringsvurdering.

Ved indsamling af produktdata blev der fokuseret på:

- at der er så konkret viden som muligt om den kemiske identitet af nanomaterialet i produktet
- at produktet er relevant for det danske og det europæiske marked (det antages generelt at produkter på det europæiske marked også kunne være på det danske marked)
- at der for hver produktkategori udvælges produkter, der dækker bredest muligt mht. forskellige i) formuleringer, ii) typer af anvendelse og iii) håndteringsmåder

Det viste sig ved søgningen i datakilderne, at for mange produkter bliver indholdet af et nanomateriale ofte kun angivet meget uklart mht. identitet, fysisk form og koncentration. Desuden var det vanskeligt at vurdere, i hvilket omfang nanomaterialet var matrix-bundet, forekom på overflader og/eller kunne frigives under brug. Ofte blev det blot anført, at produktet indeholder et nanomateriale uden yderligere specifikation eller dokumentation for dette indhold.

Endelig blev der i databaserne for flere produkter fundet fejlagtig information, og flere steder var henvisninger via links til producenter og forhandlere ikke længere aktive. Det viste sig også, at der er et vist overlap databaserne imellem, da der blev fundet flere gengangere i databaserne. Man skal således anvende data fra databaserne med en vis forsigtighed, såfremt yderligere (og evt. opdateret) dokumentation ikke kan fremskaffes for et produkt.

Lejlighedsvis viste det sig endvidere vanskeligt helt entydigt at placere produkter fra databaserne i én af de udvalgte produktkategorier. Der kan fx være vanskeligt at afgøre, hvorvidt et produkt skal kategoriseres som et rengøringsmiddel eller som et overfladebehandlings-/imprægneringsmiddel, eller om et malingsprodukt skal kategoriseres som et overfladebehandlings-/imprægneringsmiddel eller som et byggemateriale.

Især med hensyn til data for fødevarer og drikkevarer er det vigtigt at bemærke, at databaserne i praksis kun har anført nanomaterialer i forbindelse med kosttilskud, og således ikke omfatter indhold af nanomaterialer i fødevarer som sådan (dvs. fødevarer, hvor visse tilsætningsstoffer er i nanoform, indgår ikke af databaserne).

Generelt er oplysningerne om nanomaterialer i forbrugerprodukter i de tilgængelige databaser/opgørelser primært baseret på, at fabrikanten/udbyderen har påstået/ anført indhold af nanomateriale frem for konkret viden.

Ud over viden fra databaser og opgørelser blev viden om nanomaterialer i forbrugerprodukter igennem projektets forløb løbende suppleret med oplysninger fra den åbne litteratur (beskrevet i kapitel 5 i rapporten). Yderligere indgår der i dette projekt også informationer fra det parallelle delprojekt vedrørende farevurdering af nanomaterialer.

(Bilag 1, 2, 3 og 4 i bilagsrapporten indeholder yderligere oplysninger om de aktiviteter, der gennemførtes i relation til kapitel 2)

Kapitel 3: Gennemgang af tilgængelige risikovurderingsværktøjer
Denne del af projektet gennemgik udvalgte eksponerings- og risikovurderingsværktøjer og undersøgte, hvorvidt værktøjerne omfattede eksponeringsvurderings-, farekarakteriserings- og/eller risikokarakteriseringsmoduler.

Det overordnede sigte med dette er at identificere relevante modeller / værktøjer, som umiddelbart eller i tilpasset form kunne anvendes til risikovurderingen af de 20 eksponeringsscenarier, der skulle udpeges i projektet.

De relevante eksponerings- og risikovurderingsværktøjer blev identificeret i samarbejde med Miljøstyrelsen. Værktøjerne blev udvalgt på grundlag af deres specificitet m.h.t. vurdering af nanomaterialer eller deres generelle anvendelighed til vurdering af traditionelle kemikalier og dermed mulige relevans for vurdering af nanomaterialer. De udvalgte værktøjer omfattede:

- *NanoRiskCat (DTU and NRCWE)*
- *NanoSafer (NRCWE, DTI)*
- *Stoffenmanager Nano (TNO)*
- *Stoffenmanager (TNO)*
- *The ANSES tool*
- *Swiss Precautionary Matrix (Swiss consortium)*
- *ECETOC TRA*
- *ConsExpo (RIVM)*
- *DREAM (TNO and IOM)*
- *Margin of Exposure (MOE) concept (The US Soap and Detergent Industries)*

Det skal bemærkes, at der ikke kun blev bedømt værktøjer beregnet til vurdering af forbrugereksponering, idet eksponerings-/risikovurderingsværktøjer beregnet for arbejdsmiljø i visse tilfælde også blev medtaget, da elementer herfra kunne tænkes anvendt, da der ofte kan være overlap mellem arbejdsmiljø- og forbruger-eksponeringsscenarier.

Vurdering af modellerne/værktøjerne blev foretaget med udgangspunkt i en udarbejdet skabelon med relevante spørgsmål i relation til modellerne/værktøjernes indhold og anvendelsesområder. Udfyldte vurderingsskabeloner kan ses for de enkelte modeller/værktøjer i bilag 5 i bilagsrapporten.

Det samlede konklusion af denne gennemgang var, at de angivne modeller/ værktøjer varierer betydeligt bl.a. med hensyn til hvilke scenarier de omfatter, hvilket grad af kvantificering der anvendes, samt hvilke eksponeringsveje og hvilke målgrupper (og evt. undergrupper) i befolkningen de omfatter. De nano-specifikke værktøjer er generelt beregnet til kvalitative vurderinger og ikke specifikt designet til at vurdere, hvorvidt der foreligger en konkret risiko. Værktøjerne indikerer snarere, hvor der kan være en potentiel risiko, og hvor stærke indikationer der er for at iværksætte konkrete tiltag for en præventiv risikohåndtering. Ingen af værktøjerne til vurdering af nanomaterialer omfatter specifik vurdering af eksponeringsveje i forhold til eksponering gennem indtagelse, hudkontakt eller via øjnene.

I modsætning hertil er de generelle (ikke nano-specifikke værktøjer) generelt mere kvantitative med en bredere dækningsflade, fx i form af flere eksponeringsveje. Der er værd at bemærke, at antagelser vedrørende eksponering og de anvendte algoritmer til eksponeringsvurderingen i de fleste af de *ikke* nano-specifikke værktøjer er mere enkle og mere konservative (dvs. har en tendens til at overestimere) end algoritmerne i de mest avancerede nanospecifikke værktøjer til vurdering af eksponering via inhalation.

Værktøjerne anvender generelt vægtbaserede måleenheder (f.eks. mg/m³), som måske ikke altid er de mest relevante enheder, da partikel*antal* eller totalt partikel*overfladeareal* især for nanomaterialer (og især ifm. med indånding) kan være mere relevant ved vurdering af eksponering og risiko.

Alt i alt blev der ikke identificeret noget enkelt værktøj (eller kombination af værktøjer), som kunne muliggøre en passende, ensartet og harmoniseret eksponerings-/risikovurdering for alle relevante typer af nanoforbrugerprodukter. Således ville der være behov for yderligere tilpasninger for at udvikle og modificere værktøjerne for at tage højde for nanospecifikke egenskaber og opnå mere ensartede og sammenlignelige resultater, som så efterfølgende kan valideres.

For den fremtidige eksponerings- og risikovurdering i dette projekt blev det derfor overvejet:

1) - at vurdere nogle af de udvalgte scenarier med alle værktøjer (i det omfang dette er muligt, fx i forhold til hvilke typer data der er tilgængelige, og hvilke typer scenarier de enkelte værktøjer omfatter), og herudfra at foretage en ekspertbaseret vurdering;
2) - at anvende og sammensætte dele af flere relevante værktøjer;
3) - som udgangspunkt ikke at anvende konkrete redskaber, men derimod at gennemføre en case-by-case ekspertvurdering for hvert af de udvalgte scenarier.

Efter drøftelser med det eksterne ekspertpanel blev det foreslået at anvende en kombination af den anden og tredje mulighed, afhængigt af tilgængeligheden af data og de identificerede scenarier. Den nøjagtige tilgang for vurdering af forbrugereksponering og risiko i de næste faser af projektet vil så afhænge af de konkrete scenarier, der skal vurderes, samt de konkrete eksponerings- og farlighedsdata, der vil være til rådighed.

(Bilag 5 i bilagsrapporten indeholder yderligere detaljer om de aktiviteter, der blev gennemført i kapitel 3).

Kapitel 4: Eksponeringsvurdering og angivelse af vigtige faktorer, der bestemmer eksponeringen

Formålet med dette kapitel er at give et overblik over den nødvendige viden til at foretage en pålidelig, konservativ (forsigtig) eksponeringsvurdering af forbrugerprodukter indeholdende nanomaterialer. De vigtigste faktorer/parametre, der er bestemmende for forbrugereksponering, blev udpeget og beskrevet mere detaljeret i forhold til de forskellige eksponeringsveje og anvendelsesscenarier for de forskellige produktkategorier og produktformuleringer.

For at nå dette mål beskriver første del af dette kapitel relevante vejledninger og værktøjer i forbindelse med eksponeringsvurdering af *kemikalier* i forbrugerprodukter/-artikler samt vejledninger og værktøjer, der specifikt vedrører eksponering for *nanomaterialer*.

Følgende vejledninger og værktøjer blev gennemgået for at udpege de vigtigste faktorer/parametre, der har betydning for den mulige forbrugereksponering:

- RIVM (2009) exposure to nanomaterials in consumer products
- REACH guidance documents on exposure assessment from chemical products and articles

- *SCCS guidance on nanomaterials in cosmetics*
- *EFSA guidance on nanomaterials in food*
- *Environmental Defense – DuPont approach*
- *ECETOC TRA*
- *ConsExpo*
- *NanoSafer*
- *NanoRiskCat*
- *Stoffenmanager*
- *Stoffenmanager Nano*
- *ANSES*
- *Swiss Precautionary matrix*
- *Dream*
- *Margin of exposure concept*

Som nævnt har RIVM (2009) allerede foretaget en analyse af forbrugereksponering for nanomaterialer. Nøgleparametre blev af eksperter identificeret i rapporten, og disse nøgleparametre dannede fundamentet for den videre analyse af de andre vejledninger og værktøjer. Med dette som udgangspunkt blev de andre vejledninger og værktøjer derpå beskrevet (nærmere detaljer i bilag 6), og det blev vurderet, om der kunne identificeres yderligere vigtige eksponeringsparametre.

Efter at have udført denne trinvise analyse af de forskellige værktøjer og vejledninger var det muligt at udpege følgende parametre som relevante for eksponeringsvurdering af forbrugerprodukter:

Kvalitative eksponeringsparametre
• Identiteten af nanomaterialet • Produktkategori • Produkttype • Volumen af produktet/pakkedesign • Matrix for nanomaterialet (nanomaterialets tilstand i produktet, frit/matrix-bundet) • Produktets anvendelse, håndtering af produktet under anvendelse og involverede processer (forskellige livscyklustrin kan være omfattet af forskellige eksponeringsscenarier/ -vurderinger) • Overvejelser vedr. forudsigelig, ikke-tilsigtet produktanvendelse • Eksponeret kropsområde • Identifikation af de specifikke eksponeringsveje (primære og sekundære eksponeringsveje) • Direkte/indirekte anvendelse (tilsigtet human eksponering/eller eksponeringen ikke tilsigtet men en følge af anvendelsen) • Indendørs/udendørs anvendelse (særligt for inhalationseksponering) • Generering af nanomaterialer under anvendelse (særligt i forbindelse med spray og indånding) • Specifikke målgrupper (børn, unge, voksne mænd, voksne kvinder, osv.)
Kvantitative eksponeringsparametre
• Størrelsesfordeling af partikler og fraktion i nano-størrelse • Koncentration af nanomateriale i produktet • Volumen, der anvendes i én arbejdsgang • Produktets retention (fx andel der forbliver på huden ved hudkontakt) • Frigivelsesgrad/nanomaterialets migration fra produktmatrix (dermal eksponering, oral eksponering) • Eksponeret kropsoverflade (dermal eksponering)

- En artikels berøringsareal (dermal eksponering, oral eksponering)
- Volumen/ mængde af produkt frigivet til luften (indånding)
- Koncentration i luften (indånding)
- Eksponeringsvarighed
- Eksponeringshyppighed

De ***kvalitative parametre*** er primært til karakterisering af et produkts eksponeringsscenarie, men de kan indeholde nogle kvantitative elementer, f.eks. produktets pakkevolumen. De ***kvantitative parametre*** er parametre, der kan indgå i en algoritme til at opnå en kvantitativ vurdering af eksponeringen.

Nogle af ovennævnte parametre er primært vigtige i forbindelse med konkrete eksponeringsveje - dette er angivet i parentes.

Det skal understreges, at nogle parametre og typer af information må anses for at være *særligt relevante* for nanoprodukter og nanomaterialer. Disse er: Identiteten af nanomaterialet (inkl. overflademodificering og partikelstørrelsesfordeling), oplysninger i forhold til produktmatrix (vedhæftning til/ indlejring i matrix), og produktdesign/-formulering (fx pumpespray eller drivgasspray).

Mens semikvantitativ *oral og dermal eksponering*svurdering kan adresseres på en temmelig forenklet og gennemskuelig måde ved hjælp af ganske få antagelser om eksempelvis indtaget mængde eller mængde anvendt på huden, kan det være mere vanskeligt eller komplekst at opnå semikvantitative skøn for eksponering gennem indånding/ inhalation. Dette skyldes, at flere faktorer ud over den anvendte produktmængde kan påvirke eksponeringen. En vigtig parameter er koncentrationen af luft i en persons indåndingszone, som vil afhænge af flere forskellige faktorer, såsom emissionshastighed af dråber/faste partikler til luften fra produktet, luftskifte i rummet, partikelstørrelsesfordeling, sedimentationshastighed af de forskellige partikelstørrelser, personens afstand til emissionskilden (fx spray eller luftrenser) og personens indåndingshastighed og vejrtrækningsvolumen.

(Bilag 6 i bilagsrapporten indeholder yderligere detaljer om de aktiviteter, der er gennemført i kapitel 4).

Kapitel 5: Specifikke eksempler på eksponeringsvurderinger af nanomaterialer i forbruger-produkter

Ud over indsamling af data om konkrete nanoprodukter (kapitel 2) og beskrivelse af de relevante vurderingsværktøjer (kapitel 3 og 4) blev der foretaget en litteratursøgning for at indsamle viden fra den åbne litteratur om *konkrete eksempler på eksponeringsvurdering* af nanomaterialer fra forbrugerprodukter inden for de produktkategorier, der er udpeget i kapitel 2. Disse eksponeringsvurderinger viste sig enten at være udført ved hjælp af nogle af de værktøjer, der er beskrevet ovenfor, eller at være baseret på målinger. Eksemplerne bidrog således med yderligere relevante oplysninger om flere produkter i produktkategorierne. Derudover blev der under denne aktivitet også identificeret nogle nye produkter og nanomaterialer. Samlet set gav dette således et bedre grundlag for næste fase af projektet, hvor repræsentative og specifikke forbrugereksponeringsscenarier skulle udvælges (se kapitel 6), og hvor den endelige eksponeringsvurdering skulle foretages (se kapitel 7).

(Der henvises til afsnit 5.12 for sammendrag af de forskellige resultater for de forskellige produktkategorier).

Kapitel 6: Valg af eksponeringsscenarier til yderligere vurdering af eksponering og risiko

Baseret på viden fra kapitel 2 og bilag 4 (data om specifikke nanoprodukter på markedet), kapitel 3 og 4 (viden fra værktøjer, modeller og vejledninger) og kapitel 5 (specifik eksponeringsvurdering fra litteratur vedrørende produkter fra de udvalgte produktkategorier), samt en arbejdsoversigt (bilag 7 i bilagsrapporten), udarbejdede projektgruppen et udkast til en tabel med 20 repræsentative forbrugereksponeringsscenarier for forskellige nanoprodukter.

Udvælgelse af disse scenarier/produkter blev foretaget efter følgende kriterier aftalt med Miljøstyrelsen for at opnå dækning af:

- *forskellige produktkategorier og anvendelsestyper*
- *diverse formuleringer og matricer for produkter/artikler*
- *diverse typer af anvendelser/anvendelsesmetoder*
- *både lav og høj mængde produkt anvendt*
- *højt/lavt eller meget usikkert eksponeringspotentiale*
- *specifikke brugergrupper eller målgrupper i befolkningen*
- *alle relevante eksponeringsveje (dermal, oral, inhalation og øjne)*
- *anvendelse af nanomaterialer på en måde, der kan være toksikologisk betænkelig*
- *de mest anvendte nanomaterialer*

Udkastet til de repræsentative eksponeringsscenarier blev drøftet på en workshop med det eksterne ekspertpanel for at modtage kommentarer og ideer fra paneldeltagerne. Resultatet af denne proces blev valget af 20 eksponeringsscenarier (*se tabel 6-1*) til videre vurdering. På workshoppen blev det understreget af de eksterne eksperter, at selv om hvert af de 20 scenarier kan være repræsentativt for lignende produkter eller scenarier, så er de 20 scenarier langt fra repræsentative for den samlede forbrugereksponering for nanomaterialer. På den anden side kunne de valgte scenarier anses som udtryk for scenarier med varierende (fra højt til lavt) eksponeringspotentiale vurderet ud fra den nuværende viden om nanomaterialer i forbrugerprodukter.

Kapitel 7: Forbrugereksponering for nanomaterialer – eksponeringsvurdering af udvalgte scenarier

Baseret på resultaterne fra evalueringen af de eksisterende metoder og værktøjer (kapitel 3) og drøftelser med Miljøstyrelsen og den eksterne ekspertgruppe blev det besluttet at udføre en case-by-case vurdering for hvert scenarie baseret på eksisterende oplysninger og ekspertviden, og med en omhyggelig beskrivelse af usikkerheder.

På grundlag af konklusionerne i kapitel 4 blev der lavet en arbejdsskabelon til præsentation af de relevante eksponeringsparametre og den indsamlede viden samt til selve eksponeringsvurderingen for de forskellige scenarier. Med udgangspunkt i denne skabelon blev der lavet eksponeringsberegninger for hvert af de 20 scenarier (fremgår af bilag 8 i bilagsrapporten), og resultaterne fra vurderingerne blev derpå samlet i en oversigttabel (tabel 7-1). I tabellen er der angivet eksponeringsestimater for relevante eksponeringsveje for de målgrupper, der anses for mest relevante. Resultaterne er angivet i *mg* nanomateriale (*NM)/cm²* (hudkontakt), *mg NM/m³* (indånding), *mg NM/person/dag* (hudkontakt, oral indtagelse, indånding) og *mg NM/kg legemsvægt/dag* (hudkontakt, oral indtagelse, indånding). I særlige tilfælde, hvor data var til rådighed, blev eksponeringsestimater i partikelantal koncentrationer også angivet.

Der henvises til sektion 7.2, som endvidere diskuterer resultaterne af eksponeringsberegningerne m.h.t.:

-potentiale for eksponering via de forskellige eksponeringsveje (hud kontakt, oral indtagelse, indånding og øjeneksponering)

-potentiale for eksponering for de 7 specifikke nanomaterialer, der var omfattet af scenarierne
-potentiale for eksponering af de forskellige målgrupper (børn, unge og voksne) for nanomateriale

Desuden diskuteres i kapitel 7 en række væsentlige usikkerheder, som man bør have for øje.

Væsentlige usikkerheder, som man bør have for øje i de fremadrettede projektaktiviteter

På baggrund af den opnåede viden blev følgende væsentlige usikkerheder, tilknyttet vurdering af forbrugereksponering for nanoprodukter, identificeret. Det er vigtigt at have disse for øje i de fremadrettede projektaktiviteter:

- Generelt er kemisk identifikation og/eller egenskaber af nanomaterialer, der anvendes i forbrugerprodukter, ikke særligt velbeskrevne. Tilgængelige databaser/ opgørelser angiver ofte ingen eller meget generiske oplysninger om det indeholdte nanomateriale og sjældent nogen detaljer om dets karakteristika. I nogle tilfælde skyldes angivelse som et nanoprodukt ikke et egentligt nanoindhold, men derimod reaktiv kemi og dannelse af nanopartikler eller -overfladestrukturer i forbindelse med påføring af produkterne, hvilket fx er tilfældet med nogle "nanosprays".

-Koncentrationen af nanomateriale i et forbrugerprodukt er ofte ikke (præcist) angivet, og derfor bliver eksponeringsberegningen forbundet med stor usikkerhed.

-I mange tilfælde vil eksponering for nanopartikler være enten i forbindelse med *vedhæftning* til en matrix eller ved frigivelse fra en matrix. Frigivelsen og eksponeringspotentialet af et nanomateriale afgivet fra en matrix (fx fra en dråbe eller fra slibestøv) er således væsentligt dårligere belyst end fx frigivelse af et opløseligt kemikalie. Det kan således være meget usikkert, i hvilket omfang et nanomateriale kan frigives (eller kan migrere) fra produktmatrix.

-Med nogle få undtagelser tillader tilgængelige data og modeller kun en vægtbaseret eksponeringsberegning, Særligt ved indånding er det muligt at fx partikelkoncentration eller det samlede overfladeareal af partiklerne er mere relevant for en risikovurdering.

-Generelt er de aktuelle modeller til eksponeringsberegning ikke målrettet estimering af eksponering for nanomaterialer.

-For nærværende synes det mere pålideligt at foretage konservative eksponeringsestimater (eksempelvis ved vægtbaserede estimater) for oral og dermal eksponering end at estimere eksponering ved inhalation/indånding.

-Eksponering ved indånding er vanskeligere at vurdere, og fra litteraturen fremgår det særligt vanskeligt at vurdere eksponering i forbindelse med anvendelser i pumpesprays og drivgasspray-produkter. Selv om mængden af videnskabelige publikationer omhandlende disse scenarier vokser, viser et nærmere eftersyn af disse publikationer, at eksponeringskoncentrationen er meget afhængig af et betydeligt antal eksperimentelle parametre (tryk, dyse-størrelse, ventilation, forsøgsrummets størrelse, prøvens viskositet, analytiske måleteknikker, osv.). Således mangler der generelt repræsentative data for eksponering ved indånding efter spraying/sprøjtning.

-Til en vis grad gælder det samme for data mht. eksponering i forbindelse med mekanisk efterbearbejdning (slibning, formaling, m.v.) samt i forbindelse med slitage af forbrugerprodukter med indhold af nanomaterialer.

Således bør især det følgende bemærkes og holdes for øje, når der foretages risikovurdering af de 20 scenarier i næste fase af projektet:

-De 20 identificerede scenarier kan være gode eksempler på høj- (og lav-) eksponering forbundet med forbrugerprodukter, men i betragtning af den nuværende viden om nanomaterialer i forbrugerprodukter kan de ikke bruges mere generelt til at vurdere eksponeringen fra forbrugerprodukter i almindelighed.

-Ved vurdering af risici skal det bemærkes, at karakterisering af nanomaterialet i de undersøgte forbrugerprodukter generelt ikke er særligt velbeskrevet, hvilket gør det vanskeligt at sammenligne eksponeringsestimater med data, der beskriver farligheden af et tilsvarende stof, men som måske ikke er helt sammenligneligt.

-Der bør udvises forsigtighed ved vurdering af risiko ved indånding i de næste faser af projektet, da et vægtbaseret eksponeringsestimat måske ikke er den mest hensigtsmæssige parameter til vurdering af risici ved indånding.

-Generelt vil konservative metoder til beregning af eksponeringen overvurdere, hvilket naturligvis bør tages i betragtning ved den endelige bedømmelse af resultatet af risikovurderingen.

1. Introduction

1.1 Background

Nanomaterials are found in a wide range of consumer products and the commercial use of nanomaterials is anticipated to increase rapidly in the future both in quantity and diversity. It is increasingly recognised that materials in the nanoform can have unique properties as compared to the microforms and macroforms of the same material. This favours the use of nanomaterials in products, articles and technologies. At the same time, concerns in relation to the possible health and environmental properties and impacts of nanomaterials have surfaced.

The current report addresses presence and exposure of nanomaterials in consumer products, as well as an analysis of available tools, which could be used to assess exposure and risk from use of nanomaterials in consumer products. In this report, the term "nano-product" designates mixtures and articles containing nanomaterials (or claimed as a nano-product). This may cover products even with small amounts/ contents of nanomaterials. Some products groups/categories are outside the scope of this project, such as pharmaceuticals and tattoo colours, whereas medical devices (those most similar to a consumer use), food and food contact materials are within the scope. Also, the product life cycle after the initial use of the product is included (e.g. wear of a product or sanding of a painted surface) is included.

As set out in the preface, two other reports from the projects will specifically address: i) the hazardous properties of the nanomaterials used in consumer products, and ii) exposure/risks in relation to background exposure to nanoparticles/ nanomaterials from environmental sources. A final report will aim at assessing the risks for Danish consumers in relation to selected consumer products containing nanomaterials

Figure 1 provides an overview of how the different work packages (WPs) of the project should support the overall aim of the project. The current report includes the outputs of WP1 and WP2 of the project.

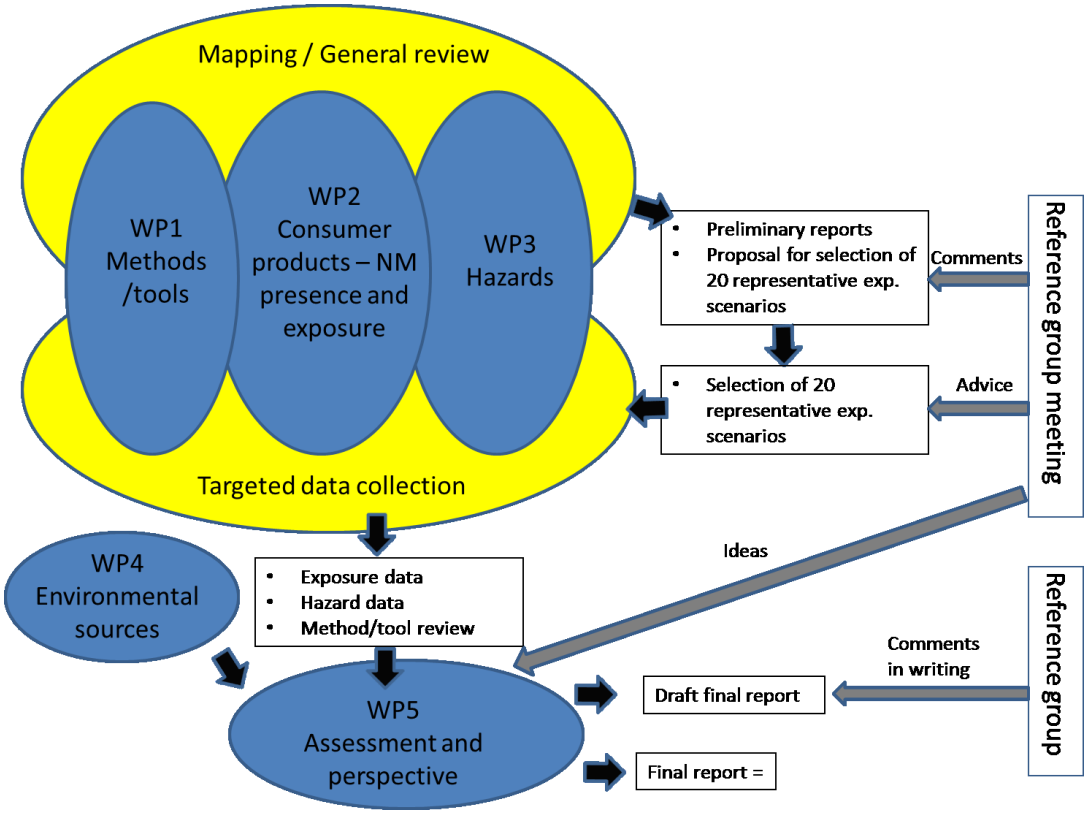

FIGURE 1-1. OVERVIEW OF PROJECT ACTIVITIES – THE CURRENT REPORT ADDRESSES WP1 AND WP2

1.2 Objectives

The overall objectives with the current report have been to:

- Assess methods/approaches/tools for assessing consumer exposure and risks from exposure to consumer nanoproducts.
- Search and select representative consumer nanoproducts from which to identify and describe a total of 20 exposure scenarios for further risk assessment.

1.3 Reader's guide to approach and methodology

In order to guide the reader, a short overview of the approach and methodology of the various chapters in this report is provided below.

1.3.1 Chapter 1. Introduction

This chapter covers background, objectives and reader's guide to approach and methodology

1.3.2 Chapter 2. Nanoproducts and consumer exposure scenarios to look for

As a starting point for the identification of relevant consumer exposure scenarios for nanomaterials, an initial look on databases/inventories on “nano-products” and reports concerning consumer use of nanoproducts was taken. Based on this initial look, a series of relevant product categories were in consultation with the Danish EPA selected for further data search and assessment.

The databases/inventories and reports were further scrutinised in order to collect and in tabular form organise specific exposure-relevant data for the different types of nanoproducts within the identified product categories.

At this stage, it has to be mentioned that a general challenge during collecting of data on specific products was the documentation of the nano-content of the claimed nanoproducts that often was very inadequate or absent.

1.3.3 Chapter 3 Review of available risk assessment tools

For the further assessment of the product categories, models/tools for exposure and risk assessment were in cooperation with the Danish EPA identified for review as to their relevance for the exposure scenarios to be undertaken in this project.

A total of 10 tools were reviewed. It should be noted that not only nanospecific tools were addressed but also tools for risk assessment of chemicals in general. Also, not only consumer specific risk assessment tools were selected, but also tools intended for the occupational environments were included, as these might be applicable for some consumer exposure scenarios as well.

The aim of the review at this stage of the project was to establish an overview of the addressed models/tools in terms of scope, requirements and coverage and to provide an initial indication of how the models/tools would be able to address the preliminary gross list of product categories and the associated exposure scenarios.

1.3.4 Chapter 4. Exposure assessment and key factors affecting exposure

The identified risk assessment tools where described in more detail with respect to their exposure part, and exposure algorithms and key exposure parameters from the tools were identified. In addition to this, also various EU guidance documents and opinions on exposure assessment and risk assessment of nanomaterials were consulted in order to identify key parameters for making exposure assessment.

1.3.5 Chapter 5. Specific nanomaterial exposure assessment

In addition to the collection of data on specific nano-products and description for the relevant assessment tools, a literature search was conducted in order to gain knowledge from the scientific literature and reports on concrete examples of exposure assessment to nanomaterials from consumer products within product categories defined in Chapter 2. These examples may either have been derived from use of some of the tools described above or been obtained by using measurements of the amount of liberated nanomaterial during product use. Thus, the examples may for some of the products in the product categories defined in Chapter 2 give additional indications in relation to the exposure potential.

1.3.6 Chapter 6. Selection of exposure scenarios for further exposure and risk assessment

Based on all nano-products identified and based on a range of selection criteria, 20 exposure scenarios (representing 20 uses/applications of 20 nano-products), considered representative for the exposure and risk of consumer use of nano-products on the Danish market, were selected.

1.3.7 Chapter 7. Consumer exposure to nanomaterials - exposure assessment of selected scenarios

For each of the selected scenarios in Chapter 6 a case-by-case exposure assessment was made based on learnings from mainly Chapter 4 and using relevant literature data from Chapter 5.
Results from the exposure assessment of the scenarios were compiled in a table (Table 7.1) to be further used in the following risk assessment phase of the project presented in a separate report for WP5.

During the elaboration of the above-mentioned chapters, several tables and working documents were elaborated. These are attached separately in an appendix report to this report.

1.4 Working process

Writing of the various chapters in this report has largely been done in a sequential manner. However, as the chapters throughout the report to some extent address the same products, the learning process has been iterative. Thus, when further/new data were obtained, e.g. concerning the content of nanomaterials in specific consumer products or new data regarding uses or exposure scenarios, this knowledge has been included as identified. This may cause some minor inconsistencies when reading the report as some data introduced late in the report not necessarily is fully coherent with the information given earlier in the report.

1.5 Terminology

When the report uses the term nanomaterial this in relation to the physical characteristics and follows the EC recommendation for definition of nanomaterial. The nanomaterial is defined in ISO/TS 80004-4 having internal structure or surface structures in the nanoscale. Nanomaterials include nano-objects and nanostructured materials. However, the report is limited to the industrially produced/engineered nanomaterials.

Nano-scale or *nano-size* generally refers to sizes below 100 nm.

The term *nano-product* is used for a product containing (or claimed to contain) manufactured nanomaterials or a product that result in nano-properties to an object after treatment (e.g., nanosprays used to generate easy-to-clean nano-films on a surface).

Product categories are defined by the purpose for a product e.g.: food, cosmetics, cleaning agents etc. However there may be some overlap in the categories, e.g. paint could be placed in the coating and impregnation category as well as in the category for construction materials. In addition, some cleaning agents could be placed in the category for coating/impregnation as well.

Product types reflect a subdivision of the product category etc. cosmetics contain product types such as shampoo, body lotion, mascara etc.

The *Formulation* of a product describes whether the product is in a spray can, whether it is a liquid or solid. Thus, a formulation may be determined by the chemical content and matrix of a product in combination with the design, volume and packaging/container of the products.

Matrix is the physical entity in which the nanomaterial is contained. The nature of the matrix may be very important by determining to which extent there is a potential for liberation of the nanomaterial, e.g. whether the nanomaterial is tightly bound in a solid matrix or more freely available in a liquid matrix.

In this report the term *nanomaterial exposure* is used as the *external exposure* of the human body to nanomaterial, thus the external exposure takes into account to which extent the nanomaterial is liberated from the matrix, however skin penetration and further systemic absorption from the dermal, oral or inhalation exposure is not considered.

An *exposure scenario* for a nano-product is understood as a qualitative and quantitative description regarding a given use of a product, which may lead to exposure to the nanomaterial with respect to dermal, oral, eye or inhalational exposure during product use by the consumer.

2. Nano-products and consumer exposure scenarios to look for

2.1 Searching for relevant product categories

As a starting point for the identification of relevant consumer exposure scenarios for nanomaterials, relevant databases/inventories on "nano-products" and relevant reports concerning consumer use of nano-products were consulted. The databases/inventories and the reports were pre-selected in consultation with the Danish EPA, see Appendix 1.

Overall it was found that the RIVM (2009) project "*Exposure to nanomaterials in consumer products*" and the Danish "*Nano database*" from DTU Environment, The Danish Ecological Council and Danish Consumer Council provided a first basis for rough evaluations on the exposure potential for various product categories and product types/formulations within the product categories.

In the RIVM (2009) study, exposure estimations for various product categories have been performed on the basis of expert judgements and graded high -/ medium-/ low-/ or unknown exposure potential.

The following information was considered important for making exposure assessment:

- Shape of nanomaterial in product
- Product form (i.e. spray, powder, liquid, solid)
- Free or fixed nanomaterial
- Concentration in product
- Direct/indirect exposure
- Indoor/outdoor use
- Duration time per use
- Frequency of use
- Exposure route.

The Danish Nano database is further considered relevant for the Danish market as it includes rather detailed descriptions of more than 1200 products claimed as nano-products. Also, it includes exposure and hazard assessment of the nanomaterials and it is a living database that is continuously updated.

In the Nano database, the specific products are ranked according to their potential ability to result in exposure (high -/ medium-/low-/ or unknown exposure potential using the colour codes red/ yellow/ green/ or grey). The ranking is mainly done based on the use pattern of the nano-product and the state of the nano-material in the matrix of the product (i.e. to which extent the nanomaterial was free or bound i.e. whether the nanomaterials was airborne, in a liquid, or e.g. bound in or onto a matrix).

Another important information source has been the recent Danish EPA (2014a) supplementary survey of products on the Danish market containing nanomaterials. This survey covers the use of nano-materials in Denmark in food and feed, food packaging, cosmetics, pesticides, medical devices and water treatment. Through contact to Danish producers, importers and trade organisations, information has been gathered on the use of specific nano-materials in the various product categories. Each nano-material was mapped out on a generic level for each product category and the report therefore does not refer to specific commercial products on the market.

Based on these data sources, the following product categories were found to have relatively high potential for consumer exposure to nanomaterials (see also Appendix 2):

Food and beverages:
- *Nano-material ingredients*
- *Food supplements*
- *Nano-material in packaging*

Cosmetics:
- *Spray, liquids, crème, lipstick, mascara, etc.*

Cleaning agents:
- *Liquids, spray, paste*

Coatings/ impregnation:
- *Liquids, spray, cloth/textile, paints, shoe polish*

Maintenance products (car, boats):
- *Liquids, spray, cloth/textile, paste*

Textiles

Construction materials:
- *Self-cleaning surfaces; cement concrete a.o*

Medical devices:
- *E.g. wound dressings containing nano-silver, dental fillings*

Air-cleaners:
- *Sprays*

Fuel and lubrication oil additives

It was further decided to include products from the following product categories as well in order to also cover some expected low-exposure scenarios:

Electronic devices
- *E.g. computers*

Appliances
- *E.g. refrigerators*

2.2 Data sources for finding information on specific nano-products on the market

In addition to the above-mentioned sources that formed the basis of the project, additional nano databases/inventories and reports were identified (see Appendix 1) and further scrutinised in order to find the most relevant data sources of information on specific nano-products to cover all the product categories selected in Section 2.1.

Each of the databases/inventories were examined with respect to the scope (what does it cover, content (which type of information), content and outcome (content and findings from the data source), exposure (which type of exposure relevant information) and the relevance in connection with this project. The outcome of this exercise is indicated in Appendix 3.

The Danish "*Nanodatabasen*" was as already mentioned considered to be a very relevant database as it is a living database with detailed information and evaluations regarding potential exposure (and potential hazard) of each product. Thus, this was used as a first-choice database when extracting data on products from various product categories. Other important and valuable databases for extracting product-specific information was considered to be the BUND database (also a living database) and the ANEC/BEUC database (last update 2012 with nano-silver products) covering to a great extent the same product categories as the Nano-database. The US Nanotech project database was also considered as a key relevant database as it has recently been updated (November 2013) and contain products from Europe. Further, this database has been upgraded with very good search options.

Applications and reference to these databases is often found in reports and scientific literature addressing nanomaterials in products, as these databases are considered the best information sources. However, when applying information from these databases, it should be stressed that the content of these databases are based on "*claims*" on the products. Thus, the databases may be biased or limited as they:

- Only address products for which the supplier can see a benefit in claiming "*nano*".
- Do not include products were the supplier is not interested in claiming "*nano*" or not knowing whether the product contains nanomaterials.
- Do not prove the content of "*nano*", i.e. it has not been verified that the products actually contain the claimed nanomaterials.

A further important information source was a mentioned in Section 2.1 a recent Danish EPA (2014a) supplementary survey of products on the Danish market containing nanomaterials. This survey covers the use of nanomaterials in Denmark in food and feed, food packing, cosmetics, pesticides, medical devices and water treatment. Through contact to Danish producers, importers and trade organisations, information has been gathered on the use of specific nanomaterials in the various product categories. Each nanomaterial was mapped out on a generic level for each product category and the report therefore does not refer to specific product examples on the market.

In Chapter 5, a review of scientific literature addressing exposure to nanomaterials from nano-products will be presented. The findings from that review will supplement the findings in this chapter and be considered in the selection of representative exposure scenarios in Chapter 6.

2.3 Strategy for extraction of product information

To cover the various product categories, formulations and exposure scenarios, it was decided to collect data of about hundred specific products and to extract data from the databases and from the website of the product suppliers to gain as much information as possible for each product. Furthermore, it was decided to collect the data in a structured approach for various parameters important for exposure assessment. Inspired by the findings of RIVM (2009), the following information should be gathered if possible:

- Product name, volume and product type
- Formulation and application method
- Nanomaterial identification
- Nanomaterial concentration in the product
- Volume of product used per event
- Duration of use (per event)
- Frequency of use
- Indoor/ outdoor use
- Target consumer group for the product

- Primary/secondary exposure route.

From this, the following table template was developed for collecting of the data from each product and product category:

Product category XX (direct or indirect exposure by use)									
1 **Product name, volume and type**	**2** **Formulation/ matrix*** Liquid/Aerosol/ Crème/Paste/ Powder/Solid **Application method**	**3** **NM ID**	**4** **Conc. of NM in product** Exact value or range [<1, 1-10, >10%]	**5** **Volume of product per use** Exact value or range [<1g, 1-10g, >10g]	**6** **Duration per event** Minutes/ Hours/ Whole day	**7** **Use frequency and site of use** Daily/ Weekly/ Monthly/ Yearly/ Indoor/ outdoor	**8** **Consumer group** All ages/Children/ Adults/Sportsmen/Hobby	**9** **Primary exposure route(s)/ (secondary exposure route)** Oral/ Dermal/ Inhalation	**10** **Comments/web-links**
The *Nanotechproject* database contains …. The *Nanodatabase* (Nordic Consumer Council) contains….. The *BUND database* …. The *ANEC-BEUC inventory* contains…									
Product category/Products: xx1									
Product name **Volume**	*Specified*								
Type of use	*Estimated*								

For each product, there is one row with *"specified"* data as obtained from the database link (or the product web-site link). The relevant web-links are given in the comment column (10). The row below contains *"estimated"* data or information. This row is filled in if data are not given in the consulted databases or web-site links. This information may be implicit or may be deduced from the way the product is presented and described. Otherwise, it is filled-in based on experience and current/general knowledge about the use of the nanomaterial and the product type. This for example relates to concentration, volume per use, duration and frequency which is generally not listed in the consulted sources of information.

Based on the information in the first eight columns, the most probable primary and secondary exposure routes during product use are identified on the basis of a qualitative exposure evaluation (presented in Column 9).

When selecting products to be assessed in the tables, the strategy was as far as possible focused on products where:

- the nanomaterial has been identified (i.e. chemistry known).
- the product should be of relevance for the Danish and European market (this was often based on assumptions. Further, it was generally assumed that products on the European market could also be on the Danish marked).
- as many different formulations, different type of use or handling within each product category as possible were covered.

2.4 Findings from the search on each of the product categories

The outcome of the search in the databases is reported for the individual products in the tables in Appendix 4. The main findings (regarding nanomaterial ID; type of formulations; exposure routes, and other findings) are briefly described in the following sub-sections.

2.4.1 Food and beverages

All the identified products referred to in Appendix 4 are food supplements. The food supplement products contained the following metallic elements claimed to be in nano form:

silver
platinum
palladium
gold

but also different organic substances apparently in the nano-size were used. The concentrations of the identified nanomaterials range from 10 ppm to <500 ppm (for nano-Ag).

Uses of nanomaterials in food products have not been presented in the databases, and thus specific food items are not included in Table 2-1.

A supplementary survey of products on the Danish market containing nanomaterials (Danish EPA, 2014a) identified in the Danish food industry the following food additives (for colouring, anticaking, etc.), which may contain particles in nanosize: silicon dioxide (E551), titanium dioxide (E171), calcium carbonate (E170), and vegetable carbon (E153). Iron, calcium and silver, and oxides thereof are not approved as food additives but are being marketed as food supplements. For use in food contact materials, nanomaterials such as silicon dioxide, titanium dioxide and titanium nitride have been approved for use.

Specific food products containing these (or other) food additives in nano-form were not identified in the databases. This may first of all be because the food items are not marketed as products containing nanomaterials and further because it may usually not be known to which extent the particulate food additives in fact contain fractions in the nm-size-range and at which levels.

The primary exposure route is of course oral as the products are intended to be ingested.

2.4.2 Cosmetics

In the examples of cosmetic products addressed in appendix 4, the following materials have been indicated to be in nanoform:

silver
in soap/ creams/ gels/ lotions for dermal application. Also in mouth wash solution and in toothpaste

gold
in cream for facial use

platinium
in cream

fullerenes
in cream at dermal application in eye region

nano-peptides
in mascara for eye lashes

silicium dioxide
in sunscreen cream and in liquid preparations for application in face and eye region

zinc oxide
in sunscreen

titanium dioxide
in sunscreen, face powder

calcium peroxide
in toothpaste

copper & copper peptides
in shampoo and facial liquid preparations

carbon black
in mascara

For the far majority of the products, the primary exposure route is the dermal route, whereas secondary routes are in relation to oral, inhalational and eye exposure. For mouthwash solution (nano-Ag) and toothpaste (nano-calcium peroxide), the primary route is the oral route.
The whole volume of a cosmetic is normally intended for direct exposure onto the body e.g. in relation to dermal or oral cavity exposure. For products that are "*leave-on*", the products remain on the body for hours, whereas most of the use volume from "rinse-off" products is washed off (e.g. soaps and shampoos) and exposure is limited to a much shorter duration.

It may be surprising that although pigments are used in a variety of cosmetics (e.g. mascara, lip stick, eye shadow, face powder, etc.), this content seems not to have led to inclusion of any cosmetics into the nano databases/inventories, although pigments, e.g. carbon black, titanium oxide, iron oxides and aluminium hydroxide, may fulfil the EU definition of "*nanomaterial*" (Danish EPA 2014a). However, this definition was established in October 2011 and it might be that pigments prior to that were not generally considered nanomaterials. However, with the new Cosmetics Regulation (Regulation No 1223/2009[1]) which entered into force in 2013, it is mandatory to label for content of ingredients in the nano form and a mandatory pre-notification scheme for products containing nanomaterials entered into force. This is expected to influence upcoming revisions of the databases/inventories. Only few toothpastes occur in the databases even though it has often been stated that they in general contain nanoparticles e.g. nano-silica and nano-TiO2.

According to the Danish EPA (2014a), nanomaterials have been used in nail polish for several years whereas the use of nanomaterials in mascara, eyeliner, face powder and foundation has been introduced within the last year.

As noted above, further knowledge concerning the use of nanomaterials in cosmetics will be available in near future. In the new Cosmetics Regulation there is a requirement for the companies to notify the use of nanomaterials in cosmetics indicating ID, particle size, physical and chemical properties, the amount used in the cosmetics, a toxicological profile, foreseeable exposure and safety data. By 11 January 2014, the Commission should have made a catalogue of all nanomaterials used in cosmetic products available, indicating the categories of cosmetic products and the reasonably foreseeable exposure conditions. This catalogue shall be regularly updated thereafter and be made publicly available. However, the work on creating this catalogue has not met this deadline as considerable inconsistencies in the notifications have been noted.

[1] *Regulation (EC) No 1223/2009 of The European Parliament and of the Council of 30 November 2009 on cosmetic products.*

2.4.3 Cleaning agents

Three different product types are addressed in Appendix 4: liquids, sprays, and cloth/wipe-based products. The indicated active nanomaterial ingredients were either:

silver
titanium dioxide
silica
micelles

Concentration levels around 1% or less than 1% (for nano-Ag) was considered as realistic estimates for these products.

The primary exposure routes were assessed to be inhalation and/or dermal exposure depending on the product type. There is subsequent risk of accidental oral exposure. The volume of the products to be used by each application of the product is typically greater than 10 g. The typical exposure duration will last for minutes, but in some cases the post application stage can result in exposure for days, e.g. this may especially be the case with textiles cleaned/ treated with a nano-product.

2.4.4 Coatings/ impregnation

For many of the products addressed in Appendix 4, no specification of the actual nanomaterial was indicated. However, products with the following nanomaterials were indicated:

titanium dioxide
silicium dioxide
silver
teflon, polytetrafluoroethylene

Only one product specifies the actual concentration of the nanomaterial. For the remaining products, the estimated nanomaterial concentrations are less than 10%, with the most products estimated to have concentrations of less than 1%. Duration of use of the products is estimated to be minutes to hours, and the frequency was estimated to vary from monthly to yearly. The primary exposure route for the nanomaterial exposure is the dermal route and for products that are sprayed, also the inhalation route.

2.4.5 Maintenance products (car, boats)

In the examples addressed in Appendix 4, the following nanomaterials have been found in the maintenance products:

silver
in anti-reflecting cleaning agents, textile impregnation, antimicrobial protection for plastic parts of car interior, odour remover inside car

silicium dioxide
in window coating for cars, car shampoo, car tires, sealant/coating and protection for cars

aluminium oxide
in polish/coating for cars

nano boron
coating for the motor protection unit

nano ceramics
in maintenance for cars

titanium dioxide
in odour remover inside car

carbon nanotubes
in polymer skeleton that are used for moulding into automotive parts for repair.

For the majority of the products, the primary exposure route is the dermal route, whereas secondary routes are in relation to oral or inhalational exposure. However, for spray/pump products such as textile impregnation and products where they require mixing before use, such as cockpit cleaner, the primary exposure route is inhalation. The latter is also assumed to cause the highest consumer exposures.

For maintenance products, the exposure is unintended, but may typically occur during use of the products. The consumers exposed will mainly be adults and car owners, who use the maintenance products. The frequency of use will mainly be monthly or yearly for the maintenance products and the duration of the event will be minutes or hours depending on the application.

2.4.6 Textiles

The nanomaterials addressed in Appendix 4 are:

silver
bamboo charcoal
titanium dioxide
teflon, polytetrafluoroethylene

The most frequently used nanomaterial in textiles seems to be Ag with antimicrobial effect. A few products contain other nanomaterials such as bamboo charcoal, Teflon and nano-TiO2, the latter as ultra violet (UV) protection. For some of the more exotic materials e.g. bamboo charcoal it may be difficult to evaluate what type of substance that is actually covered by this terminology and how the word nano should be understood in this context. For exposure to surface-bound nanomaterials, it is difficult to express "*volume of product per use*" in a meaningful manner, and thus a value of <1 g is used in Table 2-1.

The principal exposure route is the dermal route as clothes are in close contact with skin. Even though the nanomaterials are considered surface-bound, a low exposure potential may still be assumed, as e.g. textiles treated with nano-Ag may release silver particles or ions. Oral exposure may be relevant for small children sucking the textile e.g. snips from pillows.

2.4.7 Construction materials

In the examples addressed in Appendix 4, the following nanomaterials have been indicated in the construction materials:

silver
in façade protection

silicium dioxide
in plaster and cement

silicon dioxide
in coating for stone and tile protection

titanium dioxide

in tiles, surface layer for roofs and pavements, "*self-cleaning*" glass

unknown nanomaterials
in surface protection, mortar, sealant and soil stabilization products

It was anticipated that carbon nanotubes could be found in this product category, however, no specific construction materials with content of carbon nanotubes were identified.

For all of the products, the primary exposure route is the dermal route (for cement also the inhalational route), whereas secondary routes are for the majority of the products in relation to inhalational and oral exposure. Most of the nanomaterial content is unknown.

For construction materials, the exposure is unintended and the consumer will only be exposed to part of the volume of the product. The duration of the exposure depends on whether the product is quickly applied on the surface or whether it is a construction material requiring handling such as tile and cement. Consumer exposure must be assumed to be much higher for nanomaterials in powders and liquids than for nanomaterials in solid matrices.

2.4.8 Medical devices

In the examples addressed in Appendix 4, the following nanomaterials have been indicated in the medical devices:

silver
in wound dressing, coating for implants

copper
in ostomy bags

silicate
in dental filling

zirconia
in dental filling

For the ostomy bags and wound dressing, the primary exposure route is the dermal route. For dental filling (silicate or zirconia), the primary route is the oral route. For coating implants, the consumer exposure is "*systemic*". Generally, consumers of all ages may be exposed. However, ostomy bags and implants will be used more often by elderly people.

Except for dental fillings, the nanomaterials are added to enhance the antibacterial effect and thus the exposure is in that respect intended for the medical devices. For coating of implants and dental filling the duration of the event is divided into '*application*' and '*after application*' since the dental filling and implants will be embedded into the body, permanently or for a long period of time.

2.4.9 Air-cleaners

In the area of air-cleaners and sprays, two types of nano-enabled products are indicated in Appendix 4; namely solid-state and spray-based air-cleaners. The active nanomaterial ingredients were:

silver
titanium oxide
activated carbon
plant oil fatty acids, plant oils vegetable extracts (not further declared)

Solid-state air-cleaning may be assisted by UV-light or ozone treatment. In two cases, other air-cleaning agents were reported.

The most important exposure routes were inhalation and dermal for sprays and dermal exposure for handling solid-state air-cleaning systems (filters, filter changes). The typical volume of product used during each application of the products is in the order of 1-10 g. In a few cases, the actual exposure and exposure duration could be hours or longer.

2.4.10 Fuel and lubrication oil additives

In the examples addressed in Appendix 4, the following nanomaterials are indicated in fuel and lubrication oil additive products:

gold - in engine oil and as fuel catalyst

cerium oxide - as diesel catalyst

tungsten disulphide -as lubricant for engine oil

For all of the products, the primary exposure route is the dermal route during fuelling/addition of oil. The product can be added either indoor in a garage or outside on a service station.

The primary route related to combustion of the diesel would be the inhalation route. The latter is relevant for the general population (all ages) and not just the consumers fuelling the vehicles. The exposure to the products/combustion products is any case unintended.

Fuel is added regularly and the frequency of the exposure will be daily or weekly depending on the driving habits. Engine oil is added less frequently and the frequency of the exposure is therefore monthly or yearly. Exposure to traffic exhaust is very frequent/almost continuous and this is covered in another section of this project.

2.4.11 Electronic devices/products

In the examples addressed in Appendix 4, the following nanomaterials have been indicated in the electronic devices:

silver
in computer keyboard and protection coating for metal

gold
in protection coating for metal

silicon dioxide
in processor

zinc oxide
in cooling liquid

It is also known that carbon nanotubes *(*CNTs*)* are used in electronics (e.g. in semi-conductors and other solid matrices) as will be further addressed in Chapter 5. However, such uses are not generally claimed, and therefore not identified in this chapter.

For all of the products, the primary exposure route is the dermal route, whereas secondary routes may be in relation to oral and inhalational exposure.

For the cooling liquid to be applied from the bottle, actual dermal consumer exposure is expected. For the keyboard where the nanomaterials are added for antibacterial purposes, dermal exposure may also take place. The frequency of the exposure is expected to be monthly or yearly and thus limited, except for the keyboard, which will be used daily. The consumer exposure to nanomaterials in solid matrices (e.g. the processor) would require consumer intervention into the computer.

2.4.12 Appliances

In the examples addressed in Appendix 4, the following nanomaterials have been found in the electrical appliances:

silver
in refrigerator, air humidifier and in washing machine

iron
in refrigerators

c*arbon*
in refrigerators

For the far majority of the products, the primary exposure route is the dermal route, whereas secondary routes are in relation to oral or inhalational exposure. This applies for the refrigerators and the air humidifier.

For appliances, the use of nano-Ag as biocide will lead to some release of silver (as silver ions and perhaps as nano-silver) and thereby some exposure. The exposure is difficult to estimate but intuitively assessed to be low.

2.5 Overall findings regarding nanomaterials in the various product categories

Nanomaterials and products in the product categories

Overall, when searching for consumer products in the databases/inventories and the literature, a very broad and diverse picture of nanoproducts on the market appears. Especially for the broad categories of cosmetics, cleaning agents, coating/impregnation and maintenance products many different products can be found with respect to various products types/formulation and application methods.

With respect to data on food and beverages, it is important to note that the databases only present nanomaterials in food supplements and do not cover the content of nanomaterial in food products as such, which might e.g. originate from the use of additives in nanoform.

It was further noted that there are several overlaps between the databases as they often feed into each other. In addition, it was noted that it sometimes may be difficult to categorise a product into one of our chosen product categories. A cleaning agent may as an example also be a coating/impregnation agent, and a paint product can be considered relevant both for the coating/impregnation category as well as for the construction materials category.

When working with and searching in the databases, it was noted that dead links to manufacturers and vendors as well as wrong information was sometimes encountered. Thus, care has to be taken when using information from the data bases/inventories.

As an overall observation, it became clear that for many products, the nanomaterials are not properly identified, and it is difficult to assess in which state the nanomaterial is present or to which

extent the nanomaterial is matrix bound and/or released. Thus, often the content of a nanomaterial is claimed without any further specification or documentation of the nano-content.

Table 2-1 provides an overview of the identified nanomaterials found in the various product categories in Appendix 4 supplemented with data from the recent survey by Danish EPA (2014a).

It has to be noted that the table does not intend to present a complete list of nanomaterials in the product categories as this was not the objective of the project, which focused on detecting relevant consumer products with as much information as possible for assessing the exposure potential. Thus, the table reflects the experience gained during this work. Additional nanomaterials/ nanoproducts may be identified via the literature review presented in Chapter 5, as well as during the project activity addressing hazards of nanomaterials in consumer product. The entire knowledge will be taken forward to Chapter 6, where we will identify 20 representative exposure scenarios.

TABLE 2-1 NANOMATERIALS IDENTIFIED IN PRODUCTS FROM INVENTORIES/DATABASES IN THIS SURVEY

Product type	Nanomaterial chemistry identified
Food and beverages	silver, platinum, palladium, gold*
Cosmetics	silver, gold, platinium, fullerenes, nano-peptides, silicium oxide, zink oxide, titanium dioxide, calcium peroxide, copper, copper peptides, carbon black
Cleaning agents	silver, titanium dioxide, silicia, micelles
Coating/impregnation	silver, titanium dioxide, silicium dioxide, Teflon
Maintenance products (for cars and boats)	silver, titanium dioxide, silicium dioxide, silicon dioxide, aluminium oxide, nano boron, nano ceramics, carbon nanotubes
Textiles	silver, titanium dioxide, bamboo charcoal, Teflon
Construction materials	silver, titanium dioxide, silicium dioxide, silicon dioxide,
Medical devices	silver, copper, silicate, zirconia
Air-cleaners	silver, titanium dioxide, activated carbon, plant oil fatty acids, plant oils vegetable extracts
Fuel and lubrication oil additives	gold, cerium oxide, tungsten disulfide
Electronic devices/products	silver, gold, silicon dioxide, zinc oxide
Appliances	silver, iron, carbon

*It may be noted that nano-silica and nano-TiO2 is not found as ingredient in food and beverages covered by the inventories/ databases.

Data on exposure parameters

The concentration of the nanomaterial in the products is very seldom stated and for making qualified exposure assessment, this is needed. If data are not available, exposure estimations and

worst-case scenarios could be made based on current knowledge and experience in relation to the various product categories.

Rather good estimations may however be done on "*volume of product per use*" as this can often be estimated due to the product volume or general knowledge concerning use of the various consumer products. However for articles where nanomaterials are embedded into a solid or semi-solid matrix, or surface bound it may be rather difficult to make a meaningful estimation on "*volume of product per use"*. Instead, contact surface area and potential migration/release may be considered to assess the emission potential. Such a procedure has recently been applied to assess the potential consumer and environmental exposure to CNT in consumer products (Danish EPA 2014b).

With respect to duration and frequency of use, some general everyday considerations have been made, however, for some subset of the population that have specific interests in leisure activities, hobbies or specific preferences, the frequency of use may be higher and the duration per day longer.

The primary exposure route for most products is via dermal exposure. For product in the food category, the oral route is the primary route. For nearly all product categories where spray application is used, the inhalation route is generally considered the primary route and calls for attention, as the matrix here is aerosolised into tiny droplets, and the nanomaterials may be easily accessible for lung tissue exposure when inhaled. However, dermal and eye exposure associated with spraying might be highly relevant.

Further use of the information in the product category tables (Appendix 4)
At this stage, data on relevant parameters for exposure have been extracted from the most relevant databases and qualitative estimations regarding the potential for oral, dermal and inhalational exposure have been made. Further investigations and considerations are necessary in order to establish more detailed and relevant information needed for further qualitative and semi-quantitative exposure assessment of the various consumer products and exposure scenarios.

From information given in the product category tables in Appendix 4 and from the qualitative exposure estimation given in column 9 of the tables, it already seems clear that a very important factor for the further semi-quantitative approach would be the implication of the product matrix with regard to accessibility of the nanomaterial, i.e. to which extent is the nanomaterial liberated or accessible for exposure to humans. This may have a great impact on the quantitative exposure assessment that may overrule much of the quantitative information presented in the columns 1, 4, 5, 6, and 7 of the tables. E.g., there may be order-of-magnitude differences in the accessibility to nanomaterials embedded in a solid matrix compared to nanomaterials in a liquid or an aerosol.

Therefore, in the next chapters of this report, available risk assessment and exposure models will be presented and the most important parameters in relations to quantitative exposure assessment and the interplay of these when making exposure estimations will be identified and described. In addition to this, specific examples or cases with detailed exposure estimates for nanomaterials in consumer products will be described in order to obtain case-specific experience e.g. with measured exposure levels.

With further information on these aspects, it may be possible to further build on the knowledge from the tables in Appendix 4, and to select some of the products in order to define relevant and representative consumer exposure scenarios for further evaluation. This selection of scenarios will, as noted, also take into account findings from the parallel-running hazard assessment activities in the project.

3. Review of available risk assessment tools

This chapter reviews a select suite of relevant exposure and risk assessment tools. The aim of the review was to establish an overview of the addressed models/tools in terms of scope, requirements and coverage and to provide an initial indication of how the models/tools would be able to address the preliminary gross list of exposure scenarios related to the product categories identified in Chapter 2.

As the aim is to identify and examine tools for risk assessment and the potential use for nanomaterials the tools to some extent have to include several elements (or modules) in relation to exposure assessment, hazard characterisation and risks characterisation.

The current reporting will not at this stage identify which model(s) would be most suitable for the risk assessments to be performed by the end of project, but merely form a basis for the choice of risk assessment model(s) to be used or adapted to a selected set of exposure scenarios for nanomaterials. Thus, some of the information in the current reporting might be revised or further detailed in the risk assessments in the final project report, when the prioritised exposure scenarios for nanomaterials have been selected.

Although exposure to some extend will be addressed in this chapter the following Chapter 4 will go further into detail with respect to defining exposure algorithms and identifying the most important factors/parameters determining consumer exposure to nanomaterials.

3.1 Scope/objective/boundaries

The reviewed exposure and risk assessment tools were identified in cooperation with the Danish EPA. The tools were selected based on their specificity for assessing nanomaterials or for their general applicability for assessing conventional chemicals and possible relevance for assessment of nanomaterials. The tools reviewed include:

- NanoRiskCat (DTU and NRCWE)
- NanoSafer (NRCWE, DTI)
- Stoffenmanager Nano (TNO)
- Stoffenmanager (TNO)
- The ANSES tool
- Swiss Precautionary Matrix (Swiss consortium)
- ECETOC TRA
- ConsExpo (RIVM)
- DREAM (TNO and IOM)
- Margin of Exposure (MOE) concept (The US Soap and Detergent Industries).

It should be noted that we have not only addressed tools intended for risk assessment of consumer exposure. Occupational exposure/risk assessment and control-banding-type tools were also

included, as their approaches or the tools themselves might be applicable for some consumer exposure scenarios.

The reviews of the tools were conducted following an assessment template with relevant questions in relation to the approach/performance of the models/tools. A completed assessment template can be found for each tool in Appendix 5 in the appendix report**.**

Below a summary is given regarding the findings after filling out the assessment templates

3.2 Summary and comparison of the scope and approach of the assessed tools

Table 3-1 summarises the general scope and approach of the 10 assessed tools based on the evaluation listed in Appendix 5.

TABLE 3-1. : COMPARISON OF THE SCOPE AND APPROACH OF THE ASSESSED TOOLS

			Nano-RiskCat	NanoSafer	ANSES	Stoffen-manag-er nano	Swiss Precaution-ary Matrix		Stoffen-manag-er	ECETOC TRA	Cons-Expo	DREAM	Margin of expo-sure
General													
	Tier (0,1,2)		-1/0	0-1+	0	1	0		1+	0/1	0-2	0	NA
	Consumer/Occupational tool		Consumer	Occupational	Occupational	Occupational	Both		Occupational	Consumer	Consumer	Occupational	Consumer
	Background concentration taken into account		No	No	Not addressed	Yes	No		Yes	No	No	Not addressed	No
Exposure													
	Inhalation module		Exposure addressed, but not on specific route level	Yes	Yes	Yes	Exposure addressed, but not on specific route level		Yes	Yes	Yes	No	Yes
	Dermal module			No	No	No			Yes	Yes	Yes	Yes	Yes
	Oral module			No	No	No			No	Yes	Yes	No	Yes
	Matrices addressed	Solid	Yes	No	Yes	No	Yes		Yes	Yes	Not directly addressed	Yes	Not directly addressed
		Powder	Yes	Yes	Yes	Yes	Yes		Yes (included in solids	Yes		Yes	
		Solution/dispersion	Yes	No	Yes	Yes	Yes		Yes	Yes		Yes	

			Nano-RiskCat	NanoSafer	ANSES	Stoffen-manag-er nano	Swiss Precaution-ary Matrix		Stoffen-manag-er	ECETOC TRA	Cons-Expo	DREAM	Margin of expo-sure
	(Some of) the scenarios from 1.1/2.1 specifically addressed		No	No	No	No	No		No	Yes	Yes	No	Yes
	(Some of) the scenarios from 1.1/2.1* might possibly be addressed		Yes	Only nanomaterial release scenarios	Yes	Yes	Yes		Yes	Yes	Yes	Yes	Yes
	Effect of risk management measures taken into account		No	No	No	Yes	No		Yes	No	Not directly	Yes	No
	Level of quantification in exposure algorithm		Qualitativ e	Quantitative	Qualitativ e	Semi-quantitati ve	Semi-quantitative		Quantitat ive (inhalatio n module) and qualitativ e (dermal module)	Quantitativ e	Quantita tive	Semi-quantitati ve	Quantitati ve
	Metric applied		NA	Mass and Surface area	NA	NA	Mass		Mass	Mass	Mass	NA	Mass

			Nano-RiskCat	NanoSafer	ANSES	Stoffen-manag-er nano	Swiss Precaution-ary Matrix		Stoffen-manag-er	ECETOC TRA	Cons-Expo	DREAM	Margin of expo-sure
Hazard													
	Hazard module		Yes	Yes	Yes	Yes	Yes		Yes	Yes	No	No	Yes
		Hazard profile as input parameter	Yes, based on literature review	No	No	Yes, based on classificat ion	No		Yes, based on classificat ion	Yes, reference value (eg. DNEL[2])	NA	NA	Yes, NOAEL is used
		Estmation of hazard	(Yes)	Yes	Yes	No	Yes		No	No	NA	NA	No
Output													
	Communication of results		Independ ent exposure and hazard categoriza tion	Quantitative control banding	Qualitativ e control banding	Qualitativ e risk prioritizi ng band	The cumulated score allocates the substance in either a precautious level or non-precuatious level		Qualitativ e risk prioritizi ng band and quantitati ve exposure estimates (for inhaltion only)	Quantitativ e risk characteriz ation ratio	Quantita tive exposure calculati ons	Semi-quantitati ve exposure estimates in DREAM units, grouped into categories	Output is screening-level MOEs

[2] DNEL: Derived No-Effect Level

			Nano-RiskCat	NanoSafer	ANSES	Stoffen-manag-er nano	Swiss Precaution-ary Matrix		Stoffen-manag-er	ECETOC TRA	Cons-Expo	DREAM	Margin of expo-sure
	Uncertainties specifically addressed in model output		No	No	Not addressed	No	Yes (to some extent)		No	No	Yes, the results of a Monte Carlo analysis are reported in the output of the tool.	No	Not addressed
Other (specific nano features)			Specifically designed to address risk categorization of products and articles										

Table 3-1 is divided in two parts, with the first five tools specifically developed for assessment of nanomaterials. The five more general tools in the right side of the table are included in the assessment as they with appropriate caution might be used to assess exposure to nanomaterials.

3.2.1 Nano-specific tools

It was found that all the nano-specific tools are "Low Tier" tools, i.e. generally rather conservative with low level of complexity. Except for NanoSafer, the nano-specific tools use qualitative/semi-quantitative algorithms to reach conclusions. All tools lead to an output that either prioritise/rank or places a nanomaterial/nanoproduct in a control banding category. Control banding refers to categorising exposure scenarios in relation to recommended risk management.

It should be noted that all nano-specific tools have exposure as well as hazard modules thus leading to "risk-based" approaches, where some of the non-nano-specific tools discussed below only address exposure.

In relation to possible further application of these tools in this project, it should be stressed that the tools are generally not designed to explicitly confirm "no risk", but rather to prioritise areas for exposure/risk reduction. On the other hand, one might implicitly assume that "non-prioritisation"/"low banding" could indicate low/no risk, also considering that the tools generally apply conservative approaches. To this end, it should be stressed that the ANSES, NanoSafer, NanoRiskCat, and Stoffenmanager Nano tools - due to the absence of nano-specific data - also apply hazard data for the nearest analogue macro/bulk compound. Although such macro/bulk data are applied in a way that the final hazard score of the nanomaterials is higher than for the macro/bulk form, it should be noted that nanoforms might possess hazards, which are not identified based on the hazard profile for the macro/bulk form and the physicochemical hazard indicators. Depending on the level of precautionary approach taken, these potential unknown hazards, e.g. carcinogenicity or mutagenicity, could have graver implications than estimated.

The issue of exposure and dose metric is less relevant for the qualitative/semi-quantitative tools as these are inherently not operating with exposure estimates or dose descriptors, whereas it should be noted that the more quantitative NanoSafer tool includes the nano-relevant surface area metric in the final estimation of risk level.

None of the nano-specific tools has fully "built-in" default exposure scenarios for the selected product categories and exposure scenarios identified in Chapter 2. Stoffenmanager Nano is currently the only nano-specific tools pursuing this approach by requesting selection of source domains in the start of the assessment. The other nano-specific tools assess specific exposure and use scenarios using a combination of various input criteria, which often include various formats of emission potential/release potential, amount, duration, and frequency. It is upfront considered that all nano-specific tools possibly might be used to assess (some of) the exposure scenarios associated to the product categories identified in Chapter 2. In this context, it should be stressed that three of the tools are explicitly developed to be used in an occupational context and thus quite some modifications of default parameters/approaches may have to be made in order to properly address nanomaterials in consumer products. It should also be noted that three of the tools only address inhalation, whereas the two risk categorization tools, NanoRiskCat and the Swiss Precautionary Matrix, address the overall exposure potential, however without differentiating into the various exposure routes. Thus, none of the nano-specific tools explicitly address eye, oral and dermal exposure.

3.2.2 General (non-nano) tools

A number of tools for regulatory risk assessment of chemicals in general (Stoffenmanager, ECETOC TRA and ConsExpo) have also been assessed in this project as e.g. the NANEX project and the nano-specific REACH guidance indicate that these tools might be applicable (with caution) in the

context of exposure/risk assessment of some nanomaterials and consumer products. Furthermore, the Margin of Exposure approach reflecting the classical quantitative risk characterisation comparing No-Observed-Adverse-Effect-Levels (NOAELs) with exposure estimates have been assessed along with the DREAM model. The latter has been included as it might be relevant to consider, as it is specific for dermal exposure, which is a main exposure route for nanomaterials in a range of consumer products.

These tools, originating in the more classical risk assessment of chemicals, are largely quantitative in calculations and output, expect for the DREAM tool and the dermal module of Stoffenmanager. The tools are generally exposure estimation/assessment tools, although three of the tools have a "hazard module". However, the hazard modules are not made for hazard estimation, but rather a facility to enter a NOAEL/DNEL/reference value in order to be able to carry out a quantitative risk characterisation. Thus, in principle, from a hazard perspective, the tools could be used if an appropriate reference value could be estimated (done outside of the tools). As will be further addressed in the hazard assessment report, this depends on the hazard data(base) available for individual nanomaterials. Further, due to the nature of these conventional quantitative tools, it should be noted that they all base the calculations on the mass-concentration metric. This may be a problematic issue for assessment of nanomaterials, where other nano-relevant metrics such as particle size and surface area may play an important role.

As opposed to the nano-specific tools, three of the general tools (ECETOC TRA, ConsExpo and MoE) have "built-in" scenarios addressing specific exposure scenarios, several of which might be applicable for this project, in particular as these tools are also specifically targeted consumer exposure. The other two tools (Stoffenmanager and DREAM) are primarily addressing occupational exposure and have no "built-in" exposure scenarios. Nevertheless, it is assessed that these two tools might be able to address some of the exposure scenarios associated to the product categories identified in Chapter 2 after appropriate adaptation to the consumer situation, see also the following section.

It should be noted that ECETOC TRA, ConsExpo and MoE address inhalation, dermal as well as oral exposure, whereas Stoffenmanager does not address oral exposure and DREAM is specific for dermal exposure. It should also be noted that ConsExpo has a Monto Carlo simulation facility and include uncertainty in the assessment.

3.3 Initial assessment and comparison of the ability of the tools to assess relevant consumer exposure scenarios

Table 3-2 gives an initial idea as to whether the evaluated tools (possibly) could be used to address the exposure scenarios associated to the product categories identified in Chapter 2. Column two in the table specifies in which matrix the nanomaterial would/could be embedded and column three outline which exposure routes are considered primary, secondary or less/not relevant (see also table legend).

TABLE 3-2. COMPARISON OF THE ABILITY OF THE TOOLS TO ASSESS RELEVANT CONSUMER EXPOSURE SCENARIOS

Exposure scenario	Matrix	Route of exposure	Nano-Risk Cat	Nano-Safer	ANSES	Stoffen-manager nano	Swiss Precautionary Matrix	Stoffen-manager	ECETOC TRA	ConsExpo	DREAM	MOE in: Consumer Product Ingredient Safety
Food and beverages	NM Ingredient	Inhalation										
		Oral	x						x			x
		Dermal										
	Food supplements	Inhalation										
		Oral	x						x			s
		Dermal										
	NM in packaging	Inhalation										
		Oral	x						x			
		Dermal										
	Nano agrochemicals as residuals in food	Inhalation										
		Oral	x						x			
		Dermal										
Cosmetics	Spray	**Inhalation**	x	x	(x)	x	x	x	x	s		s
		Oral										

Exposure scenario	Matrix	Route of exposure	Nano-Risk Cat	Nano-Safer	ANSES	Stoffen-manager nano	Swiss Precautionary Matrix	Stoffen-manager	ECETOC TRA	ConsExpo	DREAM	MOE in: Consumer Product Ingredient Safety
		Dermal	x				x		x	s	x	s
	Liquids	*Inhalation*	x	(x)	(x)	x	x	x	x	s		
		Oral	x				x		x	s		s
		Dermal	x				x		x	s	x	s
	Powder	**Inhalation**	x	s	(x)	x	x	x	x	s		
		Oral										
		Dermal	x				x		x	s		
	Creme	Inhalation										
		Oral										
		Dermal	x				x		x	s	x	
	Tooth paste	Inhalation										
		Oral	x				x		x	s		s
		Dermal										
	Lipstick	Inhalation										
		Oral	x				x		x	s		s
		Dermal	x				x		x	s		s

Exposure scenario	Matrix	Route of exposure	Nano-Risk Cat	Nano-Safer	ANSES	Stoffen-manager nano	Swiss Precautionary Matrix	Stoffen-manager	ECETOC TRA	ConsExpo	DREAM	MOE in: Consumer Product Ingredient Safety
	Mascara	Inhalation										
		Oral										
		Dermal	x				x		x	s		
		Eye	x				x		x			
Cleaning agents	Liquids	*Inhalation*	x	(x)	(x)	x	x	x	s	s		
		Oral	x				x			s		s
		Dermal	x				x	x	s	s	x	s
	Spray	**Inhalation**	x	x	(x)	x	x	x	s	s		s
		Oral										
		Dermal	x				x	x	s	s	x	s
	Paste	Inhalation										
		Oral	x				x		s	s		
		Dermal	x				x	x	s	s	x	s
Coatings/ impregnation	Liquids	*Inhalation*	x	(x)	(x)	x	x	x	s	x		
		Oral	x				x		s	x		
		Dermal	x				x	x	s	x	x	

Exposure scenario	Matrix	Route of exposure	Nano-Risk Cat	Nano-Safer	ANSES	Stoffen-manager nano	Swiss Precautionary Matrix	Stoffen-manager	ECETOC TRA	ConsExpo	DREAM	MOE in: Consumer Product Ingredient Safety
	Spray	**Inhalation**	x	x	(x)	x	x	x	s	x		
		Oral										
		Dermal	x				x	x	s	x	x	
	Cloths	Inhalation										
		Oral										
		Dermal	x				x	x	s			
	Paints	*Inhalation*	x	(x)	(x)	x	x	x	s	x		s
		Oral										
		Dermal	x				x	x	s	x	x	
Maintenace products (cars/boats)	Liquids	*Inhalation*	x	(x)	(x)	x	x	x	s	x		
		Oral	x				x		s			
		Dermal	x				x	x	s	x	x	
	Spray	**Inhalation**	x	x	(x)	x	x	x	s	x		
		Oral										
		Dermal	x				x	x	s	x	x	
	Cloths	Inhalation										

Exposure scenario	Matrix	Route of exposure	Nano-Risk Cat	Nano-Safer	ANSES	Stoffen-manager nano	Swiss Precautionary Matrix	Stoffen-manager	ECETOC TRA	ConsExpo	DREAM	MOE in: Consumer Product Ingredient Safety
		Oral										
		Dermal	x				x	x	s	x		
	Paste	Inhalation						x				
		Oral										
		Dermal	x				x	x	s	x	x	
Textiles		Inhalation										
		Oral										
		Dermal	x				x		s			
Construction material	Cement/concrete	**Inhalation**	x	s		(x)	x	(x)	x	x		
		Oral										
		Dermal	x				x		x	x		
	Self-cleaning surfaces	*Inhalation*	x	x			x		x			
		Oral										
		Dermal	x				x		x			
Medical devices	Wound dressings	Inhalation										
		Oral										

Exposure scenario	Matrix	Route of exposure	Nano-Risk Cat	Nano-Safer	ANSES	Stoffen-manager nano	Swiss Precautionary Matrix	Stoffen-manager	ECETOC TRA	ConsExpo	DREAM	MOE in: Consumer Product Ingredient Safety
		Dermal	x				x		x			
	Tooth fillings	Inhalation										
		Oral	x				x		x			
		Dermal					x		x			
Air cleaners	Spray	**Inhalation**	x	x	(x)	x	x		x	x		
		Oral										
		Dermal	x				x	x	x	x	x	
Fuel and lubrication oil additives		*Inhalation*	x		(x)	x	x		x	x		s
		Oral										
		Dermal	x				x	x	x	x	x	
Other									x			
Shoe polish	Liquids	*Inhalation*	x		(x)	x	x		x	x		
		Oral										
		Dermal	x				x	x	x	x	x	
	Paste	Inhalation										
		Oral										

Exposure scenario	Matrix	Route of exposure	Nano-Risk Cat	Nano-Safer	ANSES	Stoffen-manager nano	Swiss Precautionary Matrix	Stoffen-manager	ECETOC TRA	ConsExpo	DREAM	MOE in: Consumer Product Ingredient Safety
		Dermal	x				x	x	x	x	x	

Legend: The table has been populated to indicate the initial results from our assessment and define whether a given tool:

- specifically "s" address the exposure scenario (with default description and assumptions for that specific scenario),
- might with caution "x" address the exposure scenario, or
- might with doubt (even further caution) "(x)" address the exposure scenario.

From this initial assessment, the results illustrate e.g.:

- That most tools have limited coverage in terms of exposure routes (as already indicated above). Inhalation exposure is the focus in most of the tools intended for exposure (control-banding-like) assessment of nanomaterials;
- That only some of the general tools (ECETOC TRA, ConsExpo and MoE) have relevant "built-in" consumer exposure scenarios "s" indications. However, none of these scenarios and exposure profiles appear to consider exposure to nanomaterials and use of nano-products; except for ConsExpo, which has the possibility to include size-distribution information. None of the tools appear to be readily applicable to assess the exposure due to use of select construction materials, medical devices, shoe polish and release from abrasion (matrix) nanocomposites;
- That common products such as cleaning agents, coatings/impregnation and maintenance products could potentially be addressed by several of the tools. Still, however, the tools make mass-based assessments and nanomaterial aspects are in principle not covered;
- That less detailed/generic tools such as the NanoRiskCat and the Swiss Precautionary Matrix could potentially be used for many/most types of exposure scenarios. One drawback with these risk categorization tools is that they might be too broad/ conservative in their scaling to be applied for risk assessment and that they do not e.g. specifically address the relevant exposure routes and levels of exposure.
- That combination of different modified and further developed tools may enable a framework for semi-quantitative risk assessment of several types of consumer products and exposure scenarios.

Overall, the results in this section are preliminary and cannot be seen in isolation from the details in the templates in Appendix 5. Sometimes the devil is in the detail and only actual application of the tools on the exposure scenarios to be selected might reveal whether it actually makes sense to use a given tool. Among the critical aspects is whether the hazard of a specific compound is assessed and defined using mass as the exposure metric and that sufficient comparability exists between the exposure characteristics in the use-phase agree with the exposure characteristics used in the toxicological tests.

3.4 Conclusions and considerations for the way forward

The overall learning from this activity is that the assessed tools vary considerably in terms of coverage, scope/approach, level of quantification, populations and exposure routes addressed etc. The nano-specific tools are generally rather qualitative, but also not specifically designed to assess whether there necessarily is a true risk, but rather to indicate where there could be a risk and how strong indications it has, which could be subject to risk mitigation. Further, none of the nanomaterial exposure assessment tools addresses eye, dermal and oral exposure specifically. The need for change in risk assessment paradigm from mass to particle-size-distribution, number concentration and specific surface area for these exposure routes needs to be documented and await conclusions from the hazard assessment activities of this project. In contrast, the general (non nano-specific tools) are generally rather quantitative with a wider coverage, e.g. in terms of exposure routes addressed. Noteworthy, the exposure assessment algorithms in most of the non nano-specific tools are simpler and more conservative than the algorithms in the most advanced nano-specific tools.

No single tool will enable a harmonised proper exposure assessment for all nano-products. Significant work effort will be required to further develop the tools with modification for incorporating nano-specific properties and harmonizing the output, not mentioning its validation.

The results show that selection/adaptation of one tool (as speculated in the project specifications) will be a major effort, which is out of the scope of the current project. One could speculate whether alternative approaches could/should be taken, such as:

- Assess some of the selected scenarios with all the tools (to the extent possible, e.g. considering data availability and tool coverage) and based on this make an expert based qualitative assessment
- Whether to apply (components of) several tools as appropriate
- Whether the project at all should apply the assessed tools, but rather perform a case-by-case expert assessment of each of the selected scenarios.

Based on discussions with the external expert panel, it was suggested to follow a combination of the second and third option depending on the data-availability and the scenarios. The exact procedures for assessment of the consumer risk in the final phases of the project will depend on the specific scenarios to be addressed, as well as the specific exposure and hazard data that might be available (identified in other part of this project). Chapter 4 will built further on the results from this activity in terms of specifying the most important exposure parameters needed for exposure assessment and subsequent chapters will address how such data could be applied.

4. Exposure assessment and key factors affecting exposure

4.1 Objective

The objective of this chapter is to provide an overview of the knowledge needed to conduct a reliable conservative exposure assessment for a nanomaterial used in a consumer product/article. The most important factors/ parameters determining the consumer exposure will be identified and described in more detail taking the relevant product and article use scenarios into consideration for the various exposure routes.

To achieve this goal the first part of this chapter describes the learnings that can be obtained from relevant guidance and, tools for exposure assessment to *chemicals*, in consumer products and articles, as well as from guidance and tools specifically addressing exposure to *nanomaterials*. The following guidance and tools were assessed for identifying the most important factors/ parameters determining consumer exposure:

- *RIVM (2009)* Exposure to nanomaterials in consumer products
- *REACH guidance on exposure assessment from chemical products and articles*
- *SCCS guidance on nanomaterials in cosmetics*
- *EFSA guidance on nanomaterials in food*
- *Environmental Defense – DuPont approach*
- *ECETOC TRA*
- *ConsExpo*
- *NanoSafer*
- *NanoRiskCat*
- *Stoffenmanager*
- *Stoffenmanager Nano*
- *ANSES*
- *Swiss Precautionary matrix*
- *Dream*
- *Margin of exposure concept*

This chapter governs greatly from the learnings from the descriptions of the risk assessment tools in Chapter 3. However, in this chapter the focus will be on the exposure part of the tools that will be described in more detail to identify methods and algorithms of the tools and to identify parameters most relevant for assessing exposure to nanomaterials from consumer products.

Together with the findings in Chapter 3, it will then be possible to select the most relevant tools for exposure and risk assessment of 20 specific scenarios that will be selected in Chapter 6.

As mentioned in Chapter 2, RIVM (2009) has already performed an analysis of consumer exposure to nanomaterials. Key parameters were identified in the RIVM (2009) study and these key

parameters will form a benchmark reference in the current analysis of the other guidance and tools. Thus, descriptions and evaluations of the other guidance and tools will be made and it will be evaluated whether additional important exposure parameters can be identified.

Learning from this exercise is important to identify the most critical exposure parameters for either a qualitative or a semi-quantitative approach for assessing consumer exposure to nanomaterials from nano-products within this project.

Note to the reader: If the reader wishes to study the detailed descriptions of single guidelines and tools, please see Appendix 6 in the appendix report.

Below the overall findings from the review of the tools and guidelines are given.

4.2 Overall findings from the search on relevant exposure parameters

4.2.1 Identification of exposure parameters

From the overview of guidance documents and tools used for exposure assessment, several key characteristics and parameters can be identified as important for a qualitative, semi-quantitative and/or quantitative assessment of exposure to nanomaterials. Below parameters are listed starting with parameters identified by RIVM (2009) and supplemented by further (sub-) parameters that have been used by others. The parameters in *italics* indicate parameters primarily for *qualitative exposure assessment*, whereas parameters in **bold** indicate quantifiable parameters to be important for **(semi-)quantitative assessment** of nanomaterials. If a parameter specifically addresses an exposure route this exposure route is indicated in a bracket ( ).

RIVM (2009) (consumer exposure, nanomaterials):

The following parameters as starting point for estimating consumer nanomaterial exposure are given:

- *Chemical ID*
- *Shape of nanomaterial*
- *Physical location/type of product (Free/ fixed nanomaterial)*
- *Product matrix/form/application (e.g. spray/ liquid/ solid)*
- *Direct/ indirect or indoor/outdoor exposure*
- *Exposure route (dermal, oral, inhalation)*
- **Concentration**
- **Exposure (event) duration**
- **Frequency of use**

REACH guidance (consumer exposure, chemicals in general):

This guidance addresses further the following parameters in order to quantify consumer exposure:

- *Type of activity or processes*
- *Level of containment of the process*
- *Fugacity,* **dustiness***, volatility*
- *Package design (e.g. design for decreasing exposure potential)*
- **Amount/ volume per use**
- **Dilution of the product during use**
- **Thickness of (diluted) product layer** (dermal exp)
- **Surface area exposed** (dermal exp)
- **Fraction remaining on skin / retention factor** (dermal exp)
- **Migration factor** (dermal exp)
- **Fraction of used amount that is ingested** (oral exp)
- **Concentration in air** (inhalation)

- **Ventilation rate of exposed person** (inhalation)

SCCS (2012a) guidance (nanomaterials, cosmetics):
Further addresses:

- *Method of application (rather similar to type of activity or processes)*
- **Foreseeable misuse**
- *Target groups (e.g. children or people with skin disease/ sensitive skin),*
- **Mass generation rate into air** (spray, inhalation)
- **Airborne fraction** (inhalation)
- *Aerosol size distribution* (inhalation)
-

EFSA (2011a) guidance (nanomaterials, food):

- **Consumption data on food items (median and high oral exposures)**

ECETOC TRA (consumer exposure, chemicals):

- **Transfer factor (may be comparable to migration factor) from matrix to dermal or gastro-intestinal tissue** (oral and dermal exposure)
- **Dilution factor in air in relation to fraction released to air** (inhalation)

ConsExpo (consumer exposure, chemicals):
In principle no further parameters are added but sub-parameters for more advanced and exact consumer exposure calculations are considered, e.g. for calculation of concentration in air where room size, room ventilation rate, particle size distributions are taken into account.

Nanosafer (occupational inhalation exposure, nanomaterials):
Nanosafer specifies some further parameters in relation to occupational inhalational exposure to nanomaterials during manufacture/ processing and industrial use:

- *Coated/ surface modified nanomaterial*
- *Specific density*
- *Specific surface area*
- *Water solubility of nanomaterial*
- *Dimension of nanomaterial*
- **Handling energy**
- **Constant release rate**
- **Respirable dustiness**

NanoRiskCat (consumer exposure, nanomaterials):
No further parameters are addressed in relation to consumer exposure to nanomaterials but the semi-quantitative exposure evaluations are made based on type of product/product use and to which extent the nanomaterial is considered free or matrix bound.

Swiss Precautionary Matrix (general exposure potential, nanomaterials):
For the semi-quantitative exposure estimation, the matrix further addresses:

- **Release factors with respect to nanomaterial release from various matrices**

Stoffenmanager + Stoffenmanager Nano (occupational inhalation exposure, chemicals + nanomaterials):
In order to grade the *occupational* inhalational exposure levels, additional parameters are mentioned:

- **Exposure reduction factor associated to control measures**
- **Exposure reduction factor associated to use of personal protective equipment**
- **Distance from task** (inhalation) (e.g. within or out-site the near-field breathing zone.; may be comparable to a dilution factor)

ANSES (occupational inhalation exposure, nanomaterials):
For occupational inhalational exposure assessment in relation to control banding, further factors in relation to liberation of nanomaterials from solids are considered:

- *Friable solids (release of nanomaterial under low stress)*
- *Dust generated by external forces (e.g. mechanical, electrical, laser forces)*(inhalation)
- *Melting?*
- *Dispersion in liquid*

*Dream (*occupational dermal exposure, chemicals):
Addresses issues in relation of emission to clothing and deposition on skin and clothing for ranking dermal exposure potential:

- *Probability and intensity of dermal exposure routes (emission, transfer and deposition) (per body part)*
- *Use of clothing (per body part) (covered vs. uncovered body parts, clothing material, repeated use of clothing)*
- *Emission to clothing and uncovered skin; and immersion of skin into agent (unlikely, occasionally, repeatedly, almost constantly)*
- *Intensity (= amount of agent) of emission*
- *Exposure route factors (= either emission, deposition, transfer)*
- *Probability of deposition on clothing and uncovered skin*
- *Intensity of deposition on clothing and uncovered skin*
- *Transfer to clothing and uncovered skin : Contact with surfaces, or tools, occurs:*
- *Intensity of transfer: Contamination level of contact surface*

Margin of exposure concept (consumer exposure, chemicals):
Does not address further parameters for external exposure assessment as already covered above.

4.2.2 Conclusions

4.2.2.1 Exposure parameters

When having an overall look of these parameters it is clear that some parameters are sub-parameters to other parameters: E.g., an air measured air concentration can be used directly for a rather precise exposure assessment. If the concentration in air has to be estimated this can be done either by using simple assumptions and few parameters or by using a more advanced approach using several sub-parameters that are equally important for determining concentration in air. The estimation can be done at a tier 0 level using only used amount of a spray for instance divided by the volume of a room. However for higher tier assessment further parameters my advance this estimate using parameters such as the distance between the spray nozzle and the breathing zone, rate of emission from the spray, rate of deposition of the various particle sizes generated, room ventilation rate and so on.

So when looking for parameters for qualitative/semi-quantitative exposure estimation for more general consumer exposure scenarios the focus would be on the more overall parameters, whereas the additional sub-parameters are important when making a more quantitative exposure assessment of a specific exposure scenario.

For the more overall qualitative/semi-quantitative assessment the following parameters seems to be the most important for characterising the exposure scenario and assess the consumer exposure potential for the nanomaterial, Table 4-15:

TABLE 4-15 IDENTIFIED IMPORTANT QUALITATIVE AND QUANTITATIVE EXPOSURE PARAMETERS

Qualitative exposure parameters
• ID of nanomaterial • Product category • Type of product • Volume/package design of the product • Matrix for the nanomaterial (nanomaterial location in the product free/matrix bound) • Product use/ handling of the product during use/application method or processes involved (various life-cycle steps may be covered by different exposure scenarios/ assessments) • Considerations regarding foreseeable misuse • Site of body area exposed • Identification of specific exposure routes (primary and secondary exposure routes) • Direct/ indirect use (intended for human exposure/or not intended but a follow by normal use) • Indoor/ outdoor use (inhalation exposure) • Generation of nanomaterial during use (especially inhalation exposure) • Specific target groups (children, teenagers, adult men, adult women, etc.)
Quantitative exposure parameters
• Size distribution of particles and fraction in nano-size • Concentration of nanomaterial in the product • Volume used per use event • Retention rate of product (e.g. dermal exposure or fraction ingested) • Degree of liberation/ migration of nanomaterial from a matrix (dermal exposure, oral exposure) • Body surface area exposed (dermal exposure) • Article surface area in contact (dermal exposure, oral exposure) • Volume released to air (inhalation) • Concentration in air (inhalation) • Duration of exposure • Frequency of exposure

The ***qualitative parameters*** is mainly for characterising the exposure scenario for a product, however, they may contain some quantitative elements e.g. the volume in which the sold. The **quantitative parameters** are parameters, which in fact can be multiplied with each other for obtaining a quantitative estimate of the exposure.

Some of the above parameters are primarily important in connection with specific exposure routes that are indicated in the brackets.

It should be stressed that some parameters and types of information are considered especially relevant for nanoproducts and nanomaterials, such as nanomaterial ID, surface coating of nanomaterial, particle distribution, details on the matrix, attachment to matrix (e.g. embedded or surface attached), and product formulation (e.g. pump spray vs propellant spray etc.).

Whereas semi-quantitative oral and dermal exposure assessment may be addressed in a rather simplistic and transparent way using rather few assumptions concerning e.g. the amount ingested or the amount applied (intentionally or unintentionally) on skin, it may be more difficult or complex to obtain semi-quantitative estimates on inhalational exposure. This is because multiple factors in addition to the volume used may affect the exposure. A key parameter is the concentration of air in a person's breathing zone, which depends on various factors, such as emission rate of droplets/solid particles into air from the product, the air exchange rate in the room (or outdoors), particle sizes, sedimentation rate of the different particle sizes, the person's distance to the emission source (e.g. spray or air cleaner), and the breathing rate/volume of the person.

To which extent these factors have been considered - or not - have to be described when making the semi-quantitative estimate in order to assess the reliability and the uncertainty of the exposure estimate.

4.2.2.2 Applicability of exposure models for consumer nanomaterial exposure assessment

Table 4-16 gives a simplified overview of the applicability of the tools based on the descriptions given above (see the more detailed analysis of this in Chapter 3 in Table 3-2).
Using Table 4-16 may ease the choice of models to use when an exposure estimate is to be elaborated for a specific use scenario.

TABLE 4-16. APPLICABILITY OF THE VARIOUS EXPOSURE TOOLS IN RELATION TO PRODUCT CATEGORIES

Tool	ECETOC TRA, Consumer part	Cons Expo	*Nano Safer*	*Nano Risk Cat*	Stoffen-manager + Stoffenm. Nano	ANSES	*Swiss Preca. Matr.*	DREAM	MoE, Cons. Prod. Ingr. Safety
Scenario application area	C	C	***W***	***C+W***	W ***W***	W	***C+W***	W	C+W
Food & Beverage	(O)	-	-	***x***	- -	-	-	-	O
Cosmetics	(I/O/D)	I/O/D	***(I)***	***x***	(I) ***(I)***	(I)	***(x*)***	(D)	I/O/D
Cleaning agents	I/O/D	I/O/D	***(I)***	***x***	(I/D) ***(I)***	(I)	***(x*)***	(D)	I/O/D
Coating/ impregn.	I/O/D	(I/O/D)	***(I)***	***x***	(I/D) ***(I)***	(I)	***(x*)***	(D)	I
Mainten. products (car/ boats)	I/O/D	(I/D)	***(I)***	***x***	(I/D) ***(I)***	(I)	***(x*)***	(D)	-
Textiles	D	(D)	-	***x***	- -	-	***(x*)***	-	-
Construct. materials	I/D	(I/D)	***I***	***x***	(I) ***(I)***	-	***(x*)***	-	-
Medical devices	(O/D)	-	-	***x***	- -	-	***(x*)***	-	-

Tool	ECETOC TRA, Consumer part	Cons Expo	*Nano Safer*	*Nano Risk Cat*	Stoffen-manager + Stoffenm. Nano	ANSES	*Swiss Preca. Matr.*	DREAM	MoE, Cons. Prod. Ingr. Safety
Air cleaners	(I/D)	(I/D)	***(I)***	***x***	(D) *(I)*	(I)	***(x*)***	(D)	-
Fuel- /oil additives	(I/D)	(I/D)	-	***x***	(D) ***(I)***	(I)	***(x*)***	(D)	I

Characters in ***bold and italics*** indicate that the tool is developed specifically for nanomaterials
C: Consumer scenarios
W: Worker scenarios
x: covered qualitatively but not on exposure route basis
x*: covered semi-quantitatively but not on exposure route basis although some specific considerations to inhalational exposure applies
I/O/D: covered (semi-)quantitatively by the indicated (**I**nhalational/**O**ral/**D**ermal) exposure routes
( ): product category not specifically addressed in the tool but the tool may be usable for this product category

As can be seen from this overview, five tools cover consumer exposure and six tools cover worker exposure. Three consumer tools ECETOC TRA, ConsExpo and MoE specifically address all exposure routes (oral, dermal, inhalation).

Four tools specifically address nanomaterials: the occupational tools Nanosafer and Stoffenmanager Nano cover occupational inhalation exposure, whereas the nano tools applicable for consumers (NanoRiskCat and Swiss Precautionary Matrix) indicate overall exposure potential and do not specify the exposure routes.
Overall, this chapter has identified and listed the most relevant parameters to consider when making either qualitative or quantitative exposure assessment in relation to nanomaterial exposure from consumer products. It has to be noted that currently, exposure estimates are to be made predominantly on a quantitative mass basis as known from general chemical exposure assessment, as it - mostly due to lack of data or knowledge - may be difficult to include nano-specific parameters for consumer exposure, as consumer exposure in general is in relation to a nanomaterial in a matrix/vehicle of a product and not the pristine nanomaterial. Models considering nanospecific parameters have been developed for occupational inhalation exposure where exposure to pristine nanomaterials may be especially relevant and of concern (e.g. Nanosafer).

In addition, this chapter describes the potential of the various exposure tools and the application of these.

When making exposure assessment for a specific consumer products (20 exposure scenarios will be selected in Chapter 6 for further assessment) the learning from this chapter will help to focus on the most relevant exposure parameters and to select the most adequate tools for the assessment.

In order to build on current knowledge, the next chapter will present data from specific assessments or measurements of nanomaterial exposure to consumers. This will contribute with additional information and give a further impression of the magnitude of the nanomaterial exposure and it may illustrate how the factors in this chapter may have impact on the exposure assessment.

5. Specific nanomaterial exposure assessments

5.1 Objective and approach

This section will gain learnings from examples of more detailed exposure assessments of nanomaterials that have been performed in published literature. The starting point for selection of these examples and descriptions is reports/surveys on consumer nano-products and exposure, in which specific exposure assessments have been done for some products. In addition to this, also data from recent original literature published within the latest years have been used. The literature has been identified through a structured web-search on ISI Web of Science (Thomson Index) and covers at about 70 references that may contain relevant information for this project. For each product group (e.g. [textiles]) the search keys were "consumer* AND product* AND expo* AND [product group] OR consumer* AND product* AND release* AND [product group]".

The exposure assessments of the specific products will be briefly described regarding methodology (e.g. to with extent measurements and/or exposure tools have been used) and the key findings and results will be presented. In addition information from these data sources will be extracted and described for the various product categories, e.g.: - has further nanomaterials been identified compared to the ones identified in the tables presented in previous chapters; - which type of nanomaterial, exposure route/ product formulations has especially been in focus: -are exposure discussed in relation to specific processes or life-cycle stages?

A general issue that is relevant across the various product categories is exposure to specific downstream life-cycle stages (e.g. in relation to tear, wear, repair, and abrasion). This will be covered separately in the end of this chapter.

5.2 Examples of nanomaterial exposure from food and beverages

5.2.1 Main findings

Most literature data regarding nanomaterials in food have been obtained for use of silica, titanium dioxide (TiO_2) and calcium carbonate ($CaCO_3$) that may contain nano-sized particles to variable degrees. Using assumptions regarding *content of food additive* in the food items, *the relative content of nano-sized particles* in the food additive, and *consumption rates* of the food items, the following exposure estimates have been derived in relation to the nanomaterial exposure:

nano-silica:	1.8 mg/kg bw day (adult)
nano-TiO2:	0.36 mg/kg bw day (adult)
	0.7 -1.1 mg/kg bw day (child below 10 years)
nano-CaCO3:	0.5- 1 mg/kg bw day (adult)
	2-3 mg/kg bw day (toddler)

From food contact materials exposure to e.g. Ag (Ag, as either ions or nanoparticles) and carbon black (as nanoparticles) may occur. However, these exposures may be quantitatively lower due to the bound state of the nanomaterial compared to nanomaterial exposure from food additives used

in food items. Recent data indicate only low Ag migration (up to 30 ng of Ag per cm^2 both as ions and as nanoparticles) from food storage materials of plastic containing 0.3 wt% of nano-Ag.

5.2.2 Specific data

Table 5-1 provides an overview of use of food additives that may occur on nanoform given by the Danish EPA (2014a).

TABLE 5-1. TYPE OF NANOMATERIAL USED FOR FOOD AND FEED PRODUCTS (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THE PRODUCT TYPE (DANISH EPA 2014A)

	Titanium dioxide	Silicon dioxide	Silicates	Calcium carbonate	Natural colorants/pigments	Nanocarrier systems
Seasoning, coffee creamer, etc. (powdery foods)	X	X	X			
Wine, fruit juice, etc. (beverages)	X	X	X	X		
Coffee, tea		X	X			
Dairy products	X			X		
Confectionary, chewing gum	X			X	X	
Baked goods	X			X		X
Sauce	X					
Poultry, sea food		X				
Cereal				X		
Feed		X	X	X	X	

Calzolai et al. (2012) also indicated other metallic food additives (used as colorants) produced in nanoforms[3]:

iron oxides (E172)
metallic silver (E174)
metallic gold (1575)

3 It should be noted that these in their nanoform are not approved for use in the EU, as the EU food additives Regulation (1333/2008) requires specific premarket approval of the nanoform of a substance. Currently, it is considered that only the premarket approvals of $CaCO_3$ and SiO_2 allow the use of these substances in their nanoform as food additives.

Below, examples of exposure estimates on some of these food additives are given from recent studies presented in the scientific literature.

Amorphous silica
Dekkers et al. (2011) made a detailed assessment of nano-silica (silicon dioxide, SiO_2) in food. The conventional form of amorphous silica is known as the food additive (E551). Specifications of commercial available qualities on the market indicate that the food additive contain nanoparticles. From analysis of two qualities (Aerosil 200F and Aerosil 380F) specific surface areas of 199 m^2/g and 388 m^2/g were determined (BET nitrogen adsorption method). Primary particle size diameters of 12 nm and 7 nm were determined using transmission electron microscopy; however, most of the primary particles formed larger aggregates and agglomerates.

The total concentrations of silica in 26 products containing E551 were found to be in the range of 0-13.7 wt%. The contents of nano-silica determined in seven products (sauce, soup, coffee cream, pancake mix, seasoning products and spicy rubs) were in the range of 0- 1 mg/g with the highest content found in coffee creamer (1 mg/g). The highest *relative* content of nano-silica (33% of the total silica-concentration) was found in instant asparagus soup; however, this product had an overall low total silica content of 0.6 mg/g.

When 2 g of the coffee cream was added to 200 mL coffee, the ready to drink content of nano-silica was measured at 22 mg/L.

Estimates of the daily intake of nanosilica from 14 food products containing E551 were made based on food intake rates from the Dutch Food Consumption Survey. From these estimates, daily exposures to nanosilica of 33 mg, 20 mg and 15 mg were found from intake of coffee creamer, seasoning mix and cheese sauce, respectively. A total daily consumption of 124 mg nanosilica (corresponding to 1.8 mg/kg bw day) was estimated from intake from the total of the 14 different food products (for 6 of the products that has not been analysed for the nanofraction as indicated above, a worst case assumption of a relative amount of nano-silica of 50% in E551 was used).

Titanium dioxide (TiO_2)
Weir et al. (2012) analysed food grade TiO_2 (E171) by electron microscopy and found a very broad particle size distribution in the range of 30-400 nm with 36% of the particles (by number) below the particle size of 100 nm. Also, E171 includes TiO_2 as both the rutile and anatase crystalline form. The titanium content was measured in a variety of food items on the US market, where the highest content of titanium was found in coconut curd and in candy and sweets including products with sugar toppings. Titanium contents above 1 mg/g food were found in chewing gum, candy, additive products, and beverages; however, the highest content of 2.5 mg/g was found in the coconut curd. Food intake estimates of E171 was made based on data from the UK National Diet and Nutrition Survey using Monte Carlo simulations for the intake rates and point estimates for the titanium content in the food items.

Realistic average exposure for the UK population was found to 2-3 mg TiO_2/kg bw day for children under the age of 10 years, whereas exposure for higher age groups were estimated to about 1 mg TiO_2/kg bw day. It was noted that 36% of this exposure may be as nano-TiO_2.

Calcium carbonate ($CaCO_3$)
EFSA (2011b) in its opinion on $CaCO_3$ as food additive (E 170) noted that $CaCO_3$ can have an amorphous or microcrystalline structure, and that particle size varies according to the form and manufacturing conditions. Particles of amorphous calcium carbonate are reported to be characteristically 40 to 120 nm diameter spherules, in contrast to the 1 to 10 μm diameters in the crystalline forms.

Nano-$CaCO_3$ (as used in some of the toxicological studies reported in this opinion) was reported to have a particle size of 60 - 100 nm when examined by SEM, although particle size determination using Sedigraph showed higher apparent particle size due to aggregation. The typical average particle size ($d_{50\%}$) of food grade calcium carbonate is stated by CCA-Europe to be about 5 µm, with an upper range ($d_{98\%}$) of 65 µm and less than 1% of particles having a diameter below 100 nm; the presence of unintentional nanoscale particles at trace levels in the product cannot be excluded.

In the EFSA (2011b) opinion, three exposure estimates based on the Comprehensive Food Consumption Database and usage data provided by industry and Member States have been calculated taking into account different sources of exposure. These were:

Scenario 1: Exposure to $CaCO_3$ /calcium from the use of $CaCO_3$ as a food additive
Scenario 2: Exposure to $CaCO_3$ /calcium from the use of $CaCO_3$ as a food additive and added nutrient source (fortification)
Scenario 3: Exposure to calcium from the use of $CaCO_3$ as a food additive and added nutrient source (fortification) and from consumption of food supplements

TABLE 5-2. ANTICIPATED EXPOSURE TO CALCIUM FROM THE USE OF $CACO_3$ IN THE THREE SCENARIOS IN ADULT, ADOLESCENT AND TODDLERS

Daily intake of calcium (mg/day)								
	Adults (60 kg)		Adolescents (50 kg)		Children (30 kg)		Toddlers (15 kg)	
	Mean	95th percentile	Mean	95th percentile	Mean	95th percentile	Mean	95th percentile
Scenario 1	200-320	320-560	230-430	380-680	230-410	350-650	170-260	245-425
Scenario 2	440-740	620-1580	530-930	930-1580	650-1700	650-1700	305-575	470-905
Scenario 3	1240-1540	1420-2380	1330-1730	1730-2380	1450-2500	1450-2500	1105-1375	1270-1705

However, EFSA (2011b) did not evaluate the relative exposure to calcium carbonate in nanoform. (If a conservative estimate of 1% of the $CaCO_3$ exposure is to be considered to be on nanoform an upper estimate for Ca-exposure from nano-$CaCO_3$ can be estimated to e.g. 13-17 mg/day for toddlers (or 0.8-1.1 mg/kg bw day). Converted to nano-$CaCO_3$ this would equal to 33-43 mg/day or 2-3 mg/kg bw day).

Pure and different surface-modified nanocrystalline 15-40 nm-size nano-$CaCO_3$ (as crystalline calcite) is available, where surface modifications have been made for use in e.g. inks, paints, PVC and polyethelyne (PE)/ polypropylene (PP) plastics. One of these types of nano-$CaCO_3$ is used for polyvinylchloride (PVC) films and rolling membranes. Whether these forms may be used in food and food-packaging material is not known.
(http://ssnano.com/inc/sdetail/calcium_carbonate_nanoparticles/247)

Silver (Ag)
EFSA has evaluated the use of various silver releasing biocides in food contact materials in 2004 and in 2005 allocating a group specific migration limit (SML) of 0.05 mg Ag/kg food. Their use in plastics has not been agreed and authorised at EU level and to date they remain on a "provisional list", which allows their use at national level (EU-Commission 2013).

Quadros et al. (2013) measured the release of silver (as Ag-ions) from various consumer products assumed to contain silver in nanoform. From sippy cups and a breast milk storage bag with a content of 0.9-24.3 mg Ag/kg product, a release of 0.93 mg Ag/kg product was measured to juice from a sippy cup, whereas no silver release was found into milk in the breast milk storage bag. Anticipating release from a cup weighing 100 g, this would result in a release of 0.09 mg of silver. For a child weighing 10 kg this would using the cup three times daily correspond to an exposure of 0.027 mg Ag/kg bw day.

Echegoyen and Nerín (2013) studied the release of silver from two different food storage containers made of polyolefins and from food storage plastic bags made of low density polyethylene or polypropylene. The Ag content in the containers and bags were in the range of 0.32-0.33 wt%. It was noted that other products on the market may contain up to 0.72 wt% Ag. The migration of silver was measured according to EU regulation 10/2011/EU using acetic acid 3% or ethanol 50% with a migration duration of 2 hours at 70 ^{o}C and 10 days at 40 ^{o}C. The highest migration ranging from 3.7 – 31.5 ng Ag/cm^2 was measured using acetic acid at 40 ^{o}C for 10 days. This migration was calculated to be far below the migration limit value for silver of 0.05 mg Ag/kg food*.

For some samples, up to 20% of the migration of Ag was due to Ag nano-particles (identified by SEM-EDX) with a diameter of 10 to 60 nm. Further, it was found that heating in a microwave oven for 2 minutes resulted in higher migration than 2 hours heating in a conventional oven. Furthermore, plastic nanoparticles were observed to be released from the food storage materials as well.

Carbon black and vegetable carbon
Carbon black that is derived from petrochemical sources should not be confused with the food additive *E153, vegetable carbon*, which is derived from carbonised material of plant origin. According to EFSA (2012) the particle size specifications on the marketed qualities of vegetable carbon, E153 indicates that currently nano-sized particles in E153 can be excluded.

Carbon black used in plastic materials and articles intended to come into contact with foodstuffs is regulated in European Directive 2007/19/EC. The maximum use level of carbon black in the polymer is set to 2.5% w/w. Requirements are set to toluene extractables with a maximum of 0.1 wt % and to a maximum benzo(a)pyrene content of 0.25 mg/kg (SCCS 2013a).

5.3 Examples of nanomaterial exposure from cosmetics

5.3.1 Main findings

Based on estimated content of nanomaterials in cosmetics and the consumption pattern of different consumer age groups the following overall estimate of nanomaterials exposure from various types of cosmetics have been made:

Body lotion (2.5%)*:	33.8	mg/kg bw day
Hand cream (2.5%):	5.57	mg/kg bw day
Skin cream (2.5%):	5.57	mg/kg bw day
Sunscreen (5%):	1.61	mg/kg bw day
Antiperspirant (0.002%):	4.50	µg/kg bw day
Shampoo (0.002%):	0.14	µg/kg bw day
Showergel (0.002%):	0.005	µg/kg bw day
Toothpaste (0.002%):	0.010	µg/kg bw day
Eye makeup (0.1%):	0.25	µg/kg bw day
Lipstick (0.3%):	2.76	µg/kg bw day
Makeup (0.1%):	42.5	µg/kg bw day

Mascara (5%): 12.5 µg/kg bw day

*( ) estimated concentration of nanomaterial in the product

These exposure estimates pertain to teenage girls, as this group was found to have the most intensive use of cosmetics. Exposure is predominantly dermal. Oral exposure is considered the dominant exposure route for toothpaste and lipstick. Eye exposure may occur for use of e.g. eye makeup and mascara.

The highest single exposure estimate was, however, found for small children and the use of sunscreen - and especially if the official recommendations for sunscreen use was followed[4]. Following these advices, a dermal exposure of *284 mg TiO2/ kg bw day* has been estimated for a sunscreen with a content of 10% nano-TiO2.

For cosmetic propellant spray formulations, measurements of the aerosols indicate no consistent differences between spray products marketed as nano-products compared to conventional spray product with respect to generation of nano-sized aerosols during use. For an antiperspirant spray containing silver nanoaerosols were generated (with a content of 6 µg Ag/g aerosol and measured as Ag-ions) leading to an average aerosol number concentration of 2 x 10^6/cm^3 in the breathing zone when using 4 g of the spray (i.e. a total of 24 µg silver). More than 10 x 10^{10} nanoparticles (aerosols) were estimated to be deposited in the respiratory tract during use.

For another mouth propellant spray containing colloidal silver a daily oral dose of 70 ng silver was estimated.

From data on cosmetic pump spray products containing titanium dioxide, a weight-based amount of aerosols below 10 µm was reported to be less than 1 wt% indicating a very low potential for exposure to nanosized aerosols from these types of (sun-screen) pump-spray products.

Data from cosmetic propellant sprays containing zinc oxide indicated that less than 0.1 wt% of the aerosols had a size below 10 µm. The large aerosol diameters of these type of sprays may pertain to the formulation with zinc and titanium dioxide as these products for skin care/ skin protection may be formulations with a high content of solid matter and/or emulsified droplets and with a rather viscous and non-volatile matrix, altogether aspects that would hamper the generation of nano-sized aerosols.

5.3.2 Specific data

The Danish EPA (2007) report on nanomaterials in consumer products established exposure scenarios for the use of nanomaterials in facial cream and sunscreen. The Technical Guidance Document on Risk Assessment for Existing Substances from 2003 was used as a basis for making the scenarios.

For facial cream (a leave-on product) a dermal exposure of 2 x 0.8 mg nanomaterial was estimated based on the use of 800 mg cream twice daily containing 0.1% nanomaterial (corresponding to *0.013 mg/kg bw day* for a woman weighing 60 kg).

4 'The SCCS based their risk assessment of sun screens on exposure to 18 grams of sun screen product/person/day, even though the amount recommended by the EU Commission is 36 grams/person/application which is the amount necessary to obtain the claimed sun protection factor. Others, e.g. the Danish EPA finds that risk assessment on UV filters and other sun screen ingredients should be based on exposure to the amount which the EU Commission, national authorities and cancer organisations worldwide recommend consumers to use and which is necessary in order to achieve the claimed sun protection factor.'

For sunscreen (a leave-on product) a dermal exposure of 3 x 52 mg nanomaterial was estimated for a 2-year-old child using 2.6 g sunscreen containing 2% nanomaterials three times daily (corresponding to *12.6 mg /kg bw day* for a child weighing 12 kg).

However, it was noted that according to a recommendation from the EU-Commission regarding effective use of sunscreen a much higher volume of sunscreen should be used (12 g) which would then correspond to a nanomaterial exposure of *56.7 mg/kg bw day* for a 2-year-old child. (Danish EPA 2007)

Lorenz et al (2011) gave an overall assessment of nanomaterial exposure from cosmetic in general. Exposure levels were modelled for 12 cosmetic products (body-lotion, hand cream, skin cream, sunscreen, antiperspirant, shampoo, shower gel, toothpaste, eye make-up, lipstick, make-up and mascara).

The exposure was evaluated based on the following algorithm:

$$Exposure_{nano} = use\ frequency\ per\ day \times retention_{product} \times use\ amount_{product} \times nanoconc._{product} / bodyweight$$

The retention factor for leave-on products was set to 1 whereas a retention factor of 0.01 was used for shampoo and toothpaste and a factor of 0.001 was used for shower gel. The amount of cosmetics used were taken from the literature e.g. US-EPA's exposure handbook and other assessments in literature, and data on the nanomaterial content in cosmetic was judged based on data from available literature.

Data with regard to use pattern of cosmetics were obtained from a German database on behaviour of youth (age above 12 years) and adults, giving data on frequency of use of the various cosmetic product.

The highest daily exposure to nanomaterials from the various products was in all cases among teenage females due to most frequent use by this group. Below figures are given *for a subgroup of teenage females* using the products at most:

Body lotion (2.5%)*:	33.8	mg/kg bw day
Hand cream (2.5%):	5.57	mg/kg bw day
Skin cream (2.5%):	5.57	mg/kg bw day
Sunscreen (5%):	1.61	mg/kg bw day
Antiperspirant (0.002%):	4.50	µg/kg bw day
Shampoo (0.002%):	0.14	µg/kg bw day
Shower gel (0.002%):	0.005	µg/kg bw day
Toothpaste (0.002%):	0.010	µg/kg bw day
Eye makeup (0.1%):	0.25	µg/kg bw day
Lipstick (0.3%):	2.76	µg/kg bw day
Makeup (0.1%):	42.5	µg/kg bw day
Mascara (5%):	12.5	µg/kg bw day

*The number in brackets indicates the estimated concentration of nanomaterial in the product

In general, the dominant exposure route was considered the dermal route. For toothpaste however, oral exposure was considered most important and for lipstick, the oral route was considered as important as the dermal route. The oral route was considered the secondary exposure route for creams, shampoo/shower gel, and makeup, whereas the inhalation was considered an important secondary route for powdered makeup and eye-makeup.

Nazarenko et al. (2011) analysed a range of spray products declared to contain nanoparticles and also corresponding "regular" products with no declared nanoparticle content, including three cosmetic product types (facial spray, hair spray and skin hydrating spray). In the nanotechnology-based cosmetics, no particles could be detected by electron microscopy, whereas particle sizes in the range of 16 to 6000 nm where found in the regular products. Analysis of the aerosols during spraying (measured by SMPS and Aerodynamic Particle Sizer (APS)) showed that the nano-products as well as the non-nano-products generated aerosols with particle sizes of 13 nm – 20 µm. It was further concluded that it might be very difficult to evaluate whether nanoparticles released during product use are actually engineered nanoparticles or whether they derive from natural product ingredients such as herbal oil emulsifications.

Nazarenko et al. (2012) looked at the potential for nanoparticle inhalational exposure from use of six cosmetic make-up powders, three of which were considered to contain nanomaterials (products from the Woodrow Wilson database). Exposure was simulated by applying the cosmetic powder preparation by brush or pads to a female mannequin head and sampling air from the nostrils of the head at a "breathing rate" of 11 litres air per minute. Using Transmission Electron Microscopy (TEM) microscopy, the exposure was characterised (not quantified by mass) and predominantly nanoparticles as agglomerates with particle sizes above 100 nm of the agglomerates were observed. Greater fractions of primary particles in nanosize were observed in two of the nanoproduct compared to the three conventional products. During application of the makeup powder the highest particle levels for nanosized particles were measured to about 10^4 particles/cm^3 for particles with a diameter at about 20 nm for both the conventional products as well as for the products claimed as nanoproducts (the highest level was measured for a conventional product). Measurements were performed using a scanning mobility particle sizer instrument. For one of the conventional products, particle levels up to 10^5 particles/cm^3 were measured for particle sizes in the range of 300-700 nm.

Nano-TiO2

NANEX (2010) made exposure evaluations of sunscreen products with a content of 10% TiO_2 using the ConsExpo tool. The ConsExpo tool was by NANEX (2010) considered the only suitable model for sunscreen products. The exposure estimates are indicated in Table 5-3 below, which also include other estimates from literature (Hansen et al., 2009 and Boxall, 2007).

TABLE 5-3 EXPOSURE ESTIMATES CALCULATED FOR NANO-TIO3 IN SUNSCEENS (NANEX 2010)

Product	Amount used (g)	Population	Hansen et al, 2009	Boxall et al., 2007	Consexpo model and manual calculation		
			Dermal ext. dose (mg/kg/day)	Inhalation exposure (mg/m3)	Inhalation exposure (mg/m3)	Dermal ext. dose (mg/kg/day)	Oral exposure (mg/kg/day)*
Sunscreen cream/lotion	8 g	Men	34	-	-	-	-
	8 g	Women	40	-	-	-	-
	8 g	2-year old children	63	-	-	-	-
	10 g	Men	-	-	-	41	-
	10 g	Women	-	-	-	49	-
	10 g	Adults	-	-	-	46	-
	10 g	3-6 months	-	-	-	483	-

Product	Amount used (g)	Population	Hansen et al, 2009	Boxall et al., 2007	Consexpo model and manual calculation		
			Dermal ext. dose (mg/kg/day)	Inhalation exposure (mg/m3)	Inhalation exposure (mg/m3)	Dermal ext. dose (mg/kg/day)	Oral exposure (mg/kg/ day)*
		old children					
	36 g	Men	154	-	-	-	-
	36 g	Women	180	-	-	-	-
	36 g	2-year old children	284	-	-	-	-
Sunscreen sprays	10 g	Men		-	46	41	0.03
	10 g	Women		-	46	49	0.03
	10 g	Adults		-	46	46	0.03
	10 g	Children		-	46	483	0.3
	30 g	Adults		35	-	-	-
Sunscreen on lips	0.1 g	Men	-	-	-	-	0.04
	0.1 g	Women	-	-	-	-	0.05
	0.1 g	Adults	-	-	-	-	0.05
	0.1 g	Children	-	-	-	-	0.48

*based on 3 applications per day

The NANEX (2010) report found that the mass-based methods/algorithms used in ConsExpo or used by Hansen et al. (2009) and by Boxall et al. (2007) for estimating the exposure were rather similar and that the differences in the obtained values pertained to different choices of various point estimates for input parameters, e.g. content of nano-TiO2, volume of product used, volume of the bathroom when spraying, etc. (e.g. Hansen et al. (2009) used a 10% content of nano-TiO2 whereas Boxall et al. (2007) used a content of 5% in the calculations (Hansen et al (2009) and Boxall et al. (2007) as cited from NANEX 2010).

It may be noted that the Hansen et al. (2009) approach in fact is identical to the Danish EPA (2007) approach described above, only Hansen et al. (2009) used a nanomaterial content (TiO2) of 10 wt%, whereas the Danish EPA (2007) used a nanomaterial content of 2 wt%.

SCCS (2013b) in its opinion on nano-TiO2 compiled data on 15 commercial available qualities of nano-TiO2 used for UV protection. The TiO2 qualities consisted of 85-100 wt% of the rutile form and 0-15 wt% of the anatase form. All qualities except one were coated, primarily with silica, alumina and dimethicone. The volume-specific surface area was in the range of 192-460 m^2/cm^3. The mean weight based particle size distribution ranged from 44 to 354 nm whereas the mean number based particle size distribution ranged from 42-85 nm.

SCCS (2013b) noted that the concentration of nano-TiO2 as an UV-filter may be up to 25 wt% in cosmetic products according to the Cosmetics Directive. In addition, it was noted that formulations in pump sprays in general generate droplets having an aerodynamic diameter above 30 µm with no more than 1 wt% below 10 µm. No specific exposure scenarios for nano-TiO2 were given by the SCCS (2013b).

Weir et al. (2012) analysed various cosmetics for the content of TiO2. In sunscreens, the concentrations measured as titanium were in the range of 10-100 mg/ g (i.e. 1-10%). Toothpaste labelled with content of TiO2 (E171) generally contained titanium in the 1-10 mg/g range (i.e. 0.1-1%).

Silver (Ag)
Quadros & Marr (2011) measured particle sizes and amount of Ag emitted from a mouth spray product containing 30 ppm of colloidal nano-Ag (using ultrafine condensation particle counter and a six-channel optical particle counter, and filter sampling for weight-based metrics). Per ml sprayed, 6.6×10^7 aerosol droplets were formed with a median diameter of 219 nm. Per spray event (0.18 ml), 55.6 ng of Ag-aerosols were generated of which only 4 ng of the aerosols had an aerosol droplet size below 250 nm.

According to the use instructions, 1-2 sprays are to be used on a daily basis, which was considered to lead to a daily load onto the mucous membrane of the oral cavity of 70 ng Ag.

Lorenz et al. (2011) measured the aerosols generated from a liquid antiperspirant propellant spray with an analysed Ag content of 6.8 mg Ag/kg (measured as total Ag). Aerosols were generated in a box with a volume of 300 L under conditions reflecting the near-field breathing zone exposure of a consumer and measured using a scanning mobility particle sizer. In addition, aerosols were collected using an electrostatic sampler for analysis by electron microscopy. No Ag particles could be detected in the aerosols. When spraying, aerosol sizes from 20 nm to 80 nm were the most dominant size fraction. An average concentration of 1.98×10^6 /cm^3 aerosols was measured in connection with use of 4 g spray over a period of 5 minutes. With an inhalation rate of 10,650 cm^3 of an adult man, the deposition of aerosols in the various respiratory tracts regions was modelled to 4.6×10^{10} aerosols for the alveolar regions; 1.3×10^{10} for the tracheobronchial region and 4.4×10^9 for the nasal region.
As no Ag particles were detected, it can be assumed that the exposure consisted of dissolved silver in the droplets.

Lem et al. (2012) reviewed nano-Ag contents in various consumer products, but the authors did not make any exposure estimations. The levels referred to in various types of cosmetics were:

Hair mousse:	20-30 wt%
Liquid, emulsions, creams, gel and sprays:	0.05-20 wt%
Wound care:	0.0005-0.04 wt%
Gel:	0.001 wt%
Cream:	0.0005-0.003 wt%
Facial mask:	0.0005-0.0015 wt%

These data has to be considered with caution as the data primarily (or maybe only) are related to products and articles on the US and Korean markets.

Fullerenes
Benn et al. (2011) analysed C_{60} and C_{70} fullerenes in cosmetic products using TEM electron microscopy and mass spectrometer. The cosmetic products were claimed to contain fullerenes (two watery serums, one lotion and two dense creams). The TEM images showed 50-100 nm agglomerated fullerenes, some of which were covered by a 20 nm layer of polyvinylpyrrolidone. C_{60} was detected in four of the products within a concentration range of 0.04-1.1 µg/g product. C_{70} was detected in two products, however, not quantified.

Nano-(ZnO

SCCS (2012c) compiled data on four qualities of nano-ZnO with UV absorbing properties for sunscreen products. The primary particle size of the four qualities were all above 21 nm with a mean weight based particle size in the range of 41-105 nm and a mean particle number based particle size of 30 to 55 nm (determined using a CPS disc centrifuge). Spray nano-ZnO formulations with gas propellant resulted in less than 5% of droplets (by weight) below 30 μm and less than 0.1% of the droplets (by weight) below 10 μm. No specific dermal or inhalational exposure scenarios for nano-ZnO were given by the SCCS (2013).

Carbon black, CI 77266

The ingredient carbon black has a long history of use as a cosmetic colorant. Typical uses of carbon black are in different types of cosmetic products, specifically makeup products, and include but are not limited to eyeliners, eye pencils, eye shadows, mascaras, blushers, brush-on-brow, foundations and nail enamels, leave-on and rinse-off skin products. Typical use concentrations range from 0.001% to 10%, with 0.001% for skin products, 5% for nail enamels and mascaras and up to 10% for other eye decorative products such as eyeliners, eye pencils and eye shadows (SCCS 2013a).

SCCS (2013a) in its opinion on carbon black (in nano-form) characterised carbon black for cosmetic use as elemental carbon obtained by partial combustion or thermal decomposition of hydrocarbons. Typically, the average primary particle diameter of commercial carbon black materials range from 10 to 100 nm, while the average aggregate/agglomerate size is in the range 100-800 nm or above. Carbon black is initially formed as roughly spherical primary particles, which, in most cases, rapidly form aggregates. An aggregate is a chain of primary carbon particles that are permanently fused together in a random branching structure. The aggregate may consist of a few or hundreds of spherical particles (or, as in the case of thermal black, primarily single spheres rather than chains). Accordingly, on the basis of their primary particle size, all carbon black materials used in cosmetics are considered as nano-structured materials.

Further, SCCS (2013a) stated that the purity of carbon black for cosmetic use should be in compliance with FDA specifications, i.e. a purity of more than 97% and with an ash content < 0.15%, total sulphur < 0.65%, total PAH < 500 ppb and benzo(a)pyrene <5 ppb, dibenz(a,h)anthracene < 5ppb, As < 3 ppm, Pb < 10 ppm, and Hg < 1 ppm.

It may be noted that SCCS (2013a) concluded the cosmetic dermal use of carbon black as safe, not at least due to the lack of systemic absorption of the substance. A potential for eye irritation of carbon black could not be completely excluded, as relevant data were lacking.

5.4 Examples of Nanomaterial exposure from cleaning products

5.4.1 Main findings

The identified literature indicates that nano-Ag is used in cleaning sprays, detergents, surface wipes and a cleaning scrubber. One paper addresses the use of nano-silica in a glass cleaner product. Some studies have identified the presence of non-declared nanomaterials in a number of cleaning sprays. The chemical identify of these nanomaterials have not been identified by the studies.

One study addressing dermal nano-Ag exposure (e.g. from wipes) finds a maximum release of 18.5 mg Ag/kg product. This release is assumed to be Ag in ionic form and considered by the authors to be very low. No actual exposure assessment is performed.

Most papers address sprays containing nano-Ag, where focus in on characterisation of the aerosol and nanomaterial content rather than actual estimation of exposure.

The study addressing nano-silica in a glass cleaner spray, estimated (using ConsExpo) that the mean concentration is 0.002 mg silica/m^3 in the surrounding of the consumer and the peak concentration 0.035 mg/m^3 shortly after spraying. An accidental scenario (spraying towards exposed person) resulted in 0.044 mg/m^3.

In general, the papers addressing sprays indicate that pump sprays result in no/low exposure due to larger aerosols generated, which deposit without causing consumer exposure to (free) nanoparticles. Propellant sprays generate much lower diameters from which liquid might readily evaporate and cause direct exposure to free nanomaterials. Smaller aerosols also stay airborne for a longer period. Thus, the spray mechanism highly influences exposure.

Further, it should be noted that propellant sprays seems to generate nano-aerosols even if they do not contain nano. These aerosols disappear when the liquid aerosol evaporates.

Overall, the literature reflects measurements in experimental chambers and shows that there are many variables (spray mechanism, room size, temperature, equipment, etc.). This may explain that many authors abstain from estimating exposure levels.

5.4.2 Specific data

Lem et al. (2012*)* reports a market-based Intellectual Property (IP) study on nanosilver applications and finds that "detergents" typically have a nano-Ag concentration in the range from 0.00001 up to 3% (w/w).

Dermal

Quadros et al. (2013*)* investigated children exposure from a number of nano-Ag-containing products, including three cleaning products; a disinfecting spray, surface wipes and a kitchen scrubber. Ag deposition onto skin was estimated by use of dermal wipes. To allow using this method for the nano-Ag-containing spray and surface wipes, these products were applied onto surface tiles, which were allowed to surface dry before wiped with the dermal wipe. For the three cleaning products, silver transfer rates of 0.3 (kitchen scrubber) to 9 µg Ag/m^2 (disinfectant spray) were identified. These values were lower than for textiles products also addressed. Overall, the authors note that exposure is expected to be to the ionic form of Ag (although further speciation research is recommended) and that the observed levels seem to be low.

Inhalation/spray
Hagendorfer et al. (2010) report from a chamber experiment conducted with a commercially available water-based nano-Ag spray. The product is supplied as a pump spray as well as a gas propellant spray. The declared Ag concentration of 1000 mg Ag/L was confirmed analytically. Particle size analysis (disregarding agglomerates possibly formed during analysis) showed a peak of 6nm and a range in the 15-60nm area as compared to a declared size of 26 nm (Dynamic light scattering). Airborne nano-aerosols/particles were measured by SMPS (Scanning Mobility Particle Sizer) and sampled on TEM-grids using an electrostatic particle sampler. The latter allowed subsequent SEM (Scanning Electron Microscopy) image analysis and elemental identification with an EDX (Energy-dispersive X-ray Spectroscopy) unit.

In control experiments, it was shown that nano-aerosols can be formed during propellant spraying even if the product does not contain nanomaterials. These purely liquid aerosols could be removed by applying a thermo-desorber before measurement. The authors conclude that that the pump sprays release relatively large droplets/aerosols, which deposit on walls and floors and do therefore not lead to exposure to free/dry nanoparticles. The propellant spray forms smaller (nm to µm range) aerosols from which the water evaporates and leads to exposure to free/dry nanoparticles. For the propellant spray, the authors showed that rapid particle loss takes place (possibly due to agglomeration and deposition of these), but that a rather stable concentration is reached within three minutes. Thereafter, particle concentration decreases very slowly indicating the potential for long-term exposure to these non-agglomerated individual particles. Generally, the paper shows a huge amount of variables in such experiments and that evaporation, deposition and agglomeration phenomena are very complex. Possibly associated with this, the paper does not propose any indicative exposure levels.

Michel et al. (2013) assessed the risks of the use of a glass cleaner supplied for consumers in "spray trigger bottles". The product is water based and contains 0.09% (w/w) spherical synthetic amorphous silica (SAS) nanoparticles as well as non-disclosed surfactants, solvents and other cleaning agents. The reported size of the primary SAS nanoparticles was 9 nm, which was confirmed with Dynamic Light Scattering (DLS) (range 4-40 nm) and TEM (range 10-20 nm). This analysis showed that the nanoparticles had a large tendency to agglomerate/aggregate, which is expected given the function of the SAS nanoparticles, in which the hydroxyl groups react with the glass surface or with each other to form siloxane bonds. This self-organisation leads to enhanced hydrophilic properties and thereby enhanced drainage, drying speed and reduced de-soiling. One spray shot corresponds to approximately 2 mL (approx. 2 g of product). The authors representing Hempel refer own data that have shown that the consumers that most frequently clean their windows do so 3-4 times per year by applying the product on dirty surfaces with a few strokes and thereafter wipe of the window using cleaning cloths. It is therefore likely that use will lead to inhalation and dermal exposure, and even inadvertent oral exposure might occur from hand to mouth or if the cleaning product is used on surfaces, which are subsequently used to handle unpackaged food. However, inhalation is assumed the main (most important) exposure route. Laser diffraction experiments were conducted to measure the aerosol droplets with open sieve (spray) and closed sieve (foam). In both cases, no aerosols below 4 µm were detected. Thus. it was concluded that aerosols were in a size range not expected to reach the alveoli. Consumer inhalation exposure was modelled with ConsExpo. It is not entirely clear which parameters are used for the modelling, but during "one cleaning event", it is estimated that the mean concentration is 0.002 mg SAS/m^3 in the surrounding of the consumer and the peak concentration 0.035 mg/m^3 shortly after spraying. An accidental scenario (spraying towards exposed person) resulted in 0.044 mg/m^3. The paper goes on with assessing risk (authors found no risk).

Nazarenko et al. (2011) analysed a range of spray products declared to contain nanoparticles and corresponding "regular" products on which nanoparticle content is not declared, including a general disinfectant. Sample analysis (TEM and Photo Correlation Spectroscopy), as well as particles in the

airborne state during simulated use (measured by SMPS and Aerodynamic Particle Sizer (APS)) show that the nano-products as well as the non-nanoproducts contain nanoparticles and result in a range of particle sizes when used (14 nm – 20 μm). This indicates that consumers can be exposed to particles, which deposit in all regions of the airway systems from nano as well as from regular sprays. Overall, the authors are, however, hesitant to draw firm conclusions due to poor ingredient lists and therefore challenges with optimising the analytical techniques towards the contained chemistry. Experiments were conducted with the supplied spray mechanism as well as with two standard nebulizers. These experiments show that particle generation and thus consumer exposure is heavily influenced by the spraying mechanism, including that smaller aerosols more likely lead to exposure to primary nanoparticles (higher likeliness of evaporation of the carrier liquid). The data also showed that generally alcohol-based products generate lower particle size distributions as compared to water-based (presumably due to quicker evaporation of alcohol compared to water).

Quadros and Marr (2011), addresses three spray products associated with nano-Ag technology of which one is a surface disinfectant. No/very few nanoparticles were found in the surface disinfectant and the authors therefore do not assess the human exposure to this product. Results for the two other products are addressed in Section 5.3. However, it should be noted that the authors in line with other authors note that spray mechanism/dynamics influence the aerosol generation/exposure, but also note that concentration of nanomaterial in the sample might influence release and exposure.

5.5 Examples of nanomaterial exposure from coating/impregnation and maintenance products

5.5.1 Main findings

Data were found on products for impregnation of surfaces using an impregnated cloth for car windows and for propellant spray products for either surface treatment of a bathroom or surface treatment of shoes and for paints.

A dermal nanomaterial exposure of 8 x 10^{-3} mg/kg bw (or a total of 560 μg) per event was estimated using a cloth for treatment of car windows impregnated with 1% nanomaterial.

Dermal nanomaterial exposure in relation to spraying bathroom surfaces was estimated to be 2 x 10^{-2} mg/kg (or a total of 1.2 mg) per event anticipating a nanomaterial content of 0.1% in the spray and assuming 1% of the sprayed amount came into contact with skin.

Inhalational exposure for the nanomaterial during 40 minutes of stay in the bathroom and use of 118 ml of the spray was calculated to be 1.9 x 10^{-3} mg/kg bw or at a total of 114 μg nanomaterial.

For shoe impregnation products (as propellant sprays), the nanoparticle concentrations in the breathing zone were measured to be about 1 x 10^5 particles/cm^3 (as liquid aerosols). During spraying, the inhalational exposure for TiO2 (1.6wt% content in the aerosols) was calculated to be 3.4 μg TiO2 per minute.

Although based on few data, this indicates that in absolute figures the dermal exposure may be more than an order of magnitude higher than the inhalational exposure for impregnation spray products. The inhalational exposure to nanomaterials from spray product may be in the microgram range per use event and within the nanogram range when expressed per kg bw. Inhalational exposure expressed in nano-particle numbers may be within the range of 1-10 x 10^9 particles per event (for a person inhaling a particle concentration level of 1 x 10^5 particles/cm^3 during several minutes).

Dermal exposure for roller painting using ConsExpo was estimated to be 13.6 mg nano-TiO2/kg bw per event.

Inhalation exposure for spray application of the paint was using ConsExpo estimated to be 0.016 mg nano-TiO2/kg bw per event.

5.5.2 Specific data

The Danish EPA (2007) study on nanomaterials in consumer products established an exposure estimate for an impregnation product for car windows. The Technical Guidance Document on Risk Assessment for Existing Substances (TGD 2003) was used as a basis for making the scenario. The liquid product with an unspecified nanomaterial content of 1% was applied using a cloth on an overall surface area of 5.4 m^2 and using 10 ml/m^2. It was assumed that 1% of the product used came into contact with the skin per event (assumed as twice yearly). Based on this, a nanomaterial exposure per event of 8 x 10^{-3} mg/kg bw was calculated for an adult man (70 kg bw).

For a spray product used for impregnation of surfaces in bathrooms, the Danish EPA (2007) study estimated a dermal nanomaterial exposure of 2 x 10^{-2} mg/kg bw and an inhalational exposure of 1.9 x 10^{-3} mg/kg bw per event for a woman (60 kg bw) using the product . This was based on a nanomaterial content in the product of 0.1% and a use of 10 ml/m^2 on a total surface area of 11.75 m^2.

For the dermal exposure, 1% of the product volume used was assumed to come into contact with skin. For the inhalational exposure, the concentration of the nanomaterial in the bathroom of 7.5 m^3 was calculated based on the amount sprayed divided by the room size. The inhalational exposure was then calculated based on a 40 minutes stay in the bathroom during application with a respiratory rate of 26 m^3/24 h during light work.

Nano-TiO2

NANEX (2010) used the ConsExpo model to calculate the dermal exposure in relation to painting (brush or roller application) with water based paint containing 25% nano-TiO2. A dermal load of nano-TiO2 was calculated to 1.05 mg/cm^2 on a skin area (both hands) of 860 cm^2 leading to a dermal exposure of 13.6 mg/ kg bw.

Using the ConsExpo model for spray application of the paint, the inhalational exposure was calculated to be 0.0157 mg nano-TiO2/kg bw during 25 minutes of exposure at an average concentration in air of 1.7 mg nano-TiO2/m^3. The dermal load and the dermal exposure was estimated to be 0.425 mg/cm^2 and 5.63 mg/kg bw, respectively. The oral (non-respirable) exposure was estimated to be 0.112 mg nano-TiO2/kg bw per event (NANEX 2010).

Chen et al. (2010) analysed the aerosols generated from a bathroom cleaner/sanitizer containing TiO2 dispensed as a propellant spray. The spraying was performed in a chamber set-up using realistic spraying conditions during 2.5 minutes. Results indicated that, while aerosol droplets were large with a count median diameter of 22 μm during spraying, the final aerosol contained primarily solid titanium dioxide particles with a diameter of 75 nm. This size reduction was due to the surface deposition of the droplets and the rapid evaporation of the aerosol propellant. In the breathing zone, the aerosol, containing primarily individual particles (>90%), had a mass concentration of 3.4 mg/m^3 or 1.6 x 10^5 particles/cm^3, with a nanoparticle fraction limited to 170 μg/m^3 or 1 .2 x 10^5 particles/cm^3 (i.e. 1 μg corresponds to 7 x 10^8 particles).

Assuming a peak TiO2 aerosol concentration of 3.4 mg/m^3 with a MMAD of 836 nm (or MMAD of 395 nm), a minute ventilation rate of 20 L/min and a deposition fraction of 11.3%, and a alveolar surface of 102 m^2, 1 minute of spraying would result in 0.0075 μg titanium dioxide per m^2 alveolar epithelium per minute or a total alveolar dose of 7.65 μg titanium dioxide. No data on the TiO2

content in the product was given; however, the sprayed aerosols contained 1.6 wt% dry weight. The nano-aerosol exposure can be calculated to 3.4 μg per minute and 2.4 x 10^9 particles per minute.

These data may be compared to the Danish data above where the exposure for a 40 minutes spray with a product concentration of 0.1% resulted in an inhalational exposure of 1.9 x 10^{-3} mg/kg bw. This exposure would have been 16 times higher i.e. 3.0 x 10^{-2} mg/kg bw (or 30 μg/kg bw) if a content of 1.6% in the product was used.

When using the Chen et al. (2010) exposure rate of 3.4 μg per minute, then 40 minutes of inhalational exposure would lead to 136 μg of inhalational exposure assuming all nano-aerosol mass is consisting of titanium dioxide (or to 96 x 10^9 titanium dioxide nanoparticles). This would for a 60 kg person correspond to a nanomaterial exposure of 2.3 μg/kg bw, which is a factor 13 lower than the calculated Danish exposure scenario. Thus, the calculated scenario may be considered as a conservative but maybe still realistic scenario as great variations may be anticipated for consumer inhalation scenarios.

Silane, siloxane and TiO2 mixed with silane and siloxane
Nørgaard et al. (2009) studied the aerosol size-distributions and chemistry during simulated application of four different easy-to-clean surface-treatment spray products and concluded with a preliminary worst-case assessment of the exposure in a 17.4 m^2 standard model room. Three of the products were pump-sprays of which one of them (NFP3) contained nano-TiO2 anatase particles.

According to the data sheets, the pump sprays, NFP1 (intended for making self-cleaning non-adsorbing floor materials) contained non-specified fluorosilane in a 2-propanol solvent and NFP2 (intended for making self-cleaning ceramic tiles) contained siloxane in an ethanol-methanol mixture. NFP3 (intended for making self-cleaning windows) contained nano-TiO2 in ethanol solvent. The fourth product (NFP4) was a pressurized spray can product for general cleaning application containing propane/butane (propellant) and kerosene. The spray tests were conducted in a 0.66 m^3 fully mixed air closed aerosol chamber in stainless steel. Product corresponding to the recommended use for 1 m^2 was sprayed onto a stainless steel plate at the recommended surface-to-nozzle-distance of 35 cm. Air-borne particles and SVOCs was sampled 20 cm behind the spray bottle to represent the position of the user inhalation zone. Nano-size particles (6-523 nm) were measured using a Fast Mobility Particle Sizer (FMPS) whereas μm-size particles (0.5 – 18.4 μm) were measured using an APS. Volatile Organic Compounds were measured using MIMs and GC-MS and GC/FID. All experiments were conducted at 25°C and 23% RH.

The results showed several sizes-modes of airborne nm- to μm-size particles after use of all the spray products. The observed particle size-distributions and concentration trends revealed complex particle formation, growth and evaporation in the air after use of these products. The gas-phase chemical analysis also showed a more complex chemistry in the products than reported by the distributer. Overall, in the tests the pump sprays generated 3.1 x 10^8 to 3.6 x 10^8 airborne particles/m^3/g product used, whereas the pressurized spray-can (NFP4) generated 2.1 x 10^{10} particles/m^3/g product used. The fluoro-silane and siloxane pump-spray products are thought to produce particles as a result of solvent evaporation and condensation of the active surface-coating ingredients. For the TiO2 anatase surface coating product (NFP3), cyclohexasiloxane and cycloheptasiloxane were found in the emissions in addition to the expected TiO2 anatase. Use of NFP4 was associated with emission of numerous volatiles, including especially alkanes, various siloxanes, and relatively high contents of limonene, an often used fragrance, but not reported in this product. Exposure assessment for NFP1 and NFP2 pump spray products showed that concentrations exceeding 1.5 x 10^6 particles/cm^3 could be reached treating a 7 m^2 surface in a 17.4 m^2 standard model room without ventilation. The particle exposure levels applying the gas propellant NFP4 spray would be approx. 100 times higher than for NFP1 and 2. NFP3 is intended

for outdoor treatment of windows, why dilution is anticipated to be very rapid reducing the level of exposure considerably.
Due to observed acute hazardous risk to the airways caused by hydroxylated per-fluorinated silanes and siloxanes (Nørgaard et al., 2010) NFP1 was taken of the Danish market on request by the Danish EPA. The specific anatase-based NFP3 is also no longer available on the Danish market, but other comparable products exist.

Zinc oxide (ZnO)
Lorenz et al. (2011) measured aerosols generated from a shoe impregnation product from a propellant gas vessel with a zinc content of 470 mg Zn/kg (analysed as Zn-ions). Aerosols were generated in a box with dimensions reflecting the near-field breathing zone exposure of a consumer and analysed using a scanning mobility particle sizer and electron microscopy. ZnO particles were further verified by the chemical analysis and electron microscopy. In addition, chlorine and fluorine were detected in the chemical analysis suggesting that acrylate polymers were present in the product. When spraying the highest particle number concentrations were obtained for particle sizes below 15 nm. The aerosol number concentration for 1 g of spraying was 7.6 x 10^4/cm^3. Zinc particles were only observed in the micrometer range of particles and particles below 100 nm was therefore considered to consist of acrylate polymers.

Consumer exposure was calculated based on use of 18.5 g of the product during 8 minutes and a measured average particle number concentration during the period of 1.14 x 10^6. When inhaling 10650 cm^3 air/ minute, the exposure of the various respiratory regions could be modelled to 4.5 x 10^{10} particles for the alveolar regions; 1.4 x 10^{10} for the tracheobronchial region and 4.8 x 10^9 for the nasal region.

Similar exposure levels could be calculated for another shoe impregnation product that only contained fluorine and chlorine and which therefore was suggested to only contain acrylate polymers.

5.6 Examples of nanomaterial exposure from textiles

5.6.1 Main findings
The number of different textiles with nanomaterials is rather wide and includes all from inner to outer clothing, shoes, blankets and textile cuddle toys for children. Ag and TiO2 are by far the most common nanomaterial used in textiles while CNT are potentially soon emerging on the European market for wearable electronic textiles. Textiles as a component in other products or articles are not covered by this analysis. The exposure route is primarily dermal, but for babies and smaller children the oral pathway, is also a likely route of exposure.

Data were found on textiles treated with Ag and TiO2. No data on use of carbon nanotubes (CNT) in textiles from the market have been found.

From the Danish market, Ag-content in textiles has been measured in the range of 0.037 µg Ag/g in a sandal to 10 300 µg Ag/g in the cuddly toy.

From migration data on a tank-top containing 12 µg Ag/g a dermal exposure to a girl (up to 9 years old) of 12.7 µg Ag/kg bw day was estimated. For a similar scenario, the ConsExpo model estimated a dermal exposure three times higher when using a content of 10 µg Ag/g in a T-shirt and a migration rate of 45%.

Such estimations may be very sensitive to different degrees of migration rates of the Ag from the textile as experimental data found here indicate a very high degree of variability (from 2% and up to

38%). Overall, these similar results from measured data and the use of the ConsExpo model indicate that ConsExpo may be an appropriate tool for estimating dermal exposure from textiles. Based on migration data on the cuddly toy (as indicated above) an oral exposure of *0.042 µg Ag/kg bw day* was estimated in relation to sucking of the toy by a child.

Migration of Ag has most often in literature been measured as Ag ions, but in one case it was indicated that silver particles < 450 nm was found in the migration fluid as well.

Wash data from textiles treated with TiO2 in the range of 2,153 to 7,149 mg Ti/g indicate generally very low migration of 0.01-0.06% of TiO2 with worst case wash out levels of 3-4%. The migration is mainly due to particulates. Based on migration data, dermal exposure from a shirt with a titanium content at 7,149 µg Ti/g textile has been estimated to be 11.6 µg Ti/kg bw for an adult person.

5.6.2 Specific data

Silver (Ag)

The Danish EPA (2012) report on nano-Ag in textiles made three consumer exposure scenarios for textiles that contained Ag based on chemical analysis. (Using EDX the content of nano-Ag particles could however, not be verified).

For a *shoe insole* with an Ag content of 19 µg Ag/g, a dermal exposure of *0.42 µg Ag/kg bw day* was estimated based of a measured migration rate of silver from the shoe insole of 0.12 µg Ag/cm²/8 hours, a skin contact area of the feet of 300 cm², a contact duration of 8 hours and a body weight of 70 kg.

For a *tank top* with a silver content of 12 µg Ag/g for 3-9 year-old girls, a dermal exposure of *12.7 µg Ag/kg bw day* was estimated based on a measured migration rate of Ag from the tank top of 0.09 µg Ag/cm²/16 hours, a skin contact area of 2,340 cm², a contact duration of 16 hours and a body weight of 16.3 kg.

For a *cuddly toy* with an Ag content of 10 300 µg Ag/g, an oral exposure due to mouthing of the toy by a 2 year-old child was estimated to be *0.042 µg Ag/kg bw/day*. This was based on a measured migration of 58 ng Ag/cm²/2 hours in artificial saliva, a mouthing area of 10 cm², a mouthing duration of 2 hours and a body weight of 13.7 kg.

A total of 18 types of textiles were examined and the Ag contents were found in the range of 0.037 µg Ag/g in a sandal to 10 300 µg Ag/g in the cuddly toy.

The NANEX (2010) project made exposure assessments using the ECHA guidance for Consumer Exposure Estimation (version 2008) and the ECETOC TRA and ConsExpo tool for consumer exposure to nano-Ag in socks (Ag content of 2.4 mg/g) and a T-shirt (Ag content 10 µg/g) .
The following results were obtained in relations to worst-case assumptions (leaching of 45% of the Ag from the textile) using the various approaches:

TABLE 5-4 DERMAL EXPOSURE TO NANO-AG FROM TEXTILES (NANEX 2010)

Product	Population	ECHA	*Models*		
		Guidance Dermal load as *(mg/cm²)*	*ConsExpo* Dermal load as *(mg/cm²)*	*ConsExpo 4.1* *Dermal external dose as* *(mg/kg/day)*	ECETOC Dermal dose as *(mg/kg/day)*
Socks	Adult	0.123	0.109	1.97	0.468
Socks	Child (10 years)	0.153	0.138	3.98	0.188
T-shirt	Adult	3.2 E-04	3.6E-04	3.46E-02	1,05E-02
T-shirt	Child (10 years)	4.1 E-04	4.8E-04	6.9E-02	3.90E-03

Compared to the Danish EPA (2012) exposure assessment for the top-tank for girls using the migration rate in artificial sweat, it can be noticed that the estimated exposure of 12.7 µg Ag/kg bw day is a factor 3 higher than the ECETOC TRA value of 3.9 µg Ag/kg bw day. (However, the ECETOC TRA figures seems a bit odd -and a typing error may have occurred- as the dermal exposure is higher for adults than for children). The ConsExpo model resulted in a dermal exposure value about three times higher than the Danish estimate.

Also, it has to be noted that the ConsExpo estimation is more conservative than the ECETOC TRA estimation (by a factor of 3-20) with the biggest difference for the child sock scenario.

With respect to dermal load from the T-shirt for a child, based on 45% leaching, the ECHA guidance-based estimate of 0.41 µg/cm² and the ConsExpo estimate of 0.48 µg/cm² is a factor 4-5 higher than the dermal load of 0.09 µg/cm² determined by the Danish EPA (2011) based on concrete migration data with artificial sweat.

Further studies have been made regarding the migration rate of Ag (and TiO2) from textiles:

Benn and Westerhoff (2008) washed six pairs of socks containing silver in pure water. The socks had an Ag-content up to 1.36 mg Ag/g textile and TEM images revealed silver particles in the range of 10 to 500 nm in diameter. Some socks released hardly any Ag (<1%) e.g. the sock with the highest Ag content, whereas other socks released 100% after 4 times 24 hours washing in distilled water. In the washing water, Ag-material was identified with diameters of one to few hundred nm in diameter. It was concluded that at least some of the Ag content in the water may be due to nano-Ag-particles.

In another study, Benn et al. (2010) found release of 0.56 µg Ag per g textile from an athletic shirt with an Ag content of 30 µg/g (i.e. nearly 2% release) after 1h washing in tap water.

Goetz et al. (2013) found Ag content in socks, shirts and trousers in the range of 18- 183 µg Ag per g textile. From a shirt with the content of 183 µg Ag per g textile, a release of 12.5 µg Ag per g textile was measured into artificial sweat after ½ hours incubation. About 60% of this amount was as particulate Ag, half of which with particle sizes below 450 nm.

Based on these measurements, a dermal exposure of 17.1 µg Ag/kg bw as total Ag and a exposure of 8.2 µg Ag/kg bw as Ag particles below 420 nm was estimated for an adult man wearing Ag-functionalized trousers and T-shirt.

For the exposure estimate, the following algorithm was used:

$$E\ (\mu g/kg) = m_{textile} \times a_{subst} \times r_{sweat} \times t_{expo} \times A_{expo} \times f_{contact} / m_{bw}$$

Where
$m_{textile}$ = weight of the textile (g)
a_{subst} = released amount of substance from fabric into sweat (µg/g/mL)
r_{sweat} = released volume of sweat per time and body weight (mL/min/m²; 1.8 and 1.25 mL/min/m² used for males and females)
t_{expo} = duration of exposure (min)
A_{expo} = body surface area covered by the fabric (m²)
$f_{contact}$ = fraction of fabric in close contact with sweat and skin
m_{bw} = body weight (kg; 77 kg and 62 kg used for men and women)

In another study from the group, eight pieces of textiles containing Ag (three of which containing nano-Ag) were examined. The initial Ag content of the textiles was between 1.5 and 2 925 mg Ag/kg. Only four of the investigated textiles leached detectable amounts of Ag during washing (in wash machines with detergent at 40 °C for 45 minutes). 34–80% of the Ag was in the form of particles larger than 450 nm. Microscopic analysis of the particles released in the washing solutions identified Ti/Si–AgCl nanocomposites, AgCl nanoparticles, large AgCl particles, nano-Ag sulfide and metallic nano-Ag, respectively. The nanoparticles were mainly found in highly agglomerated form. The fraction of Ag released in one washing/rinsing cycle compared to the initial amount was 20%, 14.8%, 23.5% and 17.6% for the four textiles releasing silver (Lorenz et al. 2012).

Quadros et al. (2013) measured the migration of Ag into tap water, saliva, sweat and urine from a children plush toy and a baby blanket containing 48.2 and 109.8 µ Ag per g textile. Highest degrees of migrations were measured into sweat and urine. Thus, 38% and 36% of the Ag in the plush toy were liberated into sweat and urine after 2 hours at 37 °C from the plush toy, whereas 4.4% and 3.4% was liberated from the baby blanket. When wiping the textiles with dermal wipes there was an Ag transfer rate of 23 µg Ag/m2 and 13.8 µg Ag/m² onto the wipes from the baby blanket and the plush toy, respectively.

From these data, it can be concluded that the migration of Ag from textiles can vary quite a lot. Therefore, a default assumption of 45% as used by NANEX (2010) may not seem quite unrealistic as worst case assumptions for dermal exposure.

Titanium dioxide (TiO2)
Windler et al. (2012) found generally low migration of 0.01-0.06% of TiO2 during washing from textiles that were sun protected with TiO2 in a concentration of 2 153 to 7 149 mg Ti/g. One textile, however, liberated 3.4% during a wash. Particle sizes in the textiles were in the range of 60 to 700 nm and particle sizes in the wash water in the range of 60-350 nm. Goetz et al. (2013) estimated a dermal exposure level of 11.6 µg Ti/kg bw based on similar migration rates measured from a TiO2-functionalized shirt with titanium content at 7 149 µg Ti/g textile. The TiO2 migration occurred mainly in form of particulates.

For TiO2 in textiles, a realistic worst-case assumption for dermal exposure may be a migration of 3-4% of the content.

Carbon nanotubes
In relation to use of carbon nanotubes (CNT) in textiles, it has been is noted that currently no CNT textiles for consumers has been found on the market (Nowack et al., 2013). An assessment of the potential dermal exposure level was performed by NANEX (2010) that suggested exposure levels of 1.7×10^2 to 8.3×10^2 mg/kg body weight/day assuming daily use, full-body dressing in a textile made with 20% CNT textile and release of 10% CNT. However, as also the authors state, this assessment seems far from realistic even as a worst case exposure scenario.

5.7 Examples of Nanomaterial exposure from construction materials

5.7.1 Main findings

Construction materials available for consumers comprise a wide group of products including e.g., cements (silica, nano-TiO2, CNT, unspecified metal oxides), nanocomposites (nanoclays), windows (silica, tungsten oxide), tiles (nano-TiO2), and protective surface coatings such as paints, lacquers, as well as antimicrobial and easy-to-clean nanofilm coatings, already discussed in section 1.3.4. Coatings/paintings may contain a range of nanomaterials such as nano-Ag, nano-copper, nano-ZnO and pohotocatalytic nano-TiO2 used as biocides, nano-ZnO and nano-TiO2 as UV-light absorber, nano-TiO2 as pigment and nanoclays as rheological modifier.

Except for paintings/coatings addressed elsewhere (Section 5.5 and 5.11), no examples on use-related release and exposure during consumer use of construction materials have been identified.

Exposure may also occur during maintenance, renovation and demolition. No data on such exposure have been identified in the literature.

5.7.2 Specific data

Kaiser et al. (2013) discusses the use or possibly upcoming use of nanomaterials in the paint and lacquer industry. Nanomaterial additives can be used as biocides (nanosilver, nanocopper, nanoZnO, photocatalytic nano-TiO2), as UV-light absorber (nanoZnO and nano-TiO2), as pigment (TiO_2 with fraction of nano-TiO2) and as hardener (amorphous silica dioxide). Silica dioxide also protects the product against corrosion and provides the product with high gloss. The paper discusses yet unresolved challenges, such as long term durability/efficiency tests; e.g. possible washout of nano bioicides and the possibility that the photo catalytically activity of nano-TiO2 besides its beneficial effects possibly also degrade the paint matrix. The paper also discusses several toxicity aspects relevant for hazard evaluation and refers the NRWCE work on release from sanding (e.g. Koponen et al., 2011, Saber et al., 2012). The paper does not address product concentrations or exposure estimates.

Based on a specific Internet/literature search on nanomaterials in building products, the findings shown in Table 5-5 has been derived in the yet on-going Danish EPA project on nanomaterials in waste (Danish EPA, 2014c).

TABLE 5-5. NANOMATERIALS AS IDENTIFIED IN BUILDING PRODUCTS (TAKEN FROM DANISH EPA, 2014C)

Type of building material	Functionality introduced	Type of introduction/ Matrix	Nano-material	Reference	Examples of commercial products
Concrete	Self-cleaning surface (photo catalytic)	Surface layer	TiO_2	[1][3]	
	Ultra strong	Mixed in matrix,	SiO2 (silica	[1]	

Type of building material	Functionality introduced	Type of introduction/ Matrix	Nano-material	Reference	Examples of commercial products
	concrete	filler to improve strength	fume) SiO_2	[4]	Dyckerhoff Nanodur (www.dyckerhoff.de)
	Corrosion reduction			[1]	
	Increased durability	Mixed in matrix	SiO_2	[1]. [3]	
	Dense and strong concrete, with better water-blocking and corrosion properties	Mixed in matrix	SiO_2	[2]	
	Improve mechanical properties	Mixed in matrix	CNT Metal oxides	[3] [4]	
Insulation material	Improved insulation properties against heath, cold, fire or a combination thereof	Aerogel (often SiO2 or carbon based)	Nanoporous material (internal structure consists of nano bubbles/ holes)	[1]. [4]	Nansulate (http://www.nansulate.com/index.html)
Coatings	Improved surface penetration, coverage, reduced layer thickness		Not identified (nano-sized dispersions)	[1]	
	Transparent coatings	Additive in the coating	Not identified (nano-sized ingredients)	[1]	
	Photo-catalytic, self-cleaning, hydrophobic properties	Additive in the coating	TiO2, ZnO, SiO2	[1]	
	Antibacterial properties	Additive in the coating	Ag, TiO_2, ZnO	[1]	
	Scratch resistance	Additive in the coating	SiO2, Aluminium oxide	[1]	
	Easy-to-clean surfaces	Additive in the coating	Carbon fluorine polymers	[1]	
	Fire retardant	Additive in the coating	TiO2, SiO2, nano-clays	[1]	

Type of building material	Functionality introduced	Type of introduction/ Matrix	Nano-material	Reference	Examples of commercial products
	Insulating properties/ corrosion protection	Additive in the coating/paint	Nano-sized cells, pores and particles, not identified	[3]	
Wood	UV-protection of wood (coating)	Additive in the coating	TiO2, ZnO, CeO2	[1]	
	Decolourisation of wood by tannin (coating)	Additive in the coating	Nano-clays	[1]	
	Water repelling wood (coating)	Not identified	SiO2, alumina	[3]	
Steel	Improves strength, has favorable corrosive-resistance properties	Nano-structured surface	Not identified		MMFX steel (www.mmfx.com)
	Steel alloys for improved strength and good ductility		Carbon, iron		Sandvik NanoFlex (http://www.smt.sandvik.com/en/products/trademarks/sandvik-nanoflex)
	Replacement of steel by CNT in steel cables	Not identified	CNT	[5]	
Glass	IR reflection	Surface coating	Tungsten oxide	[1]	
	Non-reflective glass	Surface structure/coating	Nano-porous SiO2	[1][3]	
	Fire or heat protection	Surface coating, transparent silica gel interlayer	Metal oxides, SiO2	[1]	
	Easy-to-clean properties	Surface coating	Ag, SiO2, carbon fluorine polymers	[1]	
	Photo-catalytic, self-cleaning properties	Surface coating	TiO2	[1]	Pilkington Activ [4]

[1]: van Broekhuizen *et al.* 2010.

[2]: Nano Connect Scandinavia, 2012.

[3]: NanoForum, 2006

[4]: Hanus et al. 2013

[5]: The Constructor, n.d.

5.8 Examples of nanomaterial exposure from medical devices

5.8.1 Main findings

Identified literature focuses on content and release of nano-Ag in wound dressings. The literature also to some extend addresses toxic effects seen in human case studies. When the papers do not address measurements of releases or estimations of exposure, absorption/hazards observations have been briefly addressed here to implicitly indicate that there has been a release and exposure to nano-Ag. Absorption and toxicity of dermal nano-Ag-exposure will be further address in the hazard assessment part of this project.

The wound dressing contain approx. 100-200 mg Ag/gram product corresponding to about 0.7 to 1.5 mg Ag/cm^2 body area.

The release of nano-Ag was found to be very dependent on test media and highest in the beginning, as illustrated in Table 5-6 (unit: µg/(hour cm^2).

TABLE 5-6. THE TIME DEPENDANT RELEASTE OF NANO-AG FROM WOUND DRESSINGS AS ILLUSTRATED FOR THE WOUND DRESSING ACTICOAT (ADAPTED AFTER RIGO ET AL., 2012)

	Time after application	Release µg /(hour cm^2)
Ultrapure water	0-30 min	53
	30min -2 hours	10
	2 hours – 3 days	0.0001
Normal saline solution	0-30 min	0.40
	30min -2 hours	0.008
	2 hours – 3 days	0.0009
Human serum substitute	0-30 min	161
	30min -2 hours	2.6
	2 hours – 3 days	0.0006

External exposures using the models ConsExpo and ECETOC TRA have been estimated to about 0.025 mg Ag/kg bw/day.

Internal serum Ag levels of about 25-60 µg/L have been reported in patients, indicating a significant release from the wound dressings.

Generally, total Ag levels are reported without distinguishing between whether silver released from the dressing are in ionic or (nano-)particle form.

5.8.2 Specific data

The NANEX (2010) project conducted an exposure assessment using the ECETOC TRA and ConsExpo tools for consumer exposure to nano-Ag in wound dressings. "Manual calculations" were carried out as well. The exposure scenario was built predominately on information from a clinical study by Vlachou et al. (2007). The assessment was conducted using a "worst-case scenario" since treatment of burns requiring crafting was chosen. The scenario is related to a clinical survey, and it is mentioned in NANEX that it could serve as a "realistic case" as well. From a consumer exposure point of view though, the scenario will represent a "worst case".

The input parameters for the ConsExpo tool are shown in Table 5-7.

TABLE 5-7. INPUT PARAMETER VALUES USED IN THE CONSEXPO MODEL (TABLE ADOPTED FROM NANEX 2010)

General Exposure Data	Value	Based on
Body weight, adult	60 kg	ECETOC TRA
Exposed area, adult	1486 m^2	
Thickness of layer	0.01 cm	ECETOC TRA
Diffusion coefficient	4 E-6 cm^2/s	Fan F and Bard A.J, 2002
Time of exposure	3 day	Vlachou et al, 2007
Concentration of compound	100 mg/kg	Vlachou et al, 2007

For the ECETOC TRA modelling a product ingredient concentration of 0.1 mg Ag/g wound dressing was used, and a total exposed body area of 1 486 cm^2.

The exposure estimates using the three approaches (ConsExpo, ECETOC TRA and manual calculations) are shown in Table 5-8.

TABLE 5-8. DERMAL EXPOSURE ESTIMATION (TABLE ADOPTED FROM NANEX 2010)

	Manual calculation	Models ConsExpo 4.1	ConsExpo 4.1	ECETOC TRA
Population	Dermal load (mg/cm^2)	Dermal load (mg/cm^2)	Dermal external dose (mg/kg/day)	Dermal external dose (mg/kg/day)
Burn of 1486 cm^2	1 E-02	1 E-03	2.5 E-02	2.48 E-02

There is an order of magnitude difference between dermal loads from manual calculations and ConsExpo 4.1. This is probably due to the fact that the ConsExpo model has only taken into account the use of one wound dressing, whereas a total of 15 wound dressings (100 cm^2 each) were used in the manual calculation (NANEX, 2010).

Absorption of Ag as a consequence of application of wound dressings containing nanocrystalline Ag has been documented by several studies. In a study by Vlachou et al. (2007), (which as mentioned

also served as input to the exposure estimation in NANEX (2010)) the systemic silver concentrations following usage of a nanocrystaline Ag wound dressing (Acticoat™) was investigated. A significant increase in serum Ag levels after exposure to Acticoat products was found. The median maximum serum Ag level was 56.8 µg/L, and after 6 months, the median serum level was 0.8 µg/L. No measurement of nano Ag content in the wound dressings or release rates is reported.

In another study, a 17-year old boy was treated by Acticoat nanocrystalline Ag wound dressings on several burn wounds (30% mixed depth burns). Plasma and urine Ag levels were measured and found to be profoundly elevated (107 µg/kg and 28 µg/kg, respectively) (Trop et al., 2006). No measurements of Ag content in the Acticoat was conducted in the study, but it was claimed (presumably from the manufacturer) that the average Ag crystal size was 15 nm and that the Ag coating of the Acticoat consisted of 0.2-0.3 mg Ag per mg of high density polyethylene (Trop et al., 2006).

In a more recent study, Rigo et al. (2012) investigated the Ag concentration and release from four Ag-based dressings used for the treatment of burns, where one of the investigated wound dressing, Acticoat™ Flex 3 is coated with nanocrystalline Ag particles in a concentration claimed by the producer to be between 0.69 and 1.64 mg/cm^2. The release was assessed in three matrices: ultra-pure water, a physiological saline solution and human serum substitute. The total Ag concentration for the wound dressing was found to be in agreement with that declared (1.379 ±0.091 mg/cm^2). The duration of the experiment was three days, and the release rates outlined in Table 5-9 were obtained.

TABLE 5-9. THE TIME DEPENDANT RELEASTE OF NANO-AG FROM WOUND DRESSINGS AS ILLUSTRATED FOR THE WOUND DRESSING ACTICOAT (ADAPTED AFTER RIGO ET AL., 2012)

	Time after application	Release (µg /(h cm^2)
Ultrapure water	0-30 min	53
	30min -2 hours	10
	2 hours – 3 days	0.0001
Normal saline solution	0-30 min	0.40
	30min -2 hours	0.008
	2 hours – 3 days	0.0009
Human serum substitute	0-30 min	161
	30min -2 hours	2.6
	2 hours – 3 days	0.0006

The size of the Ag nanocrystals was also determined, and the particles were found to be in the range of 200-450 nm.

In another study by the same authors, determination of total Ag content in Acticoat™ Flex 3 was conducted using different methods/quantification strategies (Roman et al., 2013). The results are

shown in Table 5-10 and again the total Ag-content measured was corresponding to that declared by the producer. However, no information about particle size is reported.

TABLE 5-10. AG CONCENTRATIONS IN THE DRESSINGS (AS ILLUSTRATED WITH ACTOCOAT) AND INTRACLASS CORRELATION (ICC) AS DETERMINED BY THE DIFFERENT METHODS/QUANTIFICATION STRATEGIES. EXPECTED VALUES ARE THOSE REPORTED FROM THE PRODUCERS (TABLE ADAPTED FROM ROMAN ET AL., 2013). PLEASE REFER TO THE ORIGINAL PAPER FOR DETAILS ON THE ANALYTICAL METHODS APPLIED.

	w/w (mg/g)	W/surface (mg/cm²)	ICC
Expected	100 to 237	0.69 to 1.64	
Open system method EC	129 ± 9	0.890 ± 0.063	0.63
Open-system method IDA	119 ± 2	0.822 ± 0.016	0.99
MW digestion EC	119 ± 8	0.827 ± 0.058	0.95
MW digestion IDA	113 ± 14	0.785 ± 0.096	0.97

Furthermore, a pilot study was conducted with the aim of obtaining an estimate of the fraction of Ag released *in vivo* on the patient, which gives an estimation of patient dose. Used Acticoat dressings were collected from patients after 3 days of treatment. Different spot samples were collected from different areas of interest on the used wound dressing and the Ag content in these were investigated by means of an extraction method using TMAH (tetramethylammonium hydroxide). The Ag content in the residual dressing represented the fraction of Ag that was not released, and the Ag present in the TMAH solution can be assumed to have been released by the dressing. The difference between the total concentration of Ag in a new unused dressing and the sum of the two fractions of Ag (in the TMAH solution and the residual dressing) was considered as an estimate of the amount of Ag that was release from the wound dressing onto the patients. It was estimated that 30-60% of the silver was released. The authors furthermore investigated the content of Ag in skin biopsies taken after 7 days of exposure to the wound dressing and found a concentration of 1.4-1.8 µg Ag/cm². The authors noted "*These values accounts for no more than 0.5% of the level estimated here, as released by the dressing, suggesting that only a minor fraction of Ag accumulates in the skin*" (Roman et al., 2013).

It is not sure whether the different Acticoat products referred to are equal with respect to Ag content and nano Ag crystal size.

Quadros et al. (2013) addressed release of nano-Ag from surface wipes. Nazarenko et al. (2011) addressed content and release of nanomaterials from a regular and from a nano-Ag containing sprays. Results from these papers are summarised in Section 5.4.

5.9 Examples of nanomaterial exposure from air cleaners

5.9.1 Main findings

Air-cleaners are here considered either products that clean the air by removing the odours by treatment of specific surfaces/products or instruments that clean air by direct removal of odours and micro-organisms. The current scientific literature only reports exposure assessment where nano-Ag or Ag+ in water droplets may be released during use of either a humidifier or different types of anti-odour/disinfectant sprays. The potential for inhalational exposure is to be considered for these products.

5.9.2 Specific data

Benn et al. (2010) investigated the Ag concentrations in a number of consumer products and assessed the release and exposure levels from these. Two of the products were two different sizes of humidifiers. The water in the small tanks contained 60 µg Ag/g plastic. The aerosolized water in the small tank contained 1.1±0.4 µg Ag/L resulting in an aerosol emission rate of 0.11±0.04 µg/hour. The large tank had an Ag-concentration of 0.19 µg Ag/L and a release rate of 0.19 µg Ag/hour into the indoor environment. The nature of the aerosolised silver was not characterised.

Quadros and Marr (2011) studied the particle emission rate from two Ag-based air-cleaner products and assessed the potential exposure during use by modelling. The two products were an anti-odour spray for hunters and a surface disinfectant. The anti-odour hunters spray was based on Ag nanoparticles and water and was intended to be sprayed directly onto the body. The surface disinfectant was based on 0.003% electrolytically generated Ag+; citric acid (4.48%); and others (95.16%). The experiments were conducted in a fully mixed 0.52 m^3 polyethylene chamber and the released aerosols were measured using a CPC, a SMPS and an OPC (Optical Particle Counter). The amounts sprayed were chosen specifically to reach a constant concentration for each product, and to further maintain the concentrations for 30 min by periodic spraying.

Analysis showed that the hunters spray contained 12.5±1.8 ppm of Ag and the surface disinfectant contained 27.5±0.4 ppm of Ag. Spray tests with two different bottles of Hunter's anti-odour spray showed very different results: The first bottle produced a bimodal size-distribution with a 20 nm and a 500 nm-mode. The second bottle produced particles mainly coarser than 500 nm. The disinfectant spray produced particle sizes comparable to the particles generated by the first Hunter's odour-spray. By mass, most of the Ag particles were found in the µm-size in the tests of the Hunter's anti-odour spray. The silver particles in the disinfectant spray had a very wide and very low-concentration distribution.

A conservative assessment of the exposure levels showed that a person using the anti-odour hunters spray by spraying 20 times (1/sec.) in a 30 m^3 room with an air-exchange rate of 0.5 per hour would inhale 0.62 ng Ag the first 10 minutes. However, the anti-odour Hunter's spray is to be sprayed onto the body, and the actual exposure levels may be significantly higher.

Quadros et al. (2013) investigated the emission from two air humidifiers; a nano-technology based manual humidifier and one with a conventional silver accessory for the water tank, respectively. The use-situations were investigated in a 36 m^3 room, with carpets and furniture to simulate a bedroom, and test conditions at less than 25°C and 40%RH. ICP-MS analysis of 5 and 17 days old tank water resulted in 0.8 ppb Ag at 5 days, but not detectable concentrations in 17 days old tank water. Condensates (300 mL water of atomized over 90 minutes) generated by the tabletop humidifier with the conventional Ag accessory, contained 2.3±0.4 ppb of Ag (measured as total Ag and most probably related to dissolved Ag-ions), suggesting a very low exposure level during regular use. (This corresponds to total liberation into air of 0.69 µg Ag over 90 minutes). No silver was detected from in the reservoir from the nanotechnology based humidifier. Also the simulated use did not result in any detectable amounts of particles emitted.
Based on these, it was concluded that there seem to be a very low – if any - release potential for silver particles from the air humidifiers.

5.10 Examples of nanomaterial exposure from electronic devices, sports equipment and appliances (general use)

5.10.1 Main findings

Exposure to nanomaterials from this type of products are not generally addressed quantitatively in the literatures, except when such products are subject to sanding, grinding, etc., which will be addressed in Section 1.3.10.

A paper qualitatively discussing exposure to CNTs from composites materials generally conclude that the expected consumer exposure is low.

Section 5.7 discussed a paper on nanoclays used in polymer nanocomposites and a number of papers addressing paints and coatings, which might also be relevant for this product category.

Literature quantifying potentially relevant exposure to nanosilver from e.g. keyboards, refrigerators, touchscreens etc. has not been identified in the current study.

5.10.2 Specific data

Nowack et al. (2013) discusses release of CNTs from various life cycle steps of CNTs used in composites (from manufacturing of the products to final disposal). Of relevance for consumer exposure are CNT-composites in: i) sports equipment, ii) electronics, and iii) textiles addressed. The latter is addressed in Section 5.6. In relation to sports equipment the authors note that release of CNTs might occur due to chemical (sweat, saliva) or mechanically (breakage or maintenance/repair) or by weathering /UV light/water). However, the authors judge overall that such release during the consumer phase has a very low likelihood. Regarding electronics, it is noted that consumers might have extensive dermal contact with these devices (laptops, mobile phones etc.) which might contain CNTs as flame retardants (although marked penetration is currently low). This may lead to dermal exposure if CNT are chemically released (sweat). As it has been shown that polymer fragments are found in household dust, it is also speculated that there could be an inhalation exposure. No quantitative data are presented, but further research in this area is proposed.

5.11 Examples of release from wear, tear and mechanical reworking

The release of nanomaterials due to wear, tear and mechanical reworking occurs or may occur for a wide range of consumer products, and therefore this crosscutting issue is covered in this separate section. The release mechanisms range from passive release by nanomaterial diffusion, nanomaterial dissolution and matrix degradation during regular use, over accidental events such as damaging a material, to influencing the materials mechanically (e.g., polishing, sanding, drilling, cutting, sawing) and during demolition. The number of publications in this topic area is growing rapidly with highest focus on nanomaterial-based composites. Some examples have already been touched upon above, but this section addresses this general issue in more detail. First search words were: nano* AND sanding OR nano* AND cutting OR nano* AND polishing OR nano* AND drilling OR nano* AND sawing OR nano* AND demolition" using ISI web of knowledge. This search resulted in 10 947 hits and was refined by the terms occupational OR consumer giving 40 hits. Title and abstract screening reduced the number to 17 hits, which were reviewed considering their potential relevance for consumer use and exposure situations.

As general conclusion, tear, wear, and sanding can result in exposure to released nanomaterials or nanomaterials present at the surface or protruding the surface of debris particles. The area is also complex due to the many different types of nanomaterials used in the different types of nanocomposite materials. The likelihood of release strongly depends on the type of product as well as the type of nanomaterial and loading. Products consisting entirely of nanomaterials, such as

ceramic nanocomposites, have a high propensity to release nanomaterial during reworking such as grinding ceramic dental replacements. High-energy processes and long-term alteration by chemical or UV-exposure (with or without rain) are prone to facilitate release and exposure to nanomaterial. Freshly dried paint and lacquer generally show good retention of doped nanomaterial during sanding, but cases do exist where their release have been documented. Loosely bound coatings such as powder treatments of wooden surfaces release nanomaterials during even gentle mechanical stress. Nanocomposite polymers were found to be associated with low risk of release in normal consumer scenarios, but many matrix degradation processes may occur that can facilitate release. Despite the knowledge in this field has grown considerably regarding release characteristics and factors enabling release during the last 5-7 years, there is still an almost complete lack of data useful for quantitative exposure assessment.

Loosely bound particulate coatings

Hsu and Chein (2007) measured the release of nanoparticles from surfaces coated with nano-TiO_2 powder coating. When three different treated surfaces (wood, polymer and tile) was exposed to UV-light (sun), a fan (wind) and scraping motions (human contact), particles with diameters in the range of 8 to 127 nm were emitted at a rate from 5.5 and up to 280 particles per minute from a 10 cm^2 surface. The particle emissions were measured with SMPS and the largest emissions of nano-TiO_2 was found for coated tiles (22 particles/cm^3). UV light seems to increase emission and emissions were affected by the rubber knife scraping motion.

Paint, lacquers and nanofilm coatings

Kaiser et al. (2013) discusses the use or possibly upcoming use of nanomaterials in the paint and lacquer industry. Nanomaterial additives can be used as biocides (nano-Ag, nano-copper, nano-ZnO, photocatalytic nano-TiO_2), as UV-light absorber (nano-ZnO and nano-TiO_2), as pigment (nano-TiO_2) and as hardener (amorphous silica dioxide). Silica dioxide also protects the product against corrosion and provides the product with high gloss. The paper discusses yet unresolved challenges, such as long-term durability/efficiency tests; e.g. possible washout of nano biocides and the possibility that the photocatalytically activity of nano-TiO_2 besides its beneficial effects, possibly also degrade the paint matrix. The paper also discusses several toxicity aspects relevant for hazard evaluation and refers the NRWCE work on release from sanding (e.g. Koponen et al., 2011; Saber et al., 2012). The paper does not address product concentrations or exposure estimates.

Dashtizadeh et al. (2011) examines scratch resistance of ceramics, steel and glass coated with a range of silica-filled water-based acrylic nanocomposite emulsions/paints specifically prepared for the study. Emulsions with 0 – 12.4% (w/w) nanosilica were used in the experiments. Highest scratch resistance was found for emulsions with 6.2% (w/w). The paper does not address particle release nor assessment of exposure.

Koponen et al. (2011) studied the size-distributions and emission characteristics of sanding dust generated by manual sanding a series of different model paint and lacquer products. The experiments were conducted on hard-coat lacquer as well as PVA (polyvinyl acetate) and Acryl paints matrices that were agreed upon by the Danish paint and adhesives association. The test materials were nano- to pigment size according to the recommended EU-definition of a nanomaterial. The actual nanomaterial in the paints were a 95 nm-size carbon black (Flammrüss 101), 7 nm nanosilica sol, 17 nm rutile UV-Titan L181, <100 nm anatase W2730X, and kaolinite flakes (ASP90) reported as 200 nm size particles. In the lacquer the nanomaterial was a <50 nm nanosilica. The nano-paints/lacquers contained between 2.5 (Flammrüss 101) and 14.7 wt% (Asp90) nanomaterial. The study was conducted inside a human exposure chamber, where the dust collection chamber of a handheld orbital sander was mounted with a tube to extract all dust generated into a mixing chamber for subsequent collection on electrostatic filters. In all emission studies, the total released aerosol passing to the dust collection chamber in the sander was by number (usually strongly) dominated by sub-µm-size particles. Online monitoring data with a

FMPS and an APS, in most cases showed that the dust size-distributions were only affected to a minor degree. This suggests that the matrix and other paint fillers dominate the general emission during sanding. However, the concentrations of the dusts were affected in different ways: In the PVA group, addition of W2730X and RD3 caused significant increase in particle number (3-5 times) and also a coarser size of µm-size dust in paint with W2730X. For the acrylic group addition of UV-Titan L181 resulted in reduced particle concentrations of FMPS-size sanding dust particles, whereas addition of nanosilica sol increased the particle concentration in the FMPS size-range by 45 times. For lacquer, a reduction to 0.13 of the reference dust concentration was observed in the FMPS-range after addition of nanosilica.

Scanning electron microscopy analysis (follow-up publication by Saber et al., 2012) showed that most of the µm-size emission particles consisted of paint aggregates and large aggregates of paint filler material. For paints, the sub-µm-size fraction of the dust generally included paint composite, free pigment particles and minor amounts of released nanomaterial. Released nanomaterial was particularly evident in the PVA-paint added nano-kaolinite, whereas released nanomaterial was not immediately identified in the experiments with UV-lacquer, where the dust appeared to consist entirely of lacquer debris particles. However, for all emissions, a more detailed nano-scale characterization work by electron microscopy might improve our understanding of nanoscale particle release. This, however, is partially hampered by the dramatic loss of sampler collection efficiency of the electrostatic precipitator used for sample collection.

Göhler et al. (2010*)* investigated the emission potential of two different coatings in a semi-automated standardized test design, where a sanding was made at a fixed pressure load of $1{\cdot}10^4$ – $5{\cdot}10^4$ Pa using a rotating abrasion wheel mounted with grain size 600 sanding paper. Sanding dust was removed by an exhaust tube and measured using an FMPS, LAP (Laser Aerosol Size Spectrometer), and a CPC. The coatings were so-called two-pack polyurethane with and without ZnO nanoparticles and white-pigmented architectural coating with and without nanoparticles of ZnO (75% smaller than 100 nm) and Fe_2O_3 (25% smaller than 100 nm). FMPS analysis of the airborne particles showed modal sizes between 90 and 100 nm for the polyurethane coating irrespective of ZnO loading or not. The airborne particles from the architectural coating, however, varied with nanoparticle doping. Sanding of the Fe_2O_3-doped architectural coating produced a bimodal size-distribution with peaks at 30 and ca. 100 nm, whereas sanding of the ZnO-doped architectural coating released 10-30 nm- and 100-200 nm-size particles. Sanding of the nanoparticle free architectural coating produced 10-20 nm- and 100-200 nm-size particles. Modelled air concentrations during sanding an area of 13 cm^2 in a 30 m^3 room with no ventilation reached from about $6.2{\cdot}10^2$ (architectural coatings) to about $6.4{\cdot}10^4$ (polyurethanes) particles/cm^3. Compared to reference materials, addition of nanoparticles increased emission levels slightly. However, no free nanoparticles were observed in the dust as observed by TEM.

Epoxy and polymer nanocomposites

Methner et al. (2012) studied the release characteristics during wet-cutting, grinding and sanding of plastic composite materials containing carbon nanofibers (CNFs) in an occupational setting. The diameters of the CNFs range from 70 to 200 nm and lengths ranging from 50 to 200 µm. The plastic nanocomposites are usually used in the aerospace industry and as carbon nanomembrane composite materials. The consumers at risk of these exposures are therefore rare, but the principle findings may still be of relevance.

Filter samples were collected to determine the mass-concentrations of dust and elemental carbon, and for qualitative TEM (Transmission Electron Microscopy) analysis. Online measurements of airborne particle concentrations were made using a CPC and for size-distributions using a laser scattering equipment and a dust track used for estimation of dust mass-concentration. Most processes lasted no longer than 5 minutes. Consequently, the measurements were done using multiple repetitions of specific tasks.

Relevant for assessment of consumer exposure risk, the paper presents two cases 1) Wet-saw cutting with no local ventilation resulted in personal exposure levels of 1 934 particles/cm^3 and detection of free CNF by TEM; 2) Sanding of the CNF-doped composite which resulted in two cases with a relatively high concentration (160 to 3 090 µg/m^3) of dust in the 300 nm to 10 µm size particles in the ambient environment around the operator, but much lower concentrations in the breathing zone. Clear detection of CNF was made using TEM in both the breathing zone and ambient air samples.

Schlagenhauf et al. (2012) assessed the release of particles from epoxy-based nanocomposites during an abrasion process. Abrasion from three samples with 0, 0.1 and 1% (w/w) CNT were analysed. Particle size distributions for abrasion from the three samples were measured to release between 8 000 to 20 000 particles/cm3 (MSPS) and 1 000 to 3 000 particles/cm^3 (APS). Sizes were estimated to be 600 nm to 2 500 nm measured by APS. Images by TEM revealed that freestanding CNTs and agglomerates were emitted during abrasion.

Wohlleben et al. (2013) investigated the surface characteristics and release of CNT from thermoplastic polyurethane with and without 3 wt% CNT under normal use (Taber abrasion), machining (sanding) and outdoor weathering (UV-light). The Taber abraser test is an established method of the coatings industry to quantify wear resistance and is described in e.g. ISO 5470–1:1999. In this case, Taber abrasion was done using S-42 sandpaper at 1 kg load and a relative velocity of 0.294 m/s. Sanding was performed using P320 sanding paper on a fixed machine and rotating the sample below. The sanding pressure load was 0.25 kg and the relative velocity of the sanding was 6.5 m/sec. Both Taber and sanding experiments were conducted in a chamber (unspecified size?) with HEPA-filtered air. Weathering was conducted with and without simulating rain according to ISO standards using a commercial weathering apparatus. The accelerated weathering simulation corresponded to 9 and 18 months of outdoor exposure in sunlight (111 W/m^2) or mixed sun (60 W/m2; n x 102 min) and rain (n x 18 min) at 50° Northern latitude. Airborne particle size-distributions were measured online by SMPS (or CPC alone) and of-line using analytical ultracentrifuge and SEM. The results showed that particles were released from both the CNT-doped and pure polyurethane during Taber abrasion and sanding. During Taber abrasion testing, the increase in particle concentration in the chamber was very low (100 particles/cm^3), but a significant amount of coarser debris particles were generated. The airborne particles had a size-peak between 20 and 100 nm. During sanding the particle concentration in the chamber increased to 6 000 to 8 000 particles/cm^3 and bursts with up to 25 000 (CNT-doped polyurethane) and 40 000 particles/cm^3 (pure polyurethane) were observed. The bursts made it impossible to size the dusts with SMPS, but analytical ultracentrifugation analysis showed that some sanding dust particles were present in the size-range below 150 nm. A high amount of coarse debris particles was also generated. Analytical ultracentrifugation analysis showed that the dusts are dominated by 10-100 µm particles. Free CNT was not observed by SEM and not detected by XPS (X-ray photon spectroscopy). It was concluded, based on uncertainties and minimum detection limits, that at least 97 wt% of the CNT remains in the polyureathane.

Weathering causes matrix degradation, protruding CNT at the sample surface and finally a highly CNT-rich crust after 9 and 18 months weathering. The CNT concentration in the most weathered samples reached 72±3 wt% at the upper 10 nm surface.

Kingston et al. (2014) reviewed the literature on release characteristics of CNT polymer matrix nanocomposites based on 134 cited references. This rather extensive work lists some of the many commercial applications and potential future applications and the typical loadings (concentrations) of CNT in polymer technologies. They also review the release properties considering the mechanical and chemical nature of the different polymer matrices. They report based on market reports that the current commercial applications of CNT polymer nanocomposites are mainly within the

automotive, aerospace, defense, electronics, energy and sporting goods sectors. Of interest regarding exposure (and risk) assessment for consumers, they construct a provisional scheme that identifies the critical conditions for matrix degradation that enables CNT release from the different polymer types (Table 5-11). It is clear that UV-irradiation and chemical exposure are the parameters inducing greatest risk of CNT release. However, a combination between weathering and subsequent mechanical reworking (e.g. sanding) for renovation will increase the likelihood of CNT exposure considerably.

TABLE 5-11. FACTORS AND CHARACTERISTICS OF MWCNT-POLYMER SYSTEMS RELEVANT FOR ESTIMATING RELEASE POTENTIAL (MODIFIED FROM KINGSTON ET AL., 2014). THE LIGHT GRAY MARKED CELLS DESCRIBE THE RELATIVE RELEASE POTENTIAL OF CNT FROM THE MATRIX COMPOSITE. THE DARK GRAY CELLS INDICATE THE INCIDENT ALONG THE LIFE CYCLE ASSOCIATED WITH GREATEST RELEASE POTENTIAL.

	Epoxy	Polyamide	Polyurethane	Polyethylene	Polycarbonate
Mechanical Characteristics	Hard/brittle	Soft, ductile	Soft, ductile, elastomer	Soft, ductile	Hard, ductile**
Photodegradation	Rapid (CNT can stabilize)	Susceptible	Susceptible	Low	Susceptible
Oxidation	Susceptible	Susceptible	Susceptible	Susceptible	Susceptible
Hydrolysis	Susceptible	Susceptible	Susceptible	Low	Susceptible (accelerated at basic conditions
Thermolysis	Low	Low	Low	Low	Low
Mechanical degradation	Low	Low	Low	Low	Low
Lifecycle*	End of life processing	End of life processing	End of life processing	End of life processing	End of life processing
Overall release potential	Low	Low	Low	Low	Low

* Life cycle stages most relevant for degradation (Manufacturing is not considered).
** Ductility decreases with CNT loading.

Concrete

Wohlleben et al. (2011) studied the emission characteristics of particles released during mechanical reworking thermoplastic and cement materials doped with CNF (Carbon nanofiber) and CNT under both worker- and consumer-like operations. As polymer materials have been discussed above, this section only contains data on the cement. Two cement types were used in the study: A Dyckerhoff CEM I with and without a 2 wt% multiwalled CNT (Nanocyl NC7000) in the dry product and a hardening-accelerated cement (Bernburg 42,5R) with or without 4 wt% (in the wet mixture) nano-sized CSH (calcium silicate hydrate) nuclei. After curing and 1-2 weeks of hardening, the two nanomaterial-free reference and the two nanomaterial-doped products were subjected to abrasion during simulated normal use, “do-it-yourself sanding” and finally long-term weathering.

Release during normal use was tested by low mechanical stress using a Taber Abraser 352G mounted with Taber S-42 sandpaper onto the taper wheel. In the set-up, the taper wheel rolls over the test sample at a pressure load of 9.81 N to exert a low mechanical stress. The rolling taper and the sample rotates a relative speed of 0.294 m/s. Aerosols were collected through a suction cap at 50 L/min and simultaneous sizing of the released aerosol was done by SMPS.

Release during sanding was analyzed using sanding paper with P320 grain size mounted on a stamp (32 mm in diameter). The sanding was performed at a pressure load of 1 N and a relative velocity of 6.49 m/s between the stamp and the disk. The released particles where sampled at 50 L/min through a suction cap located only 1 cm above the stamp and collected on a membrane filter for further investigations. The concentration and size distribution of the aerosol were measured using a SMPS.

Dry weathering tests by UV-light were performed using a Suntest™ XLS+ standard apparatus. Samples were covered by a >90% UV-transparent borosilicate glass to prevent loss of any degradation products. The nanocomposites and reference testing plates were run equivalent to 9 months in Europe at approximately 50° northern latitude. The temperature did not exceed 45°C.

All dusts and surface crusts were analysed using a range of techniques, including SEM, analytical centrifuge, XPS, and SIMS.

The normal use and sanding release studies showed no liberation of the CNT and CSH nanomaterial during the mechanical stress tests. However, for the CNT-doped cement, dust particles did contain protruding CNT. The size-distribution of the released dust was heavily dominated by particles smaller than 100 nm electrical mobility size. Noteworthy, the authors revealed that these nanosized particles were dominated by Ti-, Fe- and Ca-rich particles also found in the sandpaper, which was concluded to be the source.

Metal- and Ceramic composites

Van Landyot et al. (2012) investigated the release and exposure characteristics during reshaping and finishing ceramic composite dental replacements. Based on the listed characteristics, 5 of the 6 tested ceramic composites contained nanomaterial according to the EC nanomaterial definition: 1) Filtek Supreme XT (20 nm nano-silica and zirconia-silica clusters with primary particle sizes of 5-20 nm), 2) Premise Enamel (20 nm nano-silica), 3) Ceram X duo+ (10 nm methacrylate functionalized nano-silica and 2-3 nm methacrylate-functionalized siloxane particles), 4) Herculite XRV Ultra (20-50 nm nano-silica, 5) Gradia Direct (16 nm pyrogenic silica, 10 nm to 3.5 μm zirconia silica). The last material (Tetric EvoCeram) contained 160 nm-size mixed oxides. Common for all the nano-based ceramics was a presence of NM in high percent range 12-85 wt% and in some cases the ceramics appeared fully based on nanomaterials in the form of hybrid composites. However, the material table in the paper is not always fully clear due to formatting issues and the concentration data in some cases needs to be confirmed.

The dust emission tests were conducted inside a 27 cm x 27 cm x 42 cm (readers revision of given data) Plexiglass box. Ca. 1 g (15 mm x 13 mm x 3 mm) composite blocks were fully grinded during the test using a rough diamond bur (100 μm grain size) mounted in a dental drilling tool operated at 200,000 rpm. Dusts were collected on PUF (5-10 μm dust) and glass-fibre (< 5 μm dust) filters using IOM personal inhalable samplers and subsequently characterized by TEM. Size-class resolved dust mass-concentrations PM_1, $PM_{2.5}$, PM_5, PM_{10} (0.5 to 10 μm) were assessed by online measurements using a laser scattering instrument (Aerocet-531 Mass Particle Counter) in a dentist work situation using a grinder comparable to the one used in the laboratory experiment on a Filtek Supreme XTE nano-composite.

The results showed that grinding of all composites resulted in significant amounts of respirable dust. TEM-analysis showed that the dust consisted of both composite fragments and free nanoparticles, which were part of the composites. The nanocomposite Filtek Supreme XT released the highest amount of sub-μm size dust and the hybrid composite Z100 MP released the lowest amounts. The percentage of nano-size dust was highest during reworking the micro-hybrid composite Gradia Direct (65% by number).

Results from personal exposure measurements in the dental clinique also showed exposure to (dry) grinding dust during mechanical reworking the dental ceramics in patients. The air concentration levels at the dentist were highly elevated in episodic bursts and far above indoor reference concentrations measured in a nearby office location. From light-scattering measurements, the maximum concentrations in PM_1 (mass of particulate matter smaller than 1 μm) exceeded 60 μg/m^3, whereas the total suspended dust at the same event reached ca. 10 mg/m^3. It is concluded that this type of exposure is significant and the dentist should use respiratory protection.
In the context of consumer exposure, the results also clearly suggest that consumer exposure occurs during placement and reworking/repairing ceramic teeth. Inhalation of even fine respirable nanoparticles or composite dusts is highly likely during finishing process. Additionally, oral debris particles may not be fully rinsed out by washing the mouth and enter the gastric system.

Other contributions to the area
Patal et al. (2006) discusses applications of nanoclays in various products. Clays used for production of nanoclays belong to the smectite (2:1 phyllosilicates) group of which montmorillonite and hectorite are the most commonly used. Clay is highly hydrophilic, so the organophilic/ hydrophobic nanoclays can be obtained simply by ion exchange. 3-6% nanoclay content improves the properties (e.g. tensile strengths) of polymer nanocomposites as compared with the corresponding polymer. Nanoclay can also be used as a rheological modifier in paints, inks, emulsions or pigment suspensions. 15% content is mentioned, but it is not entirely clear whether this is the content in additive to be used when formulating products or the product concentration. Enormous nanoclay market volumes of billions of pounds are mentioned in the paper. Exposure estimations are not addressed.

5.12 Overall findings from the examples

Below main findings from the product category examples are given:

Food and beverages
This category accounts for the *highest oral nanomaterial exposure*.
Nanomaterial exposure assessments have been made for food additives such as

- Silica (E551)
- TiO2 (E171)
- CaCO3 (E170)

Nanomaterial exposure up to 3 mg /kg bw day has been estimated, due to the content of nanosized particles in these additives. Up to 50 wt% of the additive has in some cases be considered to be in the nano-size range.

Oral exposure from food contact materials containing nano-Ag seems to be low, due to low degree of migration.

(Also some exposure to nanomaterials from food supplement may occur, as indicated in the tables in appendix 4 where supplements containing 10-500 ppm of .g. nano-Ag, nano-palladium, nano-platinium, and nano-zinc have been found).

Cosmetics
This category accounts for the *highest dermal nanomaterial exposure*. Highest exposure pertains to *leave-on products* such a body lotion and sunscreen where dermal exposure to nanomaterials for small children may exceed 100 mg/kg bw day of nano-TiO2.

Inhalation may be a further exposure route, especially for cosmetics formulated as gas propellant sprays, as they may generate respirable nano-aerosols which also in some cases may contain solid

nano-particles. Formulations in pump spray with e.g. nano-TiO_2 and nano-ZnO hardly generate any aerosols in the nano-size range (or even in the respirable size range below 5 μm).

Oral exposure may occur in connection with swallowing of toothpaste (e.g. nano-TiO_2) and in connection to oral exposure of lipsticks (e.g. nano-TiO_2 from sun-protection sticks).

Eye exposure may be relevant in connection with use of eye-cosmetic e.g. mascara, eye shadow, and eyeliners (e.g. carbon black up to 10% in some products).

Teenage girls and small children seems based on the exposure estimates that have been undertaken to may be the most heavily exposed groups to nanomaterials in cosmetic products.

Cleaning products

The identified literature indicates that nano-Ag is used in cleaning sprays, detergents, surface wipes and a cleaning scrubber. One paper addresses the use of nano-silica in a glass cleaner product. Some papers have identified the presence of non-declared nanomaterials in a number of cleaning sprays.

In most literature addressing sprays containing nano-Ag, the focus is set on characterisation of the aerosol and nanomaterial content rather than actual estimation of exposure.

One paper using ConsExpo for a glass cleaner spray product containing silica estimated a mean concentration of 0.002 mg silica/m^3 in the surrounding air of the consumer and a peak concentration of 0.035 mg/m^3 shortly after spraying.

See general findings regarding spraying further down.

One study finds low dermal nano-Ag exposure (e.g. from wipes).

Coating/ impregnation

Data on exposure was found for products containing nano-TiO_2, silane/siloxane, nano-ZnO. The examples ranged from applying impregnation on car windows using an impregnated cloth, over use of liquid sprays products for shoes or bathrooms, to the application of paints with roller and by spraying.

Dermal exposure to a liquid spray product (containing 0.1% of a nanomaterial) for bathroom surface treatment was estimated to be 2×10^{-2} mg/kg per use event. The inhalation exposure was estimated to be 1.9×10^3 mg/kg bw per use event.

Dermal exposure of 13.6 mg nano-TiO_2/kg bw was estimated for roller application of paint containing 25% nano-TiO_2 using the ConsExpo exposure model. Inhalation exposure was estimated to be 0.016 mg TiO_2/kg bw per event in case of spray application of the paint. The o*ral exposure* to non-respirable aerosols from spray painting was estimated to be 0.112 mg nano-TiO_2/kg bw per event.

When measuring *particle number and particle sizes* from use of impregnation sprays about 100 times higher concentrations of nano-sized aerosols were obtained from gas propellant sprays compared to pump sprays. Highest number concentration of nano-aerosols at about 10^8 particles/ cm^3 was reported for fluoro-silane/siloxane sprays.

Use of impregnation propellant sprays containing TiO_2 or ZnO resulted in particle number concentrations of 10^5 - 10^6 particles /cm^3 and a mass concentration of about 3.4 mg/m^3 (ZnO

particles were however only observed in sizes in the micrometer range). From the ZnO spray an inhalation exposure of *a total* of 6.4 x 10^{10} particles was estimated from use of 18.5 g of the spray.

Textiles

Data has been found for textiles containing either nano-Ag or nano-TiO2.
The primary exposure route is dermal exposure with highest exposure to nano-Ag due to highest migration/dissolution rate from the textile. Migration rates up to 45% have been used for nano-Ag in textiles, whereas a worst case migration rate for nano-TiO2 of 2-3% seems more realistic.
Highest dermal exposure of 4 mg Ag/kg bw day was calculated (using ConsExpo) for a child exposure from socks with a high Ag content (2.4 mg Ag/g), whereas an exposure of 12.7 µg Ag/kg bw day was calculated from a T-shirt based on specific migration data on Ag from the shirt.
Oral exposure of 0.042 µg Ag/kg bw day has been estimated based on Ag migration data from a cuddly toy animal. Oral exposure pertains to a small child sucking the toy.

Construction materials

Construction materials available for consumers comprise a wide group of products including e.g. cements (silica, nano-TiO2, CNT, unspecified metal oxides), nanocomposites (nanoclays and CNT), windows (silica, tungsten oxide), tiles (nano-TiO2), and protective surface coatings such as paints, lacquers, as well as antimicrobial and easy-to-clean nanofilm coatings (see also "coatings/ impregnation"). Coatings/paints may contain a range of nanomaterials such as nano-Ag, nano-copper, nano-ZnO and pohotocatalytic nano-TiO2 used as biocides, nano-ZnO and nano-TiO2 as UV-light absorber, nano-TiO2 as pigment and nanoclays as rheological modifier.

Except for coatings/paintings addressed elsewhere, no examples on use-related release and exposure during consumer use of construction materials have been identified.

Medical Devices

Identified literature focuses on content and release of nano-Ag in wound dressings. The literature also addresses toxic effects seen in human case studies indicating release, exposure, uptake and toxicity of silver contained in the wound dressing. Absorption and toxicity of dermal nano-Ag exposure will be further addressed in the hazard assessment part of this project.

The wound dressing contain approx. 100-200 mg Ag/g product corresponding to about 0.7 to 1.5 mg Ag/cm^2 body area. External exposures using the models ConsExpo and ECETOC TRA have been estimated to about 0.025 mg Ag/kg bw/day. Internal serum Ag levels of about 25-60 µg/L have been reported in patients, indicating a significant release from the wound dressing.
Generally, total Ag levels are reported without distinguishing between whether silver released from the dressing are in ionic or (nano-)particle form.

Air Cleaners

In this analysis, air-cleaners are considered products that either clean the air by removing the odours by treatment of specific surfaces/products or instruments that clean air by direct removal of odours and microorganisms. Air-cleaners using the aerosol route is associated with potential risk of inhalation exposure. However, the experimental studies showed that Ag (either nano-Ag or Ag+) is released at very low concentrations during use of either a humidifier or different types of anti-odour/disinfectant sprays. However, the potential for inhalational exposure is to be considered for these products. The highest direct inhalation exposure estimate published for nano-Ag, is 0.62 ng Ag the first 10 minutes using an anti-odour spray.

Electronic devices, sports equipment and appliances for general use

Exposure to nanomaterials from this type of products are not generally addressed quantitatively in the literatures, except when such products are subject to sanding, grinding etc. summarised in the following section.

The composite materials in products maycontain e.g. carbon nanotubes (CNT), nanoclays or nanosilver (the latter as antibacterial agent in e.g. keyboards and refrigerators).

Wear/tear/mechanical reworking

Wear, tear and mechanical reworking can all result in inhalation exposure to released free nanomaterials or nanomaterials present at the surface or protruding the surface of debris particles. Less important exposure routes are dermal, oral and the eye. The likelihood of nanomaterial release strongly depends on the type of product as well as the type of nanomaterial and concentration in the products. Products consisting entirely of nanomaterials, such as ceramic nano-composites, have a high propensity to release nanomaterials during reworking such as grinding ceramic dental replacements. High-energy processes and long-term alteration by chemical or UV-exposure (with or without rain) are prone to facilitate release and exposure to nanomaterials. Freshly dried paint and lacquer generally show good retention of added nanomaterials during sanding, but cases do exist where their release have been documented. Loosely bound coatings, such as powder-treated wooden surfaces, release nanomaterials during even gentle mechanical stress. Polymer matrix nanocomposites were found to be associated with low risk of release in normal consumer scenarios, but different matrix degradation processes may occur that can facilitate release. For the above-mentioned type of release there is still an almost complete lack of data useful for quantitative exposure assessment.

Spraying

Spraying and inhalational exposure to micro- and nanosized aerosols is a general and cross-cutting issue relevant for nearly all type of products categories: cosmetics (nano-TiO2, nano-Ag, Ag'+), air-cleaning (Ag+, nano-Ag), cleaning (nano-silica, nano-Ag, Ag+, unknown), coating/impregnation and maintenance products (nano-silica, silane, siloxane, nano-TiO2, nano-ZnO, nano-Ag, Ag+, mixtures, and unspecified), construction materials (paints with nanosize pigments and various nanomaterials, easy to clean products, surface protection products), and air-cleaners (nano-Ag, Ag+).

Spraying is per default associated with risk of inhalation exposure being a process where the content of a container is dispersed in the air directed towards a target area. Dermal and oral exposure may also occur. It is observed that nanoproducts as well as the non-nanoproducts may generate aerosols with sizes in the nanometer range. As a rule of thumb, spraying using a pressurized (propellant) spray or highly volatile matrices such, as alcohol-based pump-sprays, result in very small droplets increasing the potential for direct release/ generation of nano-objects/ nanosize particles. Solutions with water-based and high-viscosity matrices (e.g. emulsions and oil) are less likely to result in generation of nano-aerosols or release of free nano-objects. However, it must be concluded that spraying results in dispersion of freely accessible nanomaterial in a liquid matrix, which is within the inhalable and often to a great extent within the respirable fraction. Assessments of mass-based exposure or dose levels indicate 1.9×10^{-3} and up to more than 100×10^{-3} mg/kg bw, with the highest value reported for a coating/impregnation and maintenance products. The actual exposure levels are very dependent on the exposure scenario and in particular the context of the scenario.

6. Selection of exposure scenarios for further exposure and risk assessment

6.1 Selection of consumer products as examples of representative consumer exposure scenarios

For getting a compiled overview of the product information collected in Chapters 2 and 4, a working table (see Appendix 7 in appendix report) was made. The table contains the relevant nanomaterials and matrices for the various product types in the various product categories (Column 1-4) as identified in previous chapters and with some input from the hazard assessment activities of the project (WP3). From this overview, specific products with specific nanomaterials was selected (marked in yellow) based on a series of selection criteria. Columns 5-9 in the table in Appendix 7 were used for specific information regarding documentation and specific information to consider further in the risk assessment.

Based on that table, the project team made a draft for Table 6-1 where 20 exposure scenarios representing various nano-products were selected as examples of representative consumer exposure scenarios.

The selection of the scenarios/products in Table 6-1 was made using the criteria below which have been agreed with the Danish EPA:

-Coverage of the various product categories and type of use
-Coverage of various formulations and matrices of the products/ articles
-Coverage of various type of use/ application methods
-Coverage of low as well as high quantitative use of the product
-Coverage of high/ low/ uncertain exposure potential
-Coverage of specific user or target group populations
-Coverage of all relevant exposure routes (dermal, oral, inhalation and eye)
-Coverage of uses of nanomaterials that may be of toxicological concern
-Coverage of most used nanomaterials

The draft table was during a workshop meeting discussed together with the reference group in order to include comments and ideas from the reference group members. Table 6-1 can be seen as the outcome of this process. It was during the workshop emphasised by the external expert that although each of the 20 scenarios may be representative for similar products/scenarios, the total of 20 scenarios could far from be said to be representative for the overall consumer exposure to nanomaterials. On the other hand, the scenarios chosen could be seen as representing possible high exposure/risk scenarios (and some low exposure/risk scenarios) given the current knowledge about nanomaterials in consumer products.

TABLE 6-1. SELECTION OF REPRESENTATIVE CONSUMER NANO-PRODUCTS FOR FURTHER RISK ASSESSMENT

No.	Product, Volume use/ application	NM	Matrix/	Prod. Vol. per use	Conc .	Duration			Frequency	User/Target group*			Exp. Route£				Potential exposure to free/ liberated NMs$			Exposure and Toxicological considerations
						mins	hours	days		c	y	a	O	D	I	E	L	M	H	
Food & Beverages																				
1	**Chewing Gum,** 20-50 g chewing	TiO2 E171	Elastomer/	1-10g, >10 g	No max limit in food	x	x		daily	**X**	x	x	**X**						x	High exposure of children? absorption/ effects? Liberation of nanomaterial from an elastomer
2	**Food items** ingestion	Silica E551	Various food matrices	>100g	< 10 g/kg in food items	x	x		daily	**X**	x	**X**	**X**						x	High dietary exposure from food additive; absorption/ effects?
3	**Food supplement, 15 ml** ingestion	Ag	Liquid	<1g	0.05%	x	x		daily			**X**	**X**						x	Direct oral exposure of nano-Ag of tox concern?
4	**Food container** **food contact**	Silica	Imbedded in polymer	-	<1%	x			daily	**X**	x	x	**X**				x			Migration of nanomaterial embedded in polymer
Cosmetics																				
5	**Sun Screen,** 100-500g dermal appl.	TiO2	Liquid	> 10 g	<25%		x	x	daily	**X**	x	x	x	**X**					x	Very high dermal expsosure of children. Absorption?
6	**Sun Screen,** 50-200g	ZnO	Liquid/ spray	>10 g	<25%		x	x	daily	**X**	x	x	x	**X**	**X**				x	Inhalation, ZnO tox.by inhal ?

No.	Product, Volume use/ application	NM	Matrix/	Prod. Vol. per use	Conc .	Duration			Frequency	User/Target group*			Exp. Route£				Potential exposure to free/ liberated NMs$			Exposure and Toxicological considerations
						mins	hours	days		c	y	a	O	D	I	E	L	M	H	
	Spray appl.																			
7	**Mascara,** 2-20 g brush appl.	CB	Paste	<1g	<10%		x	x	daily		**X**	x		**X**		**X**			x	Eye exposure/tox?
8	**Lipstick, sunscreen**	TiO2	Semisolid paste	<1	<25%	X	x		daily	**X**	x	x	**X**	**X**					x	Ingestion/absorption/ effects?
9	**Face powder,** 5-20g brush or pad Appl.	SiO2	Powder	< 1 g	No max limit	x	x		daily		**X**	x	x	**X**	**X**				x	effects (inhalation)

* c = children; y = young people; a = adult; £ O = oral; D = Dermal, I = Inhalation; E = Eye; $ C = children

No.	Product, Volume use/ application	NM	Matrix	Vol. per use	Conc .	Duration			Frequency	User/Target group*			Exp. Route£				Potential exposure to free/ liberated NMs$			Toxicological considerations
						mins	hours	days		c	y	a	O	D	I	E	L	M	H	
Surface treatment / coating																				
10a	**Paint 5 L** roller appl.	TiO_2	Viscous liquid	5L	<25%		x		monthly/ yearly		x	**X**		**X**		x			x	Very high dermal exposure
10b	**Paint sanding**	TiO_2	Solid surface layer	Several m^2	<25%		x				x	**X**	x	**X**	**X**	x			x	Potential Inhalation of nanomaterial from dust
11	**Paint 10L** Spray appl.	Ag	Viscous liquid	10L	<<1%		x		Monthly/ yearly		x	**X**		**X**	**X**	x			x	Exposure by all exposure routes, different type of tox. Concern?
12	**Easy to clean surface impregna-tion, 1L** propellant spray application	Silica	Liquid	Appr. 100 ml	<1%,	x			Monthly/ yearly			**X**		**X**	**X**	x			x	Pulmonary toxicity?
Air cleaners																				
13	**Nano-filtering system**	Ag	Embedded in solid matrix	-			x	x	daily	**X**	**X**	**X**			**X**				x	Contineus airborne exposure to Ag indoors

No.	Product, Volume use/ application	NM	Matrix	Vol. per use	Conc .	Duration			Frequency	User/Target group*			Exp. Route£				Potential exposure to free/ liberated NMs$			Toxicological considerations
						mins	hours	days		c	y	a	O	D	I	E	L	M	H	
	air filtration																			
Cleaning agents																				
14	**Disinfectant Pump sprays** 100-500ml spraying	Ag	Liquid	One spray shot about 2 g Total > 10g	<1%	x			weekly/monthly	x	x	**X**		**X**	**X**	x			x	Exposure from pump spray; Inhalation-toxicity?
15	**Disinfectant Propellant sprays** 500ml spraying	-Ag	Liquid	One spray shot about 2 g Total > 10g	<1%	x			weekly/monthly	x	x	**X**	x	**X**	**X**	**X**			x	Exposure from propellant spray; Inhalation-toxicity?
Textiles																				
16	**Piece of textile, e.g. t-shirt 100-200 g**	Ag	Solid matrix	NA	<1%		x	x	Daily	**X**	x	x	x	**X**	x				x	
Construction materials																				

No.	Product, Volume use/ application	NM	Matrix	Vol. per use	Conc .	Duration			Frequency	User/Target group*			Exp. Route£				Potential exposure to free/ liberated NMs$			Toxicological considerations
						mins	hours	days		c	y	a	O	D	I	E	L	M	H	
17	**Cement/concrete TioCem** pouring/ mixing/	TiO2	Powder -> Paste	> 10 kg	1-10%	x	x		Monthly/ yearly			**X**		**X**	**X**	x		x	x	Inhalation/ absorption?/ pulmonary tox?
Medical devices																				
18	**Wound dressing** dermal appl.	Ag	Textile like matrix	Up to large fraction of body	0.1%-20%		x	x	daily for periods	**X**	x	x		**X**					x	aborption/ effects from exposure to damaged skin?
19	**Dental fillings** dental appl. 1) applied with "spatula"; 2) subsequent sanding/polishing; 3) stay in mouth for years	zirconia	Paste	grams?	12-85%	1, 2		3	Monthly/ yearly	x	x	**X**	**1 2 3**		**2**	2		1 2 3		

No.	Product, Volume use/ application	NM	Matrix	Vol. per use	Conc .	Duration			Frequency	User/Target group*			Exp. Route£				Potential exposure to free/ liberated NMs$			Toxicological considerations
						mins	hours	days		c	y	a	O	D	I	E	L	M	H	
Composite																				
20	**Golf club containing CNT** **1) wear** **2) sanding, cutting**	CNT	Solid	-	<1%	2	1		Daily (1) Yearly (2)			**X**		**1** **2**	**2**		1	2		Inhalation of CNTs, tox?

* c = children; y = young people; a = adult; £ O = oral; D = Dermal, I = Inhalation; E = Eye; $ L = low; M = medium; H = high

X : considered most relevant as primary target group/ exposure route

x : relevant target group and exposure route as well

6.2 Criteria for selection

Below an analysis is given concerning how far the criteria for the selection have been met:

Coverage of the various product categories and type of use

Food, beverages and food contact materials (4 product scenarios)
Cosmetics (5 product scenarios)
Surface treatment, coating, cleaning, maintenance car/boats (5 product scenarios)
Textiles (1 product scenario)
Construction materials (1 product scenario)
Medical devices (2 product scenarios)
Air cleaners (1 product scenario)
Composites (1 scenario)

Consequently, no products from the product categories *fuel and oil additives electronic devices*, and *appliances* were selected. For nanomaterials used in electronic devices and appliances there seems in general to be a low potential for exposure which make these products less relevant for risk assessment. For fuel and oil additives only few products with rather specific uses (i.e. only used by few consumers) have been identified.

Coverage of various formulations and matrices of the products/ articles

The matrices cover elastomers (solids), polymers/ composites (solids), food matrices, liquids, paste, sprays, powder and textile fibres. The majority of scenarios address matrices from which high exposure could be expected; i.e. less focus on solid matrices.

Coverage of various types of use/ application methods

The selected products cover exposure scenarios with direct oral intake (food), direct and indirect dermal application (e.g. cosmetics or impregnation/coating products), as well as eye and inhalation exposure (not the least from spraying and sanding). Also, indirect exposure from nanomaterials in polymer matrices is covered. Various use/application methods are covered, including spraying, cleaning, rolling/brushing (paint), sanding, etc.

Coverage of low as well as high quantitative use of the product

The selection of the products reflects low volumes (below 1 g use of a product) with low concentrations e.g. in some food supplements (few ppm) and cosmetics to high volumes (using more than 100 g and up to several kilograms of the product) containing high concentrations (up to 25%) in surface coating (paints) and cosmetics (e.g. sunscreens).

Coverage of high/ low/ uncertain exposure potential

As indicated in the three last items above variations for the products in relation to volume used, matrix effect and application method will also lead to high variability of the exposure potential for the products.

Coverage of specific user or target group populations

Children:	9 products as primary target group (3 products as exposed as well)
Youngsters/teenagers:	3 products as primary target groups (14 products as exposed as well)
Adults:	12 as primary target group (9 products as exposed as well)

Coverage of all relevant exposure routes

From the product chosen the following distribution on the exposure routes can be found:

Dermal:	14 products as primary route (0 as secondary)

Oral:	6 products as primary route (6 products as secondary)
Inhalation:	11 scenarios as primary route (1 product as secondary)
Eyes:	2 scenarios as primary route (7 products as secondary)

Coverage of uses of nanomaterials that may be of toxicological concern

Although the highest exposure to nanomaterials may occur from food and cosmetics, the regulation associated to these sectors limit the toxicological concern for these product categories. However, for unintended and indirect exposure from the other product categories especially the inhalation exposure is considered of specific concern as dermal exposure is considered of less concern due to the high protection from the skin barrier. Thus, specific toxicological data may indicate concern for inhalational exposure to e.g. CNT, nano-TiO2, nano-ZnO and nano-silica.

Coverage of nanomaterials

Within the scope of the project, it has been foreseen to address eight NMs. Our proposals for choice of scenarios address the following eight nanomaterials.

TiO2:	6 products from 4 product categories
Ag:	7 products from 6 product categories
ZnO:	1 product from 1 product category
Carbon black:	1 product from 1 product category
Silica:	4 products from 3 product categories
Zirconium:	1 product from 1 product category
CNT:	1 product from 1 product category

The choice of these nanomaterials (except zirconium, included for other reasons) represents nanomaterials with either high tonnage levels or wide dispersive use leading to high potential for consumer exposure.
Other nanomaterials such as fullerenes, nanoclay; nano-gold; nano-plantinium; nano-palladium; nano-copper; nano-aluminium oxide; nano-siloxane; nano-polymer particles; nano-CeO2 have not been included as generally only few consumer products have been claimed to contain these nanomaterials. Nano-clays are also used in high volumes in polymers from which low release is expected and as rheological agents in e.g. paints. The term “nano-polymer” or related unspecific terms have been used in the databases and in literature but often without further precise definition and thus risk assessment of these types of nanomaterials would require further categorisation.

Further, we found many products with "unknown" identity of the nanomaterial. It cannot be ruled out that some of these nanomaterials may have specific toxicological properties. However, it is generally assumed that those nanomaterials actually identified in the project cover a wide range of inherent toxicity.

Overall

Off course the choice of 20 scenarios cannot give an overall and exhaustive view on consumer exposure to nanomaterials. Nevertheless, it is found that the 20 selected scenarios covering the various nanomaterials, products and exposure scenarios altogether represent relevant scenarios of today giving an indication of the diversity of the nanomaterial exposure potential from consumer products.

7. Consumer exposure to nanomaterials - exposure assessment of selected scenarios

This chapter further describes and attempts to assess consumer exposures associated with the exposure scenarios identified in Chapter 6.

7.1 Estimation of nanomaterial exposure

Given the findings in Chapter 3 and 4 in relation to applicability of existing models and given discussion with the reference group, it was concluded that no existing model could accommodate the variation in types of nanoproducts, exposure scenarios, matrices and exposure routes. Further, it was not the aim to develop new models in this project, but rather to assess the exposure potential with existing methodologies.

Thus, it was decided to perform a *case-by-case assessment* for each scenario based on existing information and expert knowledge, including a careful description of uncertainties.

Based on the conclusions in Chapter 4 with regards to the most relevant exposure parameters (see Table 4-15), an overall template for collection and presentation of relevant exposure parameters and data, and for performing the exposure assessment for the various scenarios was made (see Appendix 8). The evaluation of the applicability of the various exposure tools indicated in Table 4-16 was used in order to quickly identify potential tools as relevant for the specific cases.

Table 7-1 below presents the overall results from the exposure assessments made for the 20 scenarios. The exposure estimations are given for the target groups considered most relevant (or for which most specific data have been found) and for each exposure route. The results are given in the following units:

- mg *NM/cm²* (dermal load),
- *mg NM/*m³ (inhalation),
- *mg NM/person/ day* (dermal, oral, inhalation exposure) (indicated as mg/day),
- *mg NM/ kg bw/day* (dermal, oral, inhalation exposure) as appropriate (indicated as mg/kg/day).

In specific cases where data was available also exposure estimates in particle number concentrations are given.

The specific data, algorithms and methods for deriving to the exposure estimates can be found in the filled-out templates in Appendix 8, along with a discussion of the derived values.

TABLE- 7-1. NANOMATERIAL EXPOSURE ESTIMATES FOR 20 EXAMPLES OF REPRESENTATIVE CONSUMER EXPOSURE SCENARIOS COVERING VARIOUS PRODUCT CATEGORIES

FOOD & BEVERAGES								
No.	**Product**	**NM**	**Exp. Scenario (application/use) (product volume used) (NM concentration in product)**	**Target group**	**Nanomaterial Exposure***			
					Oral	**Dermal**	**Inhalation**	**Eye**
1.	Chewing Gum	TiO2 (Food grade E171 and estimated nano-part of E171)	Chewing	Children Adults	150 mg E171 and 30 mg nanoTiO2/day 8.1 mg E171 and 1.62 mg nanoTiO2/kg/day 150 mg E171 and 30 mg nanoTiO2/day 2.5 mg E171 and 0.50 mg nanoTiO2/kg/day	NCR	NCR	NCR
2.	Various food items	Silica (nano-part of E551)	Cumulative ingestion from use of E171 in various food items	Adults	124 mg/day 1.8 mg/kg/day	NCR	NCR	NCR
3.	Food supplement, liquid	Ag	Ingestion of colloid Ag from food supplement product 2.5 ml liquid containing 0.5 mg Ag/ml	Adults	1.2 mg/day 0.021 mg/kg/day	NCR	NCR	NCR

4.	Food container	Silica	Ingestion via food due to migration from container	All	≈ 0	≈ 0	≈ 0	≈ 0
COSMETICS								
No.	**Product**	**NM**	**Exp. scenario (application/use) (product volume used) (NM concentration in product)**	**Target group**	**Nanomaterial Exposure**			
					Oral	**Dermal**	**Inhalation**	**Eye**
5	Sun screen Lotion	TiO_2	Dermal: 36 g/day for Denmark and 72 g/day South of Denmark Lips: 2 to 6 applications per day 25% nanoTiO_2	Adults Children (4.5 years)	Licking on fingers + 6 lip appl. 5.5 mg/kg/day 2 and 6 lip applications: 0.24 mg/kg/day and 0.72 mg/kg/day	DK: 0.26 mg/cm² 150 mg/kg/day South of DK: 0.51 mg/cm² 300 mg/kg/day DK: 0.26 mg/cm² 223mg/kg/day South of DK: 0.51 mg/cm² 447mg/kg/day	NCR	Possible but less relevant and no data
6	Sun screen – pump spray	ZnO	Same amount as in Scenario 5 25% nanoZnO		As above scenario	As above scenario	No data, but qualitatively assessed that exposure is likely low. However, more information needed.	Possible but less relevant and no data
7	Mascara	Carbon Black	2 applications per day 12.5 mg/applications 10% Carbon Black (worst case)	Children Teenagers	NCR	0.8 mg/cm² 0.13 mg/kg/day 0.8 mg/cm2 0.044 mg/kg/day	NCR	0.5 mg/day 0.5 mg/day

				Adults		0.8 mg/cm² 0.042 mg/kg/day		0.5 mg/day
8	Lipstick sun screen	TiO_2	2-6 applications per day 28.5 mg/application 25% nanoTiO_2	Children Adults	2 and 6 lip applications: 0.88 mg/kg/day and 2.6 mg/kg/day 2 and 6 lip applications: 0.24 mg/kg/day and 0.72 mg/kg/day	1.48 mg/cm2 2 appl.: 3.5 mg/kg/day 6 appl.: 10.5 mg/kg/day 1.48 mg/cm² 2 appl.: 0.9 mg/kg/day 6 appl.: 2.7 mg/kg/day	NCR	NCR
9.	Face powder	Silica	Application in face using brush 0.51 g powder containing 100 mg nano-silica/g (10%)	Teenagers	0.43 mg/day 0.008 mg/kg/day	0.09 mg/cm² 51 mg/day 0.90 mg/kg/day	0.26 mg/m3 0.051 mg/day 0.0009 mg/kg/day 10,000 particles (20 nm)/cm³ 2 x 10⁹ particles (20 nm)/day	0.00009 mg/cm2 0.006 mg/day 0.00001 mg/kg/day

SURFACE TREATMENT/COATING

No.	Product	NM	Exp. scenario (application/use) (product volume used) (NM concentration in product)	Target group	Nanomaterial Exposure			
					Oral	Dermal	Inhalation	Eye
10a	Paint	TiO_2	Roller application 25% nanoTiO_2	Teenagers Adults	NCR	1.34 mg/cm² 4.3 mg/kg/day 0.98 mg/cm² 3.1 mg/kg/day	NCR	Possible/likely, but no data
10b	Paint	TiO_2	Sanding primer paint 100% nanoTiO2 layer	 Teenagers Adult females	Possible, but not assessed	3.9 mg/cm² 24.72 mg/kg/day 28.9 mg/kg/day	18 mg/m³ 0.238 mg/kg/day 0.247 mg/kg/day	Possible, but not assessed

				Adult males		29.8 mg/kg/day all doses = Yearly dose	0.216 mg/kg/day all doses = Yearly dose	
11	Paint	Ag	Spray painting surface with a nano-Ag paint The dermal dose is contact dose. Overspray dose is also assessed, but gives notably lower doses (0.017 to 0.056 mg/kg/d). The airborne concentration and inhaled dose is estimated using the model for overspray and results in very high exposure estimates because all overspray is considered	Teenagers Adult females Adult males	Possible, but not assessed	0.12 mg/cm^2 0.67 mg/kg/day 0.87 mg/kg/day 0.92 mg/kg/day all doses = 1 day every 5 years	109 mg /m^3 1.19 mg/kg/day 1.53 mg/kg/day 1.31 mg/kg/day all doses = 1 day every 5 years	Possible, but not assessed
12	Surface coating product, Propellant spray	silica assumed, but the group may contain silane or siloxane	Surface impregnation product with stated silica content (however silane/siloxane seems more probalble). The treatment is performed twice on the same day to complete impregnation. (2 x 2.5 mL is used) silica content 1 wt%.	Teenagers Adult females Adult males	Possible, but not assessed	0.01 mg/cm^2 0.056 mg/kg/day 0.080 mg/kg/day 0.076 mg/kg/day all doses = 1 day per year	0.0021 mg/m^3 0.000046 mg/kg/day 0.00006 mg/kg/day 0.00005 mg/kg/day all doses = 1 per years	Possible, but not assessed

AIR CLEANERS

No.	**Product**	**NM**	**Exp.scenario (application/use) (product volume used) (NM concentration in product)**	**Target group**	**Nanomaterial Exposure**			
					Oral	**Dermal**	**Inhalation**	**Eye**

13	Nano-air purifier	Ag	Filtering of air in a room	All	≈ 0	≈ 0	≈ 0	≈ 0
14	Disinfectant pump spray with Nano-Ag	Ag	Spraying an article or surface with a pump spray. 100 ml of product with 1 wt% nano-Ag is sprayed onto 4 m^2 surface during cleaning. The listed values are the daily dose, which is also weekly dose. The exposure is repeated weekly and the annual dose is therefore 52 times higher.	 Teenagers Adult females Adult males	Possible, but not assessed	0.0025 mg/cm^2 0.15 mg/kg/day 0.19 mg/kg/day 0.20 mg/kg/day doses repeated 52 times/year	3.4 – 6 x10^3 particles/cm^3 0.0043 mg/m^3 0.000015 mg/kg/day 0.00002 mg/kg/day 0.000017 mg/kg/day doses repeated 52 times/year	Possible, but not assessed
15	Dis-infectant multipur-pose sanitizer with Nano-Ag Propellant spray	Ag	Spraying a 4 m^2 textile with pressurized spray can. 100 mL product with 1 wt% nano-Ag is applied in 1 minute. No assessment for inhalation due to lack of data. Direct dermal contact with surface of inner hand.	 Teenagers Adult cfemales Adult males	Possible, but not assessed	0.0025 µg/cm^2 0.015 mg/kg 0.019 mg/kg 0.020 mg/kg Once a year, doses per event	Yes, but not assessed due to lack of emission and exposure data	Possible, but not assessed

TEXTILES

No.	**Product**	**NM**	**Exp.scenario (application/use) (product volume used) (NM concentration in product)**	**Target group**	**Nanomaterial Exposure**			
					Oral	**Dermal**	**Inhalation**	**Eye**
16	T-shirt	Ag	Exposure due to migration of Ag from textile into sweat. 1 hour	Adult females	NCR	0.036 µg/cm^2 0.25 mg/day	NCR	NCR

			soaked T-Shirt. 64-89 g T-shirt 183 µg Ag/g textile Sucking 100 cm² T-shirt	 Adult males Children	 NCR 0.0083 mg/day 0.00045 mg/kg/day	0.004 mg/kg/day 0.071 µg/cm² 0.70 mg/day 0.009 mg/kg/day MD Considered below adult values	 NCR MD	 NCR MD
CONSTRUCTION MATERIALS								
No.	**Product**	**NM**	**Exp.scenario (application/use) (product volume used) (NM concentration in product)**	**Target group**	**Nanomaterial Exposure**			
					Oral	**Dermal**	**Inhalation**	**Eye**
17	Cement	TiO_2	Repairing own house/driveway > 10 kg/day 5% nanoTiO_2	Adults	NCR	Arms/hands: 36.6 mg/kg/day Whole body: 179 mg/kg/day	Handling: 0.25 mg/m³ 0.042 mg/kg/day Grinding: 0.75 mg/m³ 0.13 mg/kg/day	Possible but no data to quantify
MEDICAL DEVICES								
No.	**Product**	**NM**	**Exp.scenario (application/use) (product volume used) (NM concentration in product)**	**Target group**	**Nanomaterial Exposure**			
					Oral	**Dermal**	**Inhalation**	**Eye**
18	Wound dressing	Ag	Dermal application of wound dressing Migration from dressing	Children	NCR	0.98 mg/cm² 118 mg/day 9.08 mg/kg/day	NCR	NCR
19	Dental replacement with nano-zirconia and	silica and zirconia	Casting and fitting with dentist tools. The ceramic consists of 5-10 wt% silica and 65-75 wt% nano-ZrO_2.	 Children	Yes, but assessment value is just a speculative	Possible, but not assessed	1 mg debris/m³ 0.009 mg/kg/day	Possible, but not assessed

	nano-silica		In general, useful date are not available for exposure assessment.	Adult females Adult males	value		0.014 mg/kg/day 0.012 mg/kg/day It should be noted that repair or tooth replacement is estimated every 10 years	
COMPOSITE								
No.	**Product**	**NM**	**Exp.scenario (application/use) (product volume used) (NM concentration in product)**	**Target group**	**Nanomaterial Exposure**			
					Oral	**Dermal**	**Inhalation**	**Eye**
20	Golf club with CNT re-enforced shaft	**CNT**	Fitting of shaft and wear and tear during use (product volume not known, NM concentration unknown)	Teenagers Adult females Adult males	Likely very low acute exposure	Likely very low to low acute exposure	Likely very low to low acute exposure	Possible negligible exposure

*NCR: not considered as a relevant exposure route
MD: missing data for estimation

7.2 Discussion of outcome

The following discussion is based on the findings presented in Table 7-1 supplemented by the data given in the filled out templates in Appendix 7. It has to be noted that when the discussion indicates *high, medium and low exposure* in relation to the various exposure routes and various nanomaterials, this concerns solely the relative exposure and as compared to other exposures and ***not*** whether the exposure may constitute a risk or not. Thus, when evaluating the exposure in this chapter, this shall not be confused with evaluation of the risk, as evaluation of risk in connection with a specific scenario require further input from a hazard evaluation for each specific nanomaterial and for each specific exposure route. The exposure data from this chapter will be used later in the forthcoming risk assessment stage of this project in which data on the hazards of the nanomaterials are included in order to compare the exposure assessments given in Table 7-1 with the hazard evaluation and characterization presented in the separate project report "Hazard assessment of nanomaterials in consumer products".

7.2.1 Scenarios covering oral exposure

For 12 scenarios, estimations have been made regarding oral exposure (food and beverages scenarios 1, 2, 3, 4; cosmetic scenario 5, 6, 8, 9; air-ventilation purifier scenario 13; textile scenario 16, dental filling scenario 19; composite scenario 20).

Food items and cosmetics represent the sources with the highest oral exposure (up to 5.5 mg NM/ kg bw/day, scenarios 5 and 6), whereas oral exposure from *textiles, air-purifiers, dental fillings, or composite* may seem rather low or in some cases even considered as absent.

However, it should be noticed that if inhalation occurs, then the inhalational dose expressed in mg NM /kg bw/day may also contribute to the oral dose as particles that do not deposit in the alveolar region may be swallowed.

7.2.2 Scenarios covering dermal exposure

For 14 scenarios, estimations have been made regarding dermal exposure (1 (food contact material); 5, 6, 7, 8, 9 (cosmetics); 10, 11, 12 (surface coating); 13 (air-ventilation cleaner); 16 (textile); 17 (construction material); 18 (medical devise); 20 (composite).

Cosmetics represent by far the highest exposure potential as these products often are intended for dermal application on a daily basis (up to 450 mg NM/kg bw/day in scenario 5).

Construction materials (scenario 17, cement) also represent a high potential for dermal exposure primarily due to the large dermal surface areas exposed. Also *the paint and sanding scenarios* (10,11) represent scenarios with potential for dermal exposure especially from sanding up to 30 mg/kg bw/day. However, the exposure to nanomaterials in sanding dust may vary considerably depending on the type of paint. In this case, scenario 11, represent sanding of a primer paint, which is reported to only contain nanomaterial suspended in a water-based medium. The paint scenario (number 10) on the other hand represents a regular paint coating where the sanding debris may predominantly be incorporated in the larger solid particles of the paint matrix.

Wound dressings (scenario 18) further represent a high dermal exposure potential.
Low dermal exposure potential relates to food-contact material (4), air-ventilation cleaner (13), composite (20) and textile (16) (the latter due to very low concentrations in the textile).

7.2.3 Scenarios covering inhalation exposure

For 11 scenarios, estimations have been made regarding inhalation exposure (6, 9 (cosmetics); 10, 11, 12 (surface coating); 13, 14, 15 (air-cleaners); 17 (cement); 19 (dental filling); 20 (composite).

Sanding and Spray-painting (10, 11) represented by far the highest potential for exposure (18-109 mg NM/m^3 and an overall exposure of 0.2-1.5 mg NM/kg bw/day). In the case of spray painting, the assessment is thought, however, to result in great overestimation because no model is able to truly estimate the inhalation exposure to overspray.

Scenario 17, cement represented an in-between scenario with an exposure level of 0.75 mg NM/m^3 and 0.13 mg NM/kg bw/day.

Also, use of face powder (9) may result in a relatively high exposure level of 0.26 mg NM/m^3 and a number-based exposure level of more than 10,000 particles per cm^3, however with a low overall exposure of 0.001 mg NM/kg bw/day and more than 2 x 10^9 particles/person/day.

In the selected cases for use of pump and propellant *spray for surface impregnation and air – cleaning* representing rather low exposure levels (up to 0.004 mg NM/m^3, scenario 14) and overall exposure (up to 0.02 mg Nm/kg bw/day, scenario 15). The relatively low estimated exposure levels are due to low contents of NM in the products and short exposure durations.

Inhalation exposure from sanding and fitting a CNT-reinforced shaft for a golf-club as a representative for sports gear (scenario 20) may only lead to very low or low acute exposure. The assessment is uncertain as both the exact location, type of the matrix and concentration in the product are unknown.

Inhalation exposure is determined by many parameters/factors that have to be considered in each scenario. Therefore, the combination of uncertainties and worst-case assumptions for each of these determining parameters are added (or multiplied) upon each other leading to scenarios that generally reflect greater variability and uncertainties than what pertains to the oral and dermal exposure estimates.

7.2.4 Scenarios covering eye exposure

For only two scenarios, quantitative estimations have been made regarding eye exposure (7 and 9) (cosmetics for mascara and face powder). Highest exposure was estimated for mascara leading to an exposure of 0.5 mg NM into the eye on a daily basis.

In general, eye exposure with respect to airborne exposure is difficult to assess and therefore great uncertainties exist in the assessments, but the mass based exposure levels are to be considered as minor compared to other exposure routes (scenario 9). However, it should be kept in mind that eye exposure –even if low- may be of concern in terms of the local exposure of the mucous membranes of the eye and possible local effects.

7.2.5 Overall dose levels from use of the various product categories and formulations

Overall *highest NM* dose can be found from *food items and food supplements* (oral exposure)*; cosmetics*, especially sunscreens (dermal and oral exposure); *surface coating, paints* (dermal and inhalation), *construction material, cement* (dermal and inhalation); *wound dressing* (dermal).

Lower dose levels pertain to *air cleaners, ventilation system and pump/propellant sprays* (inhalation scenario 13, 14, 15); *surface coating, propellant spray* (inhalation) and *textiles* (dermal).

Very low if any exposure was found in relation to the chosen scenarios for *food contact material, air cleaner (ventilation purifier),* and from *composites*.

7.2.6 Exposure to specific nanomaterials

7.2.6.1 Nano-Ti02 (scenario 1, 5, 8, 10, 17)

High *oral exposure* pertain to *food (1) and cosmetics (5, 8)* where exposures in the range of 1.6 - 5.5 mg nano-TiO_2/kg bw/day were estimated.

High *dermal exposures* were especially related to:

- *cosmetics*: up to 446 mg nano-TiO_2 for a sunscreen product *(5),*
- *construction material:* up to 179 mg nano-TiO_2/kg bw/day for cement *(17)*, and
- *sanding of paint:* up to 30 mg TiO_2/kg bw/day *(10b)*.

Still high (but lower) *dermal exposure* of up to 4.3 mg nano-TiO_2/kg bw/d was estimated for roller *application of paint (10a).*

Inhalation exposure levels (scenario *10b*, sanding of paint surface and 17 cement) was found to be in the range of 0.25-18 mg/m^3 resulting in inhaled doses in the range of 0.042- 0.25 mg/kg bw/day.

7.2.6.2 Nano-silica (scenarios 2, 4, 9, 12, 19)

High *oral exposure* pertain to *food* (2) with an accumulated exposure up to 1.8 mg nano-silica/kg bw/day. No/low oral exposure is considered to take place from the use in food contact materials (4).

The use of nano-silica in surface-coating (12) is considered very uncertain, however it is considered to be relatively low both in relation to dermal and inhalation exposure.

The use in e.g. face powder (9) result in relatively *high dermal exposure* of 51 mg/d or 0.9 mg/kg bw/d, whereas the dermal exposure, inhalation exposure and eye exposure are considered orders of magnitudes lower on a mg/kg bw/day basis.

7.2.6.3 Nano-Ag (scenario 3, 11, 13, 14, 15, 16, 18)

Highest dermal exposures pertain to the use of wound dressing (18) with an exposure estimation of 9 mg/kg bw/day.

High *dermal and inhalation* exposure pertain to *spray painting* (11) with estimated exposures of 0.9 mg/kg bw/d and 1.2 mg/kg bw/day, respectively.

Exposure from disinfection sprays (14, 15) was estimated to reach up to 0.2 mg/kg bw/day for *dermal exposure* and up to 0.02 mg/kg bw/day for *inhalation exposure* (in connection with an air concentration of 0.0025 mg Ag/m^3).

Dermal exposure from textile (16) was estimated at 0.009 mg/kg bw/day, which is to be considered as very low.

The highest *oral exposure* is from a *food supplement* (3) with an estimated exposure of 0.021 mg/kg bw/day.

Exposure from an air-ventilation purifier was considered to be very low or even absent (13).

7.2.6.4 Nano-ZnO (scenario 6)

High *oral and dermal exposure* pertain to the use in a sunscreen product (6) where exposures up to 5.5 mg nano-ZnO/kg bw/day (oral) and 446 mg ZnO/kg bw/day (dermal) were estimated.

7.2.6.5 Carbon black (scenario 7)

Relatively high *dermal load* of 0.8 mg/cm^2 was found for the use in mascara. Also, an eye exposure of 0.5 mg/day was estimated.

An upper exposure of 0.13 mg/kg bw/day was estimated for children.

7.2.6.6 Nano-zirconia (scenario 19)

The use in dental fillings for tooth replacement may result in exposure less frequent than once a year. The exposure assessment is considered very uncertain. *An inhalational dose* of up to 0.014 mg/kg bw/day was estimated.

7.2.6.7 CNT (scenario 20)

The use of CNT in a golf club was estimated to result in very low acute exposure by *dermal and inhalational exposure*.

7.2.7 Target groups

Children were considered in 8 scenarios and found to be the most exposed target group in 7 of the 20 exposure scenarios (1 (TiO_2); 5(TiO_2); 6(ZnO); 7(Carbon black);8(TiO_2), 18 (Ag), 19(Zirconia)). In scenario 16 (textile, Ag) only oral exposure was considered as dermal exposure was considered lower than for adults.

The far highest dermal and oral exposure to TiO_2 and ZnO pertain to the use of sunscreen (5, 6). High dermal exposure to nano-Ag pertains to the use in wound dressing.

Teenagers were considered in nine scenarios and found to be the most exposed target group in two scenarios: scenario 9 (nanosilica, face powder) and scenario 10 (TiO_2, roller application of paint).

Adults were considered in 16 scenarios and were the most exposed target group in nine scenarios: scenario 2 (nano-silica, food-items); scenario 3 (nano-Ag, food supplement); scenarui 10(TiO_2, sanding painted surfaces); scenarui 11 (nano-Ag, spray painting), scenario 12 (silica, surface coating), scenarios 14+15 (nano-Ag, disinfectant sprays), scenario 16 (nano-Ag, textile), scenario 17 (TiO_2, cement).

7.3 Uncertainty and knowledge gaps

It should be noted that the 20 products addressed in Chapter 6 and 7 are only a small selection of consumer products, which contain or could contain nanomaterials. Further, given availability of data, the selection is biased towards products where the manufacturer/producer has had an interest in "claiming" a content of nanomaterials. Anyway, given current knowledge, the selected products are expected to illustrate representative cases for the current situation.

Generally, the chemical identity and/or characterisation of nanomaterials applied in consumer products are not very well described. Several entries in available inventories/databases give no ("Unknown") or very generic information about the contained nanomaterial, and seldom any details about their characteristics. Also in some cases, the “nanoeffect” is due to reactive chemistry and formation of nanoscale structures after application of the products. In these cases, nanomaterials or nanoscale particles may be produced during application as in the case of some nanosprays.

Related to this, the nanomaterials concentration in a consumer product is often not indicated, and therefore the exposure estimate becomes associated with high uncertainty. In many cases, the exposure will be in association or liberated from a matrix where the transfer out of a droplet, a surface layer or the matrix a sanding fragment for example is less understood as for pure soluble chemicals.

With a few exceptions, available data and models only allow exposure estimation in the mass metric. In particular for inhalation, the number or surface area metrics might for specific cases be more relevant, e.g. in relation to further risk assessment.

In general, current exposure estimation models are not designed for estimating nanomaterial exposure.

As already noted, it appears more reliable to estimate (conservatively) oral and dermal exposures to nanomaterials (as mass based exposure estimates). In many cases it is, however, uncertain to which extent the nanomaterial can be liberated (or migrate) from the product matrix, as this may very much influence the real oral or dermal exposure to the nanomaterial. Inhalation exposure is more difficult and from reviewing the available literature, it appears particularly difficult to assess exposures following pump and propellant spray applications. Although the amount of scientific publications presenting data from studies of spray applications is growing, a closer look at these publications reveal that exposure concentration are highly dependent on a significant number of experimental parameters (pressure, nozzle size, ventilation, size of experimental chamber, viscosity of sample, analytical measurement techniques, etc.). Thus, in general, representative data for inhalation exposure following spray applications are lacking.

To some extent, the same applies for data on exposure following mechanical reworking (sanding, grinding, etc.) as well as wear and tear of nanomaterials containing consumer products.

7.4 Implications for use of data

The uncertainties described above have, between others, the following implications for further use of information collected and generated in this report:

- As also pointed out by the reference group of the project, the 20 scenarios addressed can be seen as representing very relevant consumer products with expected high as well as low exposure potentials. However, there are too many knowledge gaps in relation to where nanomaterials could potentially be found in and released from consumer products to say that (only) 20 scenarios are representative for consumer products as such.
- Given the diversity of products and matrices in which nanomaterials are found, as well as the level of available exposure estimation models, exposure (and risk assessment) of nanomaterials in consumer products must currently be made on a case-by-case basis.
- When assessing risks, it should be noted that the characterization of the nanomaterials in the investigated consumer products is generally not very well described, making it challenging to match exposure findings with hazard findings.
- Care should be taken when assessing in particular inhalation risks in the next phases of the project as the mass metric applied is probably not the most appropriate metric for assessing risk. Also, in general, the low tier exposure estimations may be very conservative which of course should be kept in mind and considered when evaluating the outcome of the risk assessment

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Exposure assessment of nanomaterials in consumer products
Under the Agreement "Better Control of Nanomaterials" (“Bedre styr på nanomaterialer”), the Danish EPA has commissioned a number of projects aiming to investigate and generate new knowledge on the presence of nanomaterials in products on the Danish market and assess the possible associated risks to consumers and the environment.

This report is the first in a series of four from a project which addresses consumer exposure and risk assessment of nanomaterials in products on the Danish market. The report:

- Evaluates existing methods/approaches/tools for assessing consumer exposure and risks associated with consumer nanoproducts.
- Identifies representative consumer nanoproducts from which to select and describe a total of 20 exposure scenarios for further risk assessment.

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