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Nanomaterials in Commercial Aerosol Products on the Danish Market

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Sources must be acknowledged.

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Foreword

The project “Prevalence of Solid Nanomaterials in Commercial Aerosol Products on the Danish Market” was carried out from February 2014 to October 2014.

This report forms part of a series of projects regarding nanomaterials in Denmark (“Better control of nano”) commissioned by the Danish Environmental Protection Agency (EPA).

The report describes the project results including a description and overview of the (possible) prevalence of solid nanomaterial in aerosol products according to literature, previous surveys, etc., a mapping of aerosol products containing solid nanomaterials on the Danish market and a preliminary risk evaluation of selected products.

The results are based purely on available literature and, for the selected products, information from the industry. No products have been subject to any form of analysis.

The project was carried out by Danish Technological Institute with COWI A/S as subcontractor. The project was managed by project manager MSc, PMP, Gitte Sørensen from February 2014 to June 2014 and by MSc Christian Holst Fischer from June 2014 to October 2014.

Health and environmental evaluations were headed by MSc Sonja Hagen Mikkelsen.

To assess the progress and results of the project, a steering committee was set up with the following members:

Flemming Ingerslev, the Danish EPA
Anne Mette Zenner Boisen, the Danish EPA
Peter Hammer Sørensen, the Danish EPA
Sonja Hagen Mikkelsen, COWI A/S
Gitte Sørensen, Danish Technological Institute

The project was financed by the Danish EPA.

Conclusion and summary

In recent years, the so-called nano-spray products have emerged. The product names with descriptions and/or marketing material of the products suggest that they contain nanomaterials. Similarly, various aerosol products that are not marked as nano-spray products may potentially contain nanomaterials.

Spraying is per default associated with risk of inhalation as exposure is a process where the content of a container is dispersed in the air and directed towards a target area; however, dermal and oral exposure might also occur. Further, nano-sized particles may differ in physical and chemical properties from the same bulk material, which might also change possible health and toxicity effects. Consequently, the use of consumer aerosol products containing nanomaterials is being debated, since there are concerns about the associated to health and environment.

The objective of the survey was to identify, map and conduct a risk evaluation of aerosol spray products containing solid nanomaterials available to consumers on the Danish market. The project has been divided into three sections:

- Aerosol products on the Danish market potentially containing nanomaterials
- Mapping of aerosol products with nanomaterials on the Danish market
- Evaluation of risk for consumers exposed to nanomaterials in aerosol products

Aerosol products on the Danish market potentially containing nanomaterials
The overall objective of the preliminary screening are is to identify and categorize the types of consumer aerosol products that potentially contain solid nanomaterials. The preliminary screening is divided into the three following sections:

Scientific literature and surveys on nanotechnology-based aerosol products
Within the last decade, a substantial number of commercially available aerosol products marketed as containing nanomaterials or based on nanotechnology have been subject to scientific reports. In addition, regular aerosol products have been included in some of the studies. The studies clearly illustrate that some of the nanotechnology-based aerosol products contains solid nanomaterials in the liquid suspension; whereas other nanotechnology-based aerosol products do not contain solid nanomaterials in the liquid suspension. Moreover, several of the studies indicate that regular aerosol products may contain a broad range of particle sizes, including some in the nano range.

Aerosol products with a claim to be nanotechnology-based
The preliminary screening of nanotechnology-based aerosol products showed that a substantial number of consumer aerosol products, which by their product name, description and/or marketing material indicate that they contain nanomaterials, are commercially available. 140 and 63 aerosol products were identified in the Woodrow Wilson database and the Nanodatabase from the Danish Consumer Council (www.nandb.dk), respectively. The databases are very similar in structure and contain many of the same products. On the Danish market, 78 products were identified. The identified products include products that may not – when further investigated – fall under the definition of the focus products of this survey. Most of the identified products are used infrequently (once/twice a year) and are mainly used by adults. The identified products have been grouped into four categories:

- Impregnation aerosol products (52 products)
  - Textiles: sprays for different textile types, shoes and leather
  - Home: sprays for tiles, concrete, metal, wood, glass and enamel
  - Cars: sprays for car paintwork and rims
  - Anti-fog: sprays for diving masks and skiing lenses
- Cleaning aerosol products (19 products)
  - Car cleaning
  - Bike cleaning
  - Home cleaning
  - Textile cleaning
- Cosmetics (1 product)
  - Sunscreen
- Others (6 products)
  - Flame retardants
  - Lubricants for bike chains

Identification of regular aerosol products that are likely to contain solid nanomaterials
Contrary to the nanotechnology-based aerosol products, the product name, product description, list of ingredients and/or marketing material of regular aerosol products do not indicate that they contain nanomaterials. Consequently, product groups rather than specific products were identified in the preliminary screening. In the preliminary screening, it was found that pigments used for spray paints may fall within the applied definition of a nanomaterial (the number of spray paints was estimated in the mapping). Moreover, a number of regular product types potentially containing nanomaterials were identified:

- Coatings
  - UV protection
  - Anti-bacterial
  - Impregnation
- Lubricants

Mapping of aerosol products with nanomaterials on the Danish Market
Mapping was conducted to gather information on aerosol products with nanomaterials on the Danish market in order to outline the prevalence of products containing nanomaterials on the Danish market as well as the types and concentrations of nanomaterials in these products.

Mapping focused on cleaning, impregnation, paint and sunscreen products, and it alone comprised products marketed in Denmark or sold on Danish/Danish language internet pages. A total of 17 companies, relevant to the selected product groups, were contacted, and they were asked to complete a short questionnaire (see Appendix 1). The findings of the mapping are summarized in the below table and text:

Products	Types	Number of companies and products identified	Nanomaterial
Cleaning	Nanotechnology -based pump sprays	7/19	According to the respondents, the products do not contain nanomaterials

Impregnation	Nanotechnology -based pump and propellant sprays	14/52	According to the respondents, some of the products do contain nanomaterial (e.g. silica and titanium dioxide)
Paints and coatings	Regular propellant sprays	72/>100	According to the respondent and literature, pigments may be used in nano-size. 72 companies was registered as manufactures or wholesalers of varnish, paint and coatings (NACE: 203000 & 467320); consequently, the number of spray paints has been estimated to be several hundred.
Sunscreens	Regular pump sprays	>50/1*	Only one sunscreen spray containing nanomaterials has been identified on the Danish market.

* ACCORDING TO THE MANUFACTURES, THE PRODUCT IS NO LONGER MARKETED ON THE DANISH MARKET

- **Cleaning:** Two Danish small-/medium-sized companies that solely focus on nanotechnology products responded to the questionnaire. Both companies specified that none of their cleaning spray products contain material that fall within the applied nanomaterial definition in this survey.
- **Impregnation:** Six companies that market nanotechnology-based impregnation sprays were approached. Two out of the six companies responded to the questionnaire. One of the respondents markets two nanotechnology-based aerosol products for car glass coating and car varnish. The glass coating spray contains a water-soluble polymer; consequently, the product is not a focus product because of the absence of solid nanomaterial in the liquid suspension. On other hand, the respondent specified that the varnish coating contains silica particles with a size of approximately 6 nm. According to the respondent, the varnish coating represents a minor share (less than 5%) of the total market for varnish coating in Denmark.
  Another respondent markets twelve nano-technology based aerosol products and specified that most of the products contain nano-sized silica and a few products contain nano-sized titanium dioxide. The respondent does not know the concentration or the particle size distribution of the nanomaterials. According to the respondent, 1/3 of the products are solvent-based and 2/3 of the products are water-based. The solvent-based products are applied on none-absorbent surfaces (e.g., glass, tiles) and the water-based on absorbent surfaces (e.g., textiles). The typical volume per square meter varies between 15-20 ml for the solvent-based and 60-80 for the water-based products. The respondent stresses that the market for nano-technology based aerosol products represents less than 1% of the total market.
- **Sunscreen:** The vast majority of Danish manufacturers offer sunscreen without nanomaterials (in order to comply with the Nordic Ecolabel 'Svanen'); therefore, only international manufacturers of sunscreen spray products were included in the mapping. However, only one company responded to the questionnaire. According to the respondent, the company does no longer market sunscreen spray products on the Nordic market that contain nanomaterials.

- **Paint and coatings:** Contrary to the nanotechnology-based aerosol products, paint and coating aerosol products do not indicate if they contain nanomaterials. However, it was found that pigments used for spray paints may fall within the applied definition of a nanomaterial. The Danish paint and coatings market consists of a very large number of importers/manufacturers. In 2012, 35 companies were registered as manufacturers of paint, varnish and similar coatings, printing inks and mastics (NACE: 203000) and 37 companies were registered as wholesalers of varnish, paint, wallpaper and floor covering, etc. (NACE: 467320). The majority of these companies market one or more spray paints; consequently, the number of spray paint on the Danish market is expected to be several hundreds.

Three companies were approached; however, only one responded to the questionnaire. The respondent specified that the company markets four different spray paints/primers for different surfaces, including metal and glass fibre. All four products contain combinations of titanium dioxide, iron oxide, iron hydroxide and carbon black that all may be termed nanomaterials if applying a number based size distribution. According to the respondent, the concentration (%w/w) of the materials varies between 0.01-7.3%.

Risk for consumers exposed to nanomaterials in aerosol products

Estimation of exposure to aerosol spray products containing nanomaterials and related risks for the consumer is a complicated affair. The respiratory system is in itself a complicated structure where exposure and uptake also depend on the breathing mode of the exposed person. Furthermore the aerosols generated from the products form a complex system of different substances involving liquid or gaseous propellants coexisting with vapours of the formulated product that contain the nanoparticles. The concentration in the aerosol spray and the size distribution of the liquid and solid parts is influenced by continuous evaporation/condensation and coalescence/agglomeration of the components. These changes affect deposition and uptake of the nanoparticles in the different compartments of the respiratory tract. Robust exposure and risk estimation therefore require characterisation of many parameters, which are generally not available.

A worst case risk evaluation has been carried out based on both supplier information, information from the literature, default values from exposure models, and a number of assumptions in order to characterise the exposure situation for two product types: a spray paint and an impregnation aerosol spray. The impregnation aerosol spray is selected even though the supplier information is very limited with regard to the contained nanomaterial.

DNELs used for evaluating the risk related to the inhalation exposure scenarios are DNEL values suggested by industry and available in the disclosed part of the REACH registration dossiers on the ECHA homepage, or derived no-effect levels (DNELs) identified in safety data sheets if no registration has been submitted and no other valid information is identified. The risk is also estimated based on relevant occupational exposure levels (OELs) or recommended exposure limits for the non-nano form of the substances or the nano-form where available. If more values have been identified, the lowest values are used to estimate the risk. Firm conclusions regarding the individual products and scenarios are difficult to draw due to limited information regarding the parameters that determine the actual exposure.

The roughly estimated risk evaluation for the inhalation route demonstrates that there may be an unacceptable risk for the consumer. Taking the uncertainties into consideration the results indicate that both aerosol spray products containing nanoparticles and aerosol spray products not containing nanoparticles in the formulation could present a risk in certain situations where aerosol products are used indoors on surfaces or objects in small rooms with lacking ventilation. It is therefore important to follow the usual recommendations of ensuring ventilation when such products are used.

Conclusion

In the survey, 78 aerosol products that through their product name, description and/or marketing material suggest that they contain nanomaterials were identified on the Danish market. The identified products were categorized into four groups: impregnation, cleaning, cosmetics and others. The mapping clearly illustrates that some of these products contain nanomaterials whereas other products do not contain nanomaterials. It was estimated that less than 2/3 of these products contains nanomaterials (equal to < 50 products). Furthermore, most of the identified products are sold to a limited extent through various web shops. In addition, a number of aerosol products that are not marketed as a nanotechnology-based aerosol product, but considered likely to contain solid nanomaterials, were identified. Depending on how existing definitions are interpreted, these may include aerosol products containing pigment e.g., spray paint and coatings. The number of aerosol products containing nanomaterials would then be several hundreds larger.

Firm conclusions regarding the individual products and scenarios are difficult to draw due to limited information regarding the parameters that determine the actual exposure.
However, the results indicate that the aerosol products with nanomaterials, may represent an inhalation risk which similar to what is seen in aerosol products not containing nanoparticles when the they are used in small, closed rooms without ventilation.

As the market survey indicates that the identified product types do not constitute a major market share, if aerosol products with pigments (paints and coatings) are excluded, exposure is not expected to be frequent for the general consumer. However, the exposure to nanoparticles in consumer products also adds to the general exposure of the public to ultrafine particles resulting from natural sources of nanoparticles, urban air pollution and indoor air pollution. The exposure to nanoparticles from consumer products covered by the present survey is expected to be low both in terms of frequency and load over the year compared to other sources of nanoparticle exposure. A single very high exposure may however still be related to serious adverse effects and should be avoided through application of adequate precautionary measures.

Opsummering og konklusion

I de senere år, er de såkaldte nanospray produkter blevet introduceret på det danske marked. Produkternes navn, beskrivelse og/eller salgsmateriale indikerer, at de indeholder nanomaterialer. Herudover kan forskellige produkter på sprayform, som ikke markedsføres som "nano", muligvis også indeholde nanomaterialer.

At spraye vil altid være forbundet med en risiko for eksponering ved indånding idet indholdet fra spraydåsen spredes i luften, men eksponering af hud eller mund kan også forekomme. Endvidere kan partikler i nanostørrelse være forskellige mht. fysiske og kemiske egenskaber i forhold til samme materiale af større størrelser, hvilket også kan påvirke de potentielle sundheds- og toksicitetseffekter. Således er brugen af sprayprodukter med indhold af nanomaterialer blevet debatteret, da der kan være bekymring for effekter på sundhed og miljø.

Formålet med denne undersøgelse har været at identificere, kortlægge og risikovurdere aerosolprodukter, der indeholder faste nanomaterialer og som er tilgængelige for forbrugere på det danske marked. Undersøgelsen er opdelt i tre hovedafsnit:

- Indledende screening af aerosolprodukter på det danske marked som muligvis indeholder nanomaterialer
- Kortlægning af aerosolprodukter med nanomaterialer på det danske marked
- Risiko for forbrugerne udsat for nanomaterialer i aerosol produkter

Indledende screening af aerosolprodukter på det danske marked som muligvis indeholder nanomaterialer
Det generelle formål med den indledende screening har været at identificere og kategorisere forbrugerprodukter på sprayform, som muligvis indeholder faste nanomaterialer. Den indledende screening blev opdelt i tre faser:

Videnskabelige rapporter og undersøgelse af aerosolprodukter baseret på nanoteknologi
Inden for det seneste årti er et betydeligt antal aerosolprodukter, som ifølge markedsføringsmateriale indeholder nanomaterialer eller er baseret på nanoteknologi, blevet undersøgt i videnskabelige studier. Derudover er almindelige aerosolprodukter inkluderet i nogle af studierne. Studierne viser tydeligt, at nogle af de aerosolprodukter, der er baseret på nanoteknologi, indeholder faste nanomateriale i væskesuspension, hvorimod andre ikke indeholder faste nanomaterialer. Endvidere indikerer flere af studierne, at almindelige aerosolprodukter kan indeholde et bredt udvalg af partikelstørrelser, herunder nogle i nanostørrelse.

Aerosolprodukter som hævdes at være baseret på nanoteknologi
Den indledende screening af aerosolprodukter baseret på nanoteknologi, viste, at et væsentligt antal af forbrugersprayprodukter, hvor produktnavnet, beskrivelsen og/eller markedsføringsmaterialet indikerer, at de indeholder nanomaterialer, er tilgængelige på markedet. Således blev 140 og 63 aerosolprodukter identificeret i henholdsvis Woodrow Wilson-databasen og forbrugerrådets Nano-database (nandb.dk). Databaserne ligner hinanden meget i struktur og indeholder nogle af de samme produkter. 78 produkter blev identificeret på det danske marked, dog er det muligt at flere af produkterne ikke falder ind under definitionen ved nærmere undersøgelse. De fleste af de

identificerede produkter anvendes sjældent (en/to gange om året), og de anvendes især af voksne. De identificerede produkter blev inddelt i fire kategorier:

- Imprægneringsprodukter (52 produkter)
  - Tekstiler: spray til forskellige typer tekstil, sko og læder
  - Hjem: spray til fliser, beton, metal, træ, glas og emalje
  - Biler: spray til bilmaling og fælge
  - Antidug: spray til dykkermasker og skibriller
- Rengøringsprodukter på spray (19 produkter)
  - Rengøring af bil
  - Rengøring af cykel
  - Rengøring af hjem
  - Rengøring af tekstiler
- Kosmetik (1 produkt)
  - Solcreme
- Andre (6 produkter)
  - Brandhæmmere
  - Smøremiddel til cykelkæder

Aerosolprodukter med sandsynligt indhold af nanopartikler som ikke bliver omtalt
I modsætning til aerosolprodukter, der er baserede på nanoteknologi, så indikerer produktnavnet, produktbeskrivelsen, ingredienserne og/eller markedsføringsmaterialet af almindelige aerosolprodukter ikke om produktet indeholder nanomaterialer. I den indledende screening blev det vist, at de pigmenter, der bruges til spraymaling, i nogle tilfælde kan karakteriseres som et nanomateriale. Endvidere blev et antal almindelige produkter, der muligvis indeholder nanomaterialer, identificeret:
- Coatings
  - Maling
  - UV-beskyttelse
  - Antibakteriel
  - Imprægnering
- Smøremidler

Kortlægning af aerosolprodukter med nanomaterialer på det danske marked
Formålet med kortlægningen har været at give et overblik over udbredelsen af aerosolprodukter der indeholder nanomaterialer på det danske marked samt at undersøge typen og koncentrationen af nanomaterialet i produkterne.

Kortlægningen fokuserede på rengøring, imprægnering, maling og solcreme, og omhandlede kun produkter, der markedsføres i Danmark eller sælges på danske/dansksprogede internetsider. I alt 17 firmaer, som er relevante for de udvalgte produktgrupper, blev kontaktet, og bedt om at udfylde et spørgeskema (se bilag 1). Kortlægningens resultater er opsummeret i det nedenstående tabel og tekst:

Produkt	Type	Antal virksomheder og produkter identificeret	Nanomateriale
Rengøring	Baseret på nanoteknologi –	7/19	Ifølge respondenterne indeholder produkterne ikke nanomaterialer

	pumpe spray		
Imprægnering	Baseret på nanoteknologi – pumpe spray og drivgas	14/52	Ifølge respondenterne indeholder nogle af produkterne ikke nanomaterialer (eks. silika and titandioxid)
Maling og coatings	Regulær - drivgas	72/>100	Ifølge respondenten og litteratur anvendes pigmenter i nogle tilfælde i nanostørrelse. 72 virksomheder er registreret som fremstiller eller importør af maling og coatings (NACE: 203000 & 467320). På denne baggrund skønnes det at der findes flere hundred spraymalinger på det danske marked
Solcreme	Regulær - pumpe spray	>50/1*	Kun en solcreme spray med indhold af nanomateriale blev identificeret på det danske marked

* I FØLGE PRODUCENTEN MARKEDESFØRES PRODUKTET IKKE LÆNGERE PÅ DET DANSKE MARKET.

- **Rengøring:** To danske SMV'ere, som udelukkende fokuserer på nanoprodukter, svarede på spørgeskemaet. Begge firmaer specificerede, at ingen af deres sprayprodukter indeholder materiale, som kommer ind under den definition af nanomateriale, som anvendes i denne kortlægning.
- **Imprægnering:** Der blev taget kontakt til seks firmaer, som markedsfører imprægneringsspray baseret på nanoteknologi. To ud af de seks firmaer svarede på spørgeskemaet. En af respondenterne forhandler to sprayprodukter, baseret på nanoteknologi til bilglasbelægning og billak. Sprayen til glasbelægninger indeholder vandopløselige polymerer og falder derfor ikke inden for den her anvendte definition af et nanomateriale (ikke et fast nanomateriale). På den anden side, understregede respondenten, at lakbelægningen indeholder silikapartikler med en størrelse på ca. 6 nm. Ifølge respondenten repræsenterer lakbelægningen en mindre andel (mindre end 5 %) af hele markedet for lakbelægninger i Danmark.
  Den anden respondent forhandler 12 nanoprodukter på sprayform, og det blev specificeret, at de fleste produkter indeholder silika i nanostørrelse og nogle få produkter indeholder titandioxid i nanostørrelse. Respondenten kender ikke koncentrationen eller partikelstørrelsesfordelingen af nanomaterialerne. Ifølge respondenten er 1/3 af produkterne opløsningsbaserede, og 2/3 af produkterne er vandbaserede. De opløsningsbaserede produkter anvendes på ikke-vandsugende overflader (fx glas, fliser), og de vandbaserede anvendes på vandsugende overflader (fx tekstiler). Den typiske volumen pr. kvadratmeter varierer mellem 15-20 ml for de opløsningsbaserede og 60-80 for de vandbaserede produkter. Respondenten understreger, at markedet for sprayprodukterne baseret på nanoteknologi repræsenterer mindre end 1 % af hele markedet.
- **Solcreme:** De fleste danske producenter tilbyder solcreme uden nanomateriale (for at overholde det nordiske miljømærke 'Svanen'); derfor blev der kun inkluderet internationale producenter af spraysolcreme i kortlægningen. Kun et firma besvarede spørgeskemaet. I henhold til respondenten, sælger firmaet ikke solcreme på sprayform som indeholder nanomaterialer på det nordiske marked.

- **Maling og coatings:** I forhold til de aerosol produkterne baseret på nanoteknologi, indikerer maling og coating produkter ikke om de indeholder nanomaterialer. I den indledende screening, blev det i midlertidig vist at pigmenter, som anvendes i spraymaling muligvis anvendes i nanostørrelse. Det danske marked for maling og belægninger består af et stort antal importører/fabrikanter. I 2012, var 35 firmaer registrerede som fabrikanter af maling, lak og lignende belægninger, trykfarve og mastiks (NACE: 203000), og 37 firmaer var registrerede som grossister inden for lak, maling, tapet og gulvbelægninger osv. (NACE: 467320). Størstedelen af disse firmaer sælger en eller flere spraymalinger. Derfor skønnes der at være flere hundrede slags spraymaling på det danske marked.

Der er taget kontakt til tre firmaer, men kun et firma svarede på spørgeskemaet. Respondenten specificerer, at firmaet sælger fire forskellige spraymalinger/grundere til forskellige overflader, herunder metal og glasfiber. Alle fire produkter indeholder kombinationer af titandioxid, jernoxid, jernhydroxid og carbon black, som alle muligvis kan karakteriseres som et nanomateriale. I henhold til respondenten varierer koncentrationen (%w/w) af materialerne mellem henholdsvis 0,01-7,3 %.

Risiko for forbrugerne udsat for nanomaterialer i aerosol produkter
Etablering af skøn over eksponeringen for aerosolprodukter, der indeholder nanomaterialer og de dermed forbundne risici for forbrugeren er en kompliceret affære. Åndedrætssystemet har i sig selv en kompliceret opbygning, hvor eksponering og optagelse også afhænger af vejrtrækningen hos den eksponerede person. Endvidere danner aerosoler genereret fra produkterne et komplekst system af forskellige stoffer, der omfatter flydende eller gasformige drivmidler sammen med dampe af det formulerede produkt, der indeholder nanopartikler. Koncentrationen i aerosolsprayen og størrelsesfordelingen af de flydende og faste komponenter er påvirket af kontinuerlig fordampning / kondensation og sammensmeltning / agglomerering af komponenterne. Disse ændringer påvirker aflejring og optag af nanopartikler i de forskellige dele i luftvejene. Troværdig eksponerings- og risikoestimering kræver derfor karakterisering af mange parametre, der i reglen ikke er tilgængelige.

En worst case risikovurdering er foretaget på grundlag af oplysninger fra leverandører, fra litteraturen, information om standardværdier fra eksponeringsmodeller og en række antagelser med henblik på at karakterisere eksponeringssituationen for to produkttyper: en spraymaling og en solcreme på aerosolform. Solcremen er valgt selvom leverandøroplysninger tyder på, at solbeskyttelsesprodukter er ikke tilgængelige som aerosolprodukter på det danske marked.

DNEL-værdier, som anvendes til at estimere risici relateret til eksponeringsscenarierne for indånding er værdier foreslået af industrien og til rådighed i den offentlige del af REACH-registreringsdossiererne på ECHA hjemmeside, eller i sikkerhedsdatablade, hvis der ikke er fremsendt nogen registrering, og anden valid information ikke er identificeret. I de tilfælde hvor DNEL-værdier specifikke for nano-formen af stofferne er identificeret, eller hvor der er identificeret lavere grænseværdier (eller anbefalede grænseværdier) for erhvervsmæssig eksponering, er disse værdier anvendt til at estimere risikoen.

Faste konklusioner vedrørende de enkelte produkter og scenarier er derfor vanskeligt at drage på grund af begrænset information om de parametre, der bestemmer den aktuelle eksponering.

Den anvendte fremgangsmåde til risikoevaluering viser, at det kan være en uacceptabel risiko for forbrugeren. Tager man usikkerhederne i betragtning, indikerer resultaterne at både aerosolprodukter med indhold af nanopartikler og aerosolprodukter uden indhold af nanopartikler, kan udgøre en risiko på grund af indånding især i situationer, hvor aerosolprodukter anvendes indendørs på overflader eller genstande i små rum med manglende ventilation. Det er derfor vigtigt at følge de sædvanlige anbefalinger om brug af ventilation, når sådanne produkter anvendes.

Konklusion
I kortlægningen blev 78 sprayprodukter, som gennem deres produktnavn, beskrivelse og/eller markedsføringsmateriale indikerer, at de indeholder nanomaterialer, identificeret på det danske marked. De identificerede produkter blev inddelt i fire produktkategorier: imprægnering, rengøring, kosmetik og andre. Kortlægningen viser tydeligt, at nogle af produkterne indeholder

nanomaterialer, mens andre produkter ikke indeholder nanomaterialer. Det skønnes at mindre end 2/3 af produkterne indeholder nanomaterialer (svarende til <50 produkter). Endvidere, skønnes det at mange af de identificerede produkter kun sælges i begrænset omfang fra internetbutikker. Herudover er et antal sprayprodukter identificeret, som ikke markedsføres som nanosprayprodukter, men hvor det vurderes sandsynligt at de indeholder nanomaterialer. Afhængig af hvordan definitionen på et nanomateriale fortolkes, kan disse omfatte sprayprodukter med indhold af pigmenter fx maling og coatings. Antallet af sprayprodukter med nanomaterialer på det danske marked vil i så fald være flere hundrede større.

Endelige konklusioner vedrørende de enkelte produkter og scenarier er vanskelige at drage. Det skyldes ikke mindst begrænset information om de parametre, der bestemmer den konkrete eksponering fra en spray. Resultaterne indikerer dog, at aerosolprodukter med nanopartikler, kan udgør en inhalationsrisiko for forbrugerne, på samme måde som det ses for aerosolprodukter, hvis de anvendes i små lukkede rum uden ventilation. Da markedsundersøgelsen indikerer, at de identificerede produkttyper ikke udgør en større markedsandel, hvis der ses bort fra aerosolprodukter med pigmenter (maling og belægninger), forventes eksponering ikke at være hyppigt forekommende for den almindelige forbruger. Eksponering for nanopartikler i forbrugerprodukter bidrager også til den øvrige eksponering af offentligheden for ultrafine partikler som følge af naturlige kilder til nanopartikler, luftforurening i byerne og indendørs luftforurening. Eksponeringen for nanopartikler fra forbrugerprodukter omfattet af denne undersøgelse forventes dog at være lav i løbet af året, både med hensyn til hyppighed og belastning og i forhold til andre kilder til eksponering for nanopartikler.

1. Introduction to the survey

This report describes the use of consumer aerosol products containing solid nanomaterials.

In recent years, so-called nano-spray products have emerged. These products may have product names with descriptions and/or marketing materials suggesting that they contain nanomaterials. Similarly, various aerosol products that are not marked as nano-spray products may potentially contain nanomaterials.

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; thus, dermal and oral exposure may also occur. Further, nano-sized particles may differ in physical and chemical properties from the same bulk material, which may also change possible health and toxicity effects. Consequently, the use of consumer spray products containing nanomaterials are being debated, since there are concerns about the associated to health and environment.

1.1 Objective of the survey

The objective of the survey is to identify and map aerosol products containing solid nanomaterials available to consumers on the Danish market. The survey comprises alone products marketed in Denmark or sold on Danish/Danish language internet pages. Conclusively, a risk evaluation of selected products/product groups is conducted.

1.2 Survey methods

The project is divided into three sections: a preliminary screening, a mapping of products and a risk evaluation.

1.2.1 Preliminary screening

A preliminary screening has been carried out to identify aerosol products, which by their product name, description and/or marketing material suggest that they contain nanomaterials. The identified products are catalogued and described with regard to the function, overall prevalence and dispensing system (pump vessel or propellant gas vessel). The preliminary screening is based on:

- Previous surveys and recent scientific literature/reviews on aerosol products generating nano-sized aerosols and/or containing solid nanoparticles.
- Relevant databases, including online nanodatabases such as the Woodrow Wilson database and the Nano database by the Danish Consumer Council's and the Danish Ecological Council.
- Visits in a number of retail shops, including furniture and interior shops, sports and outwear shops, shoe shops and department stores.
- Google search using combinations of a number of relevant key words in order to find shops and web-shops selling aerosol products, which by their product name, description and/or marketing material suggest that they contain nanomaterials. The following key words have been used: nano, nanoparticles, spray, film, aerosol, impregnation, textiles, clothing, shoes, self-cleaning, cleaning, car, universal, coating, sunscreen, cosmetic, vitamin, health, UV block, sun protection, anti-bacterial, lubricant.

In addition, a preliminary screening of regular aerosol products potentially containing nanomaterials has been carried out. The screening is based on the general knowledge of nanomaterial applications, literature as well as the knowledge acquired from nanomaterial suppliers, and products groups rather than specific products are identified.

1.2.2 Mapping of products

In the mapping of products, only products containing solid nanomaterials are included, see section 1.4 and 1.5. The mapping has been carried out during spring and summer of 2014.

Industry contact

Manufacturers/importers/retailers of aerosol products, registered during shop visits and via internet pages were contacted, asking them to complete a short questionnaire (see Appendix 1). The companies that did not respond to the first enquiry were contacted again with a request to complete the questionnaire, and the contact was supplemented by an interview to clarify further, when relevant.

1.2.3 Risk evaluation

Assessment of the risk to consumers from exposure to nanomaterials in aerosol products requires information not only about the chemical content in the aerosol can but also detailed information about spray nozzle, the application scenario and conditions, as well as the dynamics of the physical-chemical parameters characterising the spray cloud. This information will in general not be available and therefore a more simplified approach is used based on the ECHA guidance documents for exposure assessment and risk characterisation of chemicals in general, information from the supplier of the selected products, default parameters obtained from the literature and own assumptions. Furthermore, DNEL values for all relevant exposure routes and endpoints have not been identified and derivation of appropriate DNEL's for the nanomaterials in question are outside the scope of this project. Therefore the risk characterisation ratio (RCR) is calculated based on the derived no-effect levels (DNELs) suggested by industry for worker exposure, and on occupational exposure levels (OELs) not specific for the nano-form of the substances in order to estimate the risk related to two selected exposure scenarios.

It should be emphasized that calculations are based on a number of assumptions allowing only a rough evaluation of a worst case risk.

Two scenarios have been selected. One illustrating exposure to an aerosol paint spray based on information on the chemical content from the supplier. The other scenario involves spray application of a theoretical impregnation product. Although there are indications that cosmetic products containing nanoparticles are not prevalent on Danish or EU market due to the possible health risk and recommendations from authorities to avoid such products, a scenario is included. This is because sunscreens are used by the general population and all age groups, and because products are also obtained from the Internet and during vacations abroad where the control may be less stringent.

1.3 Structure of the report

The report reflects the main contents and the delimitation process throughout the project. This means that the chapters have been structured as described below:

- A preliminary screening outlining and categorizing the aerosol products on the Danish market potentially containing nanomaterials (chapter 2)
- Mapping of aerosol products with nanomaterials on the Danish market (chapter 3)
- Risk evaluation of selected products/product groups (chapter 4)

1.4 The nanomaterial definition applied in the survey

In the literature, industry and legislation, several diverse definitions of a nanomaterial are in use, exemplified by the different definitions suggested by e.g. the International Organization for Standardization (ISO), by the European Food Safety Authority (EFSA) and by Organisation for

Economic Co-operation and Development (OECD) as recommended by the European Commission. This heterogeneity complicates a common understanding and, thereby, also discussions on prevalence and effects of nanomaterials and their use.

In this survey, a nanomaterial is defined according to the Recommendation of the EU Commission on the definition of nanomaterials (2011/696/EU). In addition, only solid nanomaterials (i.e. melting point ≥ 25 °C) are considered a nanomaterial in this survey.

Recommendation of the EU Commission on the definition of nanomaterials (2011/696/EU)

"Nanomaterial" means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.

"Particle", "agglomerate" and "aggregate" are defined as follows:
(a) "Particle" means a minute piece of matter with defined physical boundaries;
(b) "Agglomerate" means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components;
(c) "Aggregate" means a particle comprising strongly bound or fused particles."

1.5 Inclusion and exclusion of products in the survey

Aerosol products containing nanomaterials may be confused in a number of ways with generally used terms such as nano-sprays and nano-aerosols as well as many other spray products associated with nanotechnology or nanoparticles in some way. For these reasons, a clear description of the product in focus in this survey is needed. Only the presence of solid nanomaterials (i.e. melting point ≥ 25 °C) in the can determines if the aerosol product is considered a focus product for this survey.

The products must be spray products intended to form an aerosol using propellant gas or a pump vessel, and the gas/liquid in the spray must contain a solid nanomaterial. This means that the size of aerosol droplets is unimportant and that the state, result and function of the content of the can after spraying (e.g. if it forms an aerosol of nano-sized droplets, a nanofilm or a nanostructured surface) is not important to determine if the definition is fulfilled.

Product examples

Examples of products falling within and outside the definition of the focus products of this survey is presented below:
INCLUDED - Aerosol products emitting nano- and/or micro-sized aerosol droplets that contain solid nanomaterial in the liquid suspension, e.g.:

- Lubricant with nanoparticles
- Sunscreens with nano-sized UVblockers (e.g. titanium dioxide)

EXCLUDED - Products emitting nano- and/or micro-sized aerosol droplets, that do <u>not</u> contain solid nanoparticles in the liquid suspension, e.g.:

- Impregnators with organo-functionalized silanes (melting point <25 °C)
- Antiperspirants containing metal oxides (e.g. aluminium) with an average particle size

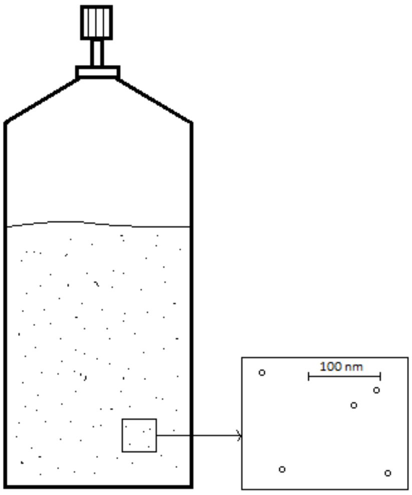

IMAGE 1
THE BOX IN THE RIGHT SIDE OF THE IMAGE REPRENSENT AN ENLARGED SECTION OF THE SPRAY SOLUTION: CIRCLES REPRESENTS THE NANOPARTICLES (MP>25) AND THE SURROUNDINGS THE SOULTE/GAS.

larger than 100 nm (number concentration)

2. Aerosol products on the Danish market potentially containing nanomaterials

The overall objective of the preliminary screening is to identify and categorize the type of consumer aerosol products that potentially contain solid nanomaterials. This includes:

- Aerosol products, which by their product name, description and/or marketing material suggest that they may contain nanomaterials. These product types are from this point referred to as nanotechnology-based aerosol products
- Aerosol products that are not marketed as a nanotechnology-based aerosol product, but are considered likely to contain solid nanomaterials

The preliminary screening is divided into three separate sections:

- A review of scientific literature on nanotechnology-based aerosol products (section 2.1)
- Identification of nanotechnology-based aerosol products on the Danish market (section 2.2)
- Identification of regular spray products (not marketed as a nanotechnology-based aerosol product) that are likely to contain solid nanomaterials (section 2.3)

As a result of the broad approach of including products in any way suggesting relation to nanotechnology, which is applied in this preliminary screening phase, the identified products will include products that do not – when further investigated – fall under the definition of the focus products of this survey.

2.1 Scientific literature and surveys on nanotechnology-based aerosol products

Within the last decade, a substantial number of commercially available aerosol products marketed as containing nanomaterials or based on nanotechnology have been subject to scientific reports. The overall findings for each paper are summarized in Table 1 with a more comprehensive description in the subsequent sections. The objectives and/or definition of a nanomaterial in most of these studies differ from the ones used in this survey, and, consequently, the results are interpreted in relation to the definition used in this survey as given in the table and descriptions below. In some literature the particle size distribution is presented as a volume distribution, making it difficult to determine if the material may be termed nanomaterials (<100 nm) when applying the number-based particle size distribution conditions according to 2011/696/EU (see the text box below). Further, as most literature and surveys focus on the international market, some products identified in this section may not be present on the Danish market.

Paper	Products tested	Findings
(Nørgaard, Jensen et al. 2009)	Four nanofilm aerosol products	Only the photocatalytically active glass coating contained solid nanoparticles; however, the size distribution of the particles was not determined. Consequently, it cannot be determined if the product fall under the definition of the focus products of this survey.
(Quadros and Marr 2011)	Three silver-containing aerosol products	In one product, nearly 70% of the silver particles were nano-sized (mass%). This product is expected to fall under the definition of the focus products of this survey. The nanosilver content was found to be much lower in the remaining two products (<<50%).
(Nazarenko, Han et al. 2011)	Six nanotechnology-based and five regular aerosol products (same functionalities)	Only three of the nanotechnology-based aerosol products contained solid nanoparticles, the remaining three nanotechnology-based aerosol products did not contain solid particles. Moreover, nano-sized particles were detected in most of the regular products.
(Lorenz, Hagendorfer et al. 2011)	Three nanotechnology-based and one regular aerosol products	Two of the nanotechnology-based sprays were found to contain nanoparticles with an average size of 8 nm 23 nm, respectively. Both of the products are expected to fall under the definition of the focus products of this survey. The regular spray was found to contain structures in the microrange.
(Chen, Afshari et al. 2010)	One nanotechnology-based bathroom/sanitizer spray	The aerosol droplets contained solid particles with a diameter of 75 nm, with 65% of the particles being smaller than 100 nm (number concentration). Consequently, the product fall under the definition of the focus products of this survey
(Hagendorfer, Lorenz et al. 2009)	One nanotechnology-based aerosol product	The product contained particles with a main size mode of 6 nm and a second broader size fraction of size range 15-60 nm. The product is expected to fall under the definition of the focus products of this survey
(Bekker, Brouwer et al. 2014)	Two nanotechnology-based and two regular aerosol products (same functionalities)	Both nanotechnology-based aerosol products contained a large number of silica (SiO_2) particles in the size range of 50–200 nm. The majority of particles in the regular aerosol products were observed in the microrange
(Michel, Scheel et al. 2013)	One nanotechnology-based glass cleaning spray	The product is water based and contains 0.09% (w/w) spherical synthetic amorphous silica (SAS) nanoparticles, with primary SAS particles of size range 10-20 nm. Consequently, the product is expected to fall under the definition of the focus products of this survey

TABLE 1
LITERATURE OVERVIEW OF NANOTECHNOLOGY-BASED CONSUMER AEROSOL PRODUCTS.

In a study by Nørgaard et al., the emission data on volatile organic compounds and aerosol particles emitted during simulated use of four commercial nanofilm-generating sprays were investigated. Three of the products were pump-sprays of which one of them (NFP3) contained TiO2 anatase nanoparticles. 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 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 results demonstrate that only NFP3 contains solid nanoparticles (titanium dioxide) in the liquid suspension (Nørgaard, Jensen et al. 2009). However, the size distribution of the particles was not measured; consequently, it cannot be determined if the given product is covered by the definition applied in this survey. The specific anatase-based NFP3 is also no longer available on the Danish market, but other comparable products exist.

Hagendorfer et al. analysed one commercially available water-based nanosilver spray, using a propellant gas spray and a pump spray dispenser. The dispersion of the product was found to contain aggregated nanosilver clusters in a size range of 20-100 nm, with single particles in a main size mode of 6 nm and a second broader size fraction of size range 15-60 nm. The pump spray situation showed no measurable nano-sized aerosol droplet release, whereas in the case of the gas spray, a significant release was observed; indicating that the release of nano-sized aerosol droplets is affected by the spray vessel type (Hagendorfer, Lorenz et al. 2009).

Similarly, Quadros et al. investigated three aerosol products claiming to contain silver nanoparticles or ions, namely an anti-odour spray, a surface disinfectant and a throat spray. The three products were found to contain silver particles smaller than 100 nm; however, most of the silver in anti-odour spray and the surface disinfectant were found to be ionic silver or associated with larger particles (>450 nm). On the other hand, more than 70% of the silver content (by mass) was found to be nano-sized in throat spray. Analysis showed that the anti-odour spray contained 12.5±1.8 ppm of Ag, the surface disinfectant contained 27.5±0.4 ppm of Ag and the throat spray contained 23,7 ±1.2 ppm of Ag (Quadros and Marr 2011). Consequently, this product is likely to be covered by the definition applied in the survey.

In a recent study by Nazarenko et. al,, six nanotechnology-based consumer aerosol products and five regular consumer aerosol products performing similar functions were tested. The products include personal care sprays (body/facial mists, hair care sprays), cleaning spray products and multi-purpose disinfectant sprays. Three of the nanotechnology-based consumer aerosol products were shown to not contain any solid particles (not visible using TEM photomicrographs). In addition, it was found that the remaining three nanotechnology-based aerosol products contained a broad range of particles, including some in the nano-range. Similarly, the regular aerosol products were found to contain a broad range of particle sizes, including some in the nano range (14 nm – 20 μm). This indicates that consumers can be exposed to nanoparticles from nanotechnology based as well as regular aerosol products; however, the authors are hesitant to draw firm conclusions due to poor ingredient lists and therefore challenges with optimising the analytical techniques toward the contained chemistry (Nazarenko, Han et al. 2011).

Using a similar approach, Bekker et al. examined two nanotechnology-based aerosol products and two regular aerosol products performing similar functions: impregnators for smooth materials, including leather and suede, and antiperspirant sprays. Characterization of the dispersions showed that both nanotechnology-based aerosol products contained a large number of silica (SiO_2) particles in the size range of 50–200 nm. In addition, the analysis of the nanotechnology-based antiperspirant spray showed a small number of magnesium oxides, iron and iron oxides, and silica particles in the size range of 100–200 nm. No particles in the nanorange could be identified in the regular impregnator spray. Analysis of the regular antiperspirant sprays showed a very small number of nano-sized silica particles, while the majority of particles were observed in the micro-range (Bekker, Brouwer et al. 2014). Consequently, only the examined nanotechnology-based aerosol products are likely to be covered by the definition applied in the survey.

Lorenz et. al analysed three commercially available nanotechnology-based aerosol products; two shoe impregnators and one plant treatment. The plant treatment spray and one of the shoe impregnator sprays were found to contain nanoparticles with an average size of 8 nm and 23 nm, respectively. Consequently, the examined products are likely to be covered by the definition applied in the survey. The shoe impregnation product, using a propellant gas vessel, was found to found to contain 470 mg zinc/kg. The plant treatment spray was found to contain 9.1 mg silver/kg. Also chlorine and fluorine were detected in the chemical analysis suggesting that acrylate polymers were present in the products. In addition, an antiperspirant claiming to contain silver was analysed in the study, but was found to contain structures in the micro-range (Lorenz, Hagendorfer et al. 2011).

Chen et. al. analysed a commercially available aerosol product marketed as containing nano-sized titanium dioxide and intended to be used as a bathroom cleaner dispensed as a propellant spray. The spraying was performed in a chamber set-up using realistic spraying conditions during 2.5 minutes. The study indicated that, while aerosol droplets were large with a median particle size of app. 22 µm during spraying, the aerosol contained primarily solid titanium dioxide particles with an average diameter of 75 nm (number based), with 65% of the particles being smaller than 100 nm (Chen, Afshari et al. 2010). Consequently, the examined product is likely to be covered by the definition applied in the survey.

Michel et al. assessed the risks of the using a glass cleaner containing 0.09% (w/w) spherical synthetic amorphous silica (SAS) nanoparticles as well as a 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). Consequently, the examined product is likely to be covered by the definition applied in the survey. The analyses showed that the nanoparticles had a tendency to agglomerate/aggregate, which was expected since the SAS nanoparticles are designed to react with the glass surface or with each other to form siloxane bonds (Michel, Scheel et al. 2013).

Influence of the spray type (pump spray versus propellant spray)

Droplet/aerosol formation and thus consumer exposure is heavily influenced by the spraying mechanism and type of solution. Spraying using propellant sprays (pressurized) or highly volatile matrices such as alcohol-based pump-sprays can generate very small droplets (nm-/µm-range). Smaller aerosols are more likely leading to exposure of primary nanoparticles because of the higher likeliness of carrier liquid evaporation. On the other hand, water-based solutions and high yiscosity matrices (e.g., emulsions and oils) can form relatively large droplets/aerosols less likely to generate nano-aerosols or release free solid nanoparticles (Hagendorfer, Lorenz et al. 2009). Consequently, the potential for direct release/ generation of nanoparticles is higher for propellant sprays and alcohol-based pump sprays than for other pump-driven products.

Nanoparticle size distribution measurement

The nanoparticle size distribution can be determined using numerous commercially available instruments for analysis of, powders and particles in a suspension. The particle size distribution can be measured/calculated based on a number of different models/theories and working principles which can result in either a number- or a volume/mass-based size distribution. Commonly microscopes or image analysers construct their beginning result as a number distribution whereas results from e.g. laser diffraction and dynamic light scattering typically come as volume-based size distributions. For example, one 100-nm particle equals the same volume as a thousand 10-nm particles, and as such it has huge impact in the size distribution whether a number- or a volume-based approach is used Consequently, a number-based size distribution will provide a lower average particle size than a volume-based size distribution.

2.2 Preliminary screening of nanotechnology-based aerosol products

The identity and concentration of all ingredients added to commercial products do often not appear in the product information. In many cases, therefore, it is difficult or impossible to determine whether a nanotechnology-based consumer aerosol product contains solid nanoparticles. In the sections below, all aerosol products, which by their product name, description and/or marketing material suggest that they may contain nanomaterials, have been included.

2.2.1 Databases

A total of 141 products were, at the time of examination, categorized with the potential exposure pathway “Inhalation” in the Consumer Product Inventory in the Project on emerging nanotechnologies (Woodrow Wilson). A review of these products shows that 63 are aerosol products. Among these products, 15 were randomly picked, and their availability on the Danish market was investigated and the application of aerosol products was assigned to each product. Four of the randomly picked products could be identified on the Danish market, whereas the remaining 11 were solely sold outside Denmark. In Image 2, the aerosol products (national and international market) have been grouped into six categories based on their application. The identified products are predominated by car care, cleaning and cosmetic aerosol sprays.

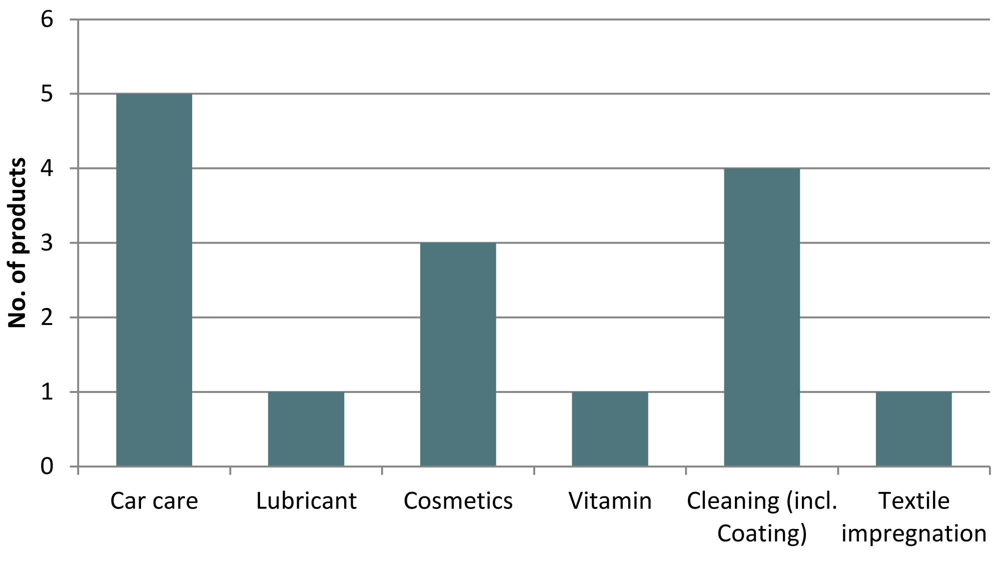

IMAGE 2
GROUPING OF 15 RANDOMLY PICKED AEROSOL PRODUCTS FROM THE CONSUMER PRODUCT INVENTORY IN THE PROJECT ON EMERGING NANOTECHNOLOGIES (WOODROW WILSON)

In addition to the Woodrow Wilson database, the Nanodatabase by the Danish Consumer Council's and the Danish Ecological Council was examined. The two databases are very similar in content and composition, and both include products from most of the world. At the time of examination, 168 products were categorized as “airborne”. A thorough examination of these products shows that approximately 140 of these products are aerosol products[1]. Assuming that the ratio of products available on the Danish market compared to products solely marketed outside Denmark is similar to what was found for the Woodrow Wilson nanodatabase, the Nanodatabase is estimated to contain approximately 35-40 aerosol products available on the Danish market.

2.2.2 Internet search and shop visits

A total of 78 aerosol products were identified on the Danish market by searching the internet and visiting shops and stores. This is comparable fewer than the number of aerosol products in the Woodrow Wilson database; however, this finding was anticipated given that the use of nanotechnology has been a subject of public debate in Denmark due to increasing concerns about the human and environmental effects of nanomaterials. Consequently, nanotechnology-based aerosol products are expected to be more prevalent outside Denmark.

In the preliminary screening, 10 shops were visited, including retail shops, furniture and interior shops, sports and outwear shops, shoe shops and department stores. In Image 3, the identified aerosol products are grouped based on their application. A further description of each category is given in the sections below.

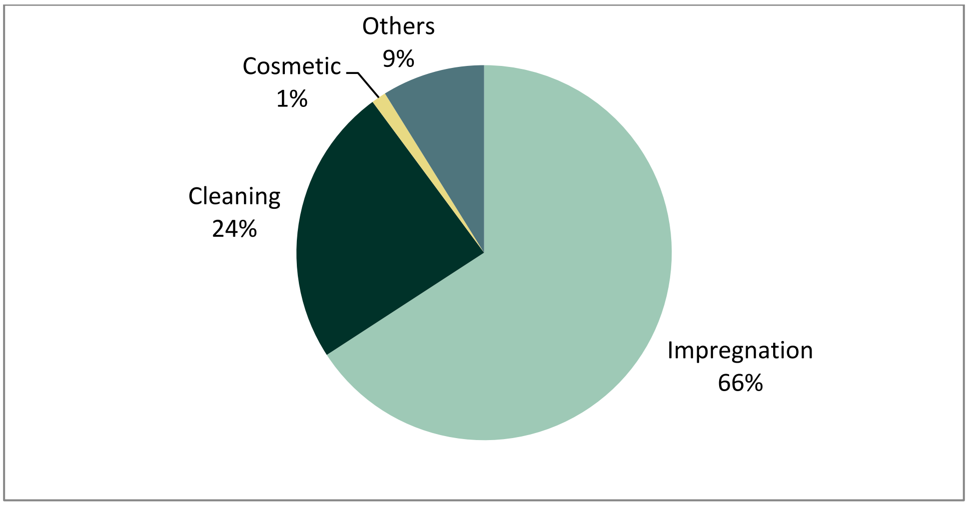

IMAGE 3
CATEGORIZATION OF THE IDENTIFEID NANOTECHNOLOGY-BASED AEROSOL PRODUCTS ON THE DANISH MARKET

2.2.2.1 Impregnation

The bulk of products identified in the preliminary screening are impregnation aerosol products (52 products), constituting 2/3 of the aerosol products identified in total. All products are DIY products and mainly used by adults.

A relatively new type of impregnation aerosol product for impregnating various surfaces are nanofilm spray products (see textbox below). Most of the nanofilm sprays induce non-stick and/or self- cleaning properties when applied to surfaces.

Nanofilm sprays

Recently, a new generation of waterproofing and/or dirt repelling spray products have been

[1] Due to incomplete description of some products, the exact number cannot be determined.

developed, the so-called nanfilm sprays. A variety of nanofilm spray are sold in e.g. DIY stores and supermarkets. Like the more traditional products, the nanofilm sprays are used to achieve easy-to-clean surfaces because impurities adhere poorly to the nanofilm (hydrophobic or ultrahydrophobic) (Larsen, Dallot et al. 2014).
The nanofilm-generating sprays are available for a wide range of different surfaces, including bathroom tiles, floors, textiles, and windows. Normally the products are sprayed onto a surface, and a film is formed by self-organization during evaporation of the solvent. The film arises in a sol-gel process involving hydrolysis and condensation reactions between organo-functionalized silanes and in some cases nanoparticles of, e.g., metal oxides or silica. The result is an interconnected rigid network of functionalized organo siloxanes. The melting point of organo-functionalized silanes is commonly well below 25 °C. For some products, the nonstick and selfcleaning abilities are achieved by mimicking the leaves of the lotus plant (Nørgaard, Jensen et al. 2009).

In this survey, only the nanofilm spray products containing solid nanoparticles is covered by the definition applied in this survey.

The majority of impregnation spray products are marketed by three online shops specialized in nanotechnology-based products. Almost 85% of the identified impregnation spray products were found to use a manual pump vessel. In Image 4, the identified impregnation spray products have been further grouped into subcategories based on the application.

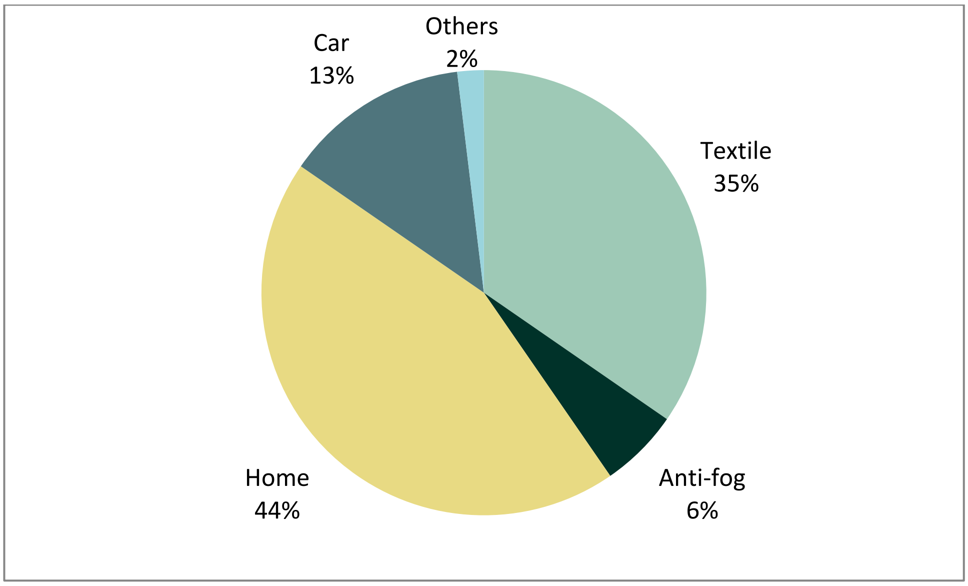

IMAGE 4
SUBCATEGORIZATION OF THE IDENTIFIED IMPREGNATION SPRAY PRODUCTS

Home
The subcategory "Home" constitutes almost half of the identified impregnation spray products (23 products) and covers an impressive range of applications, including impregnation of tiles, concrete, metal, wood, glass and enamels. The products are marketed by just five different companies and are mainly retailed from three online shops specialized in nanotechnology-based products.

Textile
More than 1/3 of the identified impregnation spray products are impregnation products intended for application on different textiles, shoes and leather (18 products). In contrast to the subcategory

“Home”, these products are marketed by 11 different companies, including retail stores and online shops.

Car
Seven impregnation spray products for impregnating car paintwork and rims were identified. The products are marketed by four different companies.

Anti-fog
Two anti-fog spray products for diving mask and skiing lenses, solely sold from online shops, were identified.

Others
One spray product for ski waxing was identified in the preliminary screening.

2.2.2.2 Cleaning
Almost a quarter of the total number of identified aerosol products are cleaning products (19 products). Eight of the products are intended for car cleaning (A/C, rim, paintwork and windows); four products for bike cleaning; four products for general cleaning and two products for textile cleaning. Ten of the identified products are marketed by three online shops specialized in nanotechnology-based products. The majority of cleaning spray products, mainly used by adults, were found to use a manual pump vessel.

2.2.2.3 Cosmetics
Contrary to the other regular aerosol products, the use of nanomaterials in cosmetic products are readily identified because, the nano-scale ingredients must be labelled by adding ‘nano’ after the INCI name of the nano-scale ingredient in the list of ingredients (see the textbox below). Consequently, four retails stores (Matas, Salling, Magasin and Naturskøn) were visited and the lists of ingredients were examined on a comprehensive number of aerosol products.
Nanomaterials and nanotechnology have a widespread influence in the cosmetics industry where changed properties obtained from incorporation of nano-scale components include colour, transparency, solubility, etc. In 2006, the European Commission estimated that 5% of cosmetic products contained nanoparticles and there are currently three main applications of nanomaterials in cosmetics: (*i*) nanoparticles as UV filters, (*ii*) delivery vehicles for active ingredients and (*iii*) colourants (ObservatoryNANO (b) 2010).

Sunscreen
The Danish sunscreen market consists of more than 30 different brands, including large international brands, smaller international brands targeted at narrow customer segments and purely Danish brands. Manufacturers most often produce a number of different brands (including private label), and, likewise, importers and retailers offer several brands. The majority of sunscreen products are non-spray format types, while aerosol products represent 29% of the sunscreen format types launched on the European market in 2013, and with pump sprays being predominant over propellant sprays (Osterwalder, Sohn et al. 2014). Similar tendencies are observed on the Danish market, where non-spray sunscreen products predominate significantly over the merely two propellant sunscreen sprays identified.

Sunscreen products are commonly divided into two subcategories: physical sunscreens and chemical sunscreens. Physical sunscreens use physical UV filters (mineral-based), while chemical sunscreens use chemical UV filters (e.g. avobenzone, bemotrizinol, bisoctrizole, octinoxate, octocrylene, oxybenzone) (Osterwalder, Sohn et al. 2014). The majority of chemical UV filters are solubilized in the product; consequently, these are not categorized as nanomaterials. However, particulate UV filters may be used to counteract formulation challenges arising from limited solubility of some chemical UV filters, and bisoctrizole was the first example of a particulate chemical UV filter with a melting point of 195 °C and an average particle size of 0.16 µm (Osterwalder, Sohn et al. 2014). In a recent survey by The Danish Consumer Council, three sunscreen products from Piz Buin containing the nano-sized chemical UV filter bemotrizinol were identified; however, none of the identified products were aerosol products from either shop visits or webshops.[2]

In the preliminary screening, it was not possible to identify any sunscreen spray products containing a nano-sized chemical UV filter.

In a the survey by The Danish Consumer Council, 14 sunscreen products from Nivea, Garnier, Vichy and La Roche-Posay containing nano-sized titanium dioxide were identified (labelled in the list of ingredients); however, none of the identified products were aerosol products.[3] Similarly, a large number of non-spray products containing nano-sized titanium dioxide are identified in the preliminary screening, while just one sunscreen spray product with nano-sized titanium dioxide was identified.

Personal care sprays
Several personal care sprays not marketed as nanotechnology-based products (facial mist, body mist, hair care and antiperspirant) were included in the scientific literature reviewed in section 2.1. The examined products were found to contain a broad range of particle sizes, including some in the nanorange (Nazarenko, Han et al. 2011; Bekker, Brouwer et al. 2014). This indicates that regular personal care sprays may contain nanoparticles; however, it is estimated that the majority of products most likely do not fall under the definition of the focus products of this survey.

European cosmetics regulation

The European cosmetics industry must comply with Regulation (EC) 1223/2009 on cosmetic products. Nanomaterials are specifically considered in Article 16, which states that nanomaterials shall be notified to the European Commission with material details, including information on identity, particle size, properties, quantities, safety data, etc. This provision does not apply to nanomaterials used as colorants, UV filters or preservatives (listed in Annex, IV, V and VI of (EC) 1223/2009). From July 2013, nano-scale ingredients must furthermore be labelled by adding 'nano' after the INCI name of the nano-scale ingredient in the list of ingredients according to the regulations article 19 on labelling. This applies to all ingredients, not only the categories subjected to notification. These steps are taken to allow consumers to access the information on nano-scale ingredients in products as well as for the Commission to survey the developments in the use of nanomaterials in cosmetics. A catalogue of all nanomaterials used in cosmetic products placed on the market (including those used as colorants, UV filters and preservatives) is under preparation by the Commission, indicating the categories of cosmetic products and the reasonably foreseeable exposure conditions.

[2] Personal communication with The Danish Consumer Council.
[3] Personal communication with The Danish Consumer Council.

2.2.2.4 Others

The category “Others” consists of six products, including four flame retardant sprays for treatment of textiles, wood and paper and two lubricants for bike chains.

2.2.3 Summary

The preliminary screening of nanotechnology-based aerosol products shows that a substantial number of consumer aerosol products, which by their product name, description and/or marketing material suggest that they contain nanomaterials, are commercially available. 141 and 63 aerosol products were identified in the Woodrow Wilson database and the Nanodatabase from the Danish Consumer Council (www.nanodb.dk), respectively. The databases are very similar in structure and contain many of the same products. On the Danish market, 78 products were identified. The identified products have been grouped into four categories:

- Impregnation aerosol products (52 products)
  - Textile: sprays for different textile types, shoes and leather.
  - Home: sprays for tiles, concrete, metal, wood, glass and enamel.
  - Car: sprays for car paintwork and rims.
  - Anti-fog: sprays for diving mask and skiing lenses.
- Cleaning spray products (19 products)
  - Car cleaning
  - Bike cleaning
  - Home cleaning
  - Textile cleaning
- Cosmetic (1 product)
  - Sunscreen
- Others (6 products)
  - Flame retardants
  - Lubricants for bike chains

As a result of the broad approach of including products in any way suggesting relation to nanotechnology, the identified products include products that may not – when further investigated – fall under the definition of the focus products of this survey.

Professional application

During the preliminary screening of nanotechnology-based aerosol products, a substantial number of Danish companies conducting nanotechnology-based impregnation/coatings of roof titles, floors, windows, textile and cars (rim, paintwork and windows) has been identified. However, none of these companies markets consumer products, and are thus not included in the survey.

2.3 Identification of regular aerosol products potentially containing solid nanomaterials

The review of scientific literature clearly illustrates that regular aerosol products (e.g. antiperspirants, disinfectants) that in general are not necessarily associated with nanomaterial and nanotechnology may contain a wide range of particles, including some in the nano-range. Consequently, it cannot be precluded that some regular aerosol products may contain solid nanomaterials and thereby be relevant to the present project.

In contrast to the nanotechnology-based aerosol products, the regular aerosol products do not indicate by their product name, product description, lists of ingredients and/or marketing material if they contain nanomaterials. Thus, the preliminary screening of regular aerosol products potentially containing nanomaterials is based on the general knowledge of nanomaterial applications, literature as well as the knowledge acquired from nanomaterial suppliers, and products groups rather than specific products are identified.

2.3.1 Paint and coatings

Paint

Pigments are added to provide colour or tone to a product and are widely used for spray paints. In Environmental Project no. 45, 2004, a number of spray paints available on the Danish market were examined. The spray paints contained aluminium, carbon black, titanium dioxide, copper and/or zinc oxide pigments in concentrations ranging from 1-10%. According to literature, typical size ranges of pigments used in brush paint are (Lambourne and Strivens 1999):

- Carbon black: 10-80 nm
- Organics: 10-1000 nm
- Inorganic: 100-5000 nm
- Titanium dioxide 220-240 nm

From the above given intervals, it may be assumed that only carbon black and organic pigment can be categorized as nanomaterials. However, other scientific studies and literature indicate that pigments may fall within the nanomaterial definition when using a number-based size-distribution. Consequently, at present time there is no consensus whether or not pigments are categorized as nanomaterial and it cannot be precluded that spray paints contain nano-sized pigments

UV protection

Several UV-protection sprays for protection/preservation of textiles (umbrellas, tents, clothing, etc.) and wood are available on the Danish market. The presence of an UV filer is not described for most of the products; however, the products are likely to contain either a chemical or physical UV filter. As detailed in section 2.3.1, some chemical and physical UV filters can potentially be in nanosize.

Anti-bacterial

In recent years, nanosilver has been incorporated in everyday products, including various aerosol products, to add antimicrobial properties. Recently, the use of nanosilver has been debated due to increasing concerns about the human and environmental toxicity of nanosilver; however, no anti-bacterial sprays with silver were identified on the Danish market in the preliminary screening.

Impregnation

More people are utilizing textiles to provide extra protection from the sun. Recently, a number of products, containing nano-sized zinc, have been developed to further improve the UV protection of the textile, but none of these were identified at the Danish market.

2.3.2 Lubricants

Many scientific research papers have been published on the tribological properties of nanoparticles-based lubricants. Results show that they deposit on the rubbing surface and improve the tribological properties of the base oil, displaying good friction and wear reduction characteristics even at concentrations below 2%wt (Hernández Battez, González et al. 2008). Various companies markets nanoparticle lubricant additives, such as molybdenum, silica and borate, and thus, it is likely that nanoparticles are used in lubricant sprays.

2.3.3 Summary

In contrast to the nanotechnology-based aerosol products, the regular aerosol products do not indicate by their product name, product description, lists of ingredients[4] and/or marketing material that they contain nanomaterials. In the preliminary screening, it was found that with the existing definitions of nanomaterials spray paints in general are likely to contain nanomaterials. In addition, a number of regular aerosol products potentially containing nanomaterials have been identified:

- Coatings
  - Paints
  - UV-protection
  - Anti-bacterial
  - Impregnation
- Lubricants

[4] With the exception of cosmetic products

3. Mapping of aerosol products with nanomaterials on the Danish market

The mapping is conducted to gather information on aerosol products with nanomaterials on the Danish market with the purpose of outlining the prevalence of products containing nanomaterials on the Danish market as well as the types and concentrations of nanomaterials in these products.

The mapping is focused on cleaning, impregnation and paints and sunscreens, and it comprises alone products marketed in Denmark or sold on Danish/Danish language internet pages. Companies relevant to the selected product groups were contacted, asking them to complete a short questionnaire (see Appendix 1).

The degree of detail of the questionnaire responses varied a lot, and for some of the responses, only a few of the questions were answered. Some of the completed questionnaires were followed by a telephone interview to clarify further. The full questionnaire scheme is given in Appendix 1.

3.1 Cleaning products

In the mapping, five companies were identified as marketing nanotechnology-based cleaning sprays; two major international companies offering a full product range of cleaning products, coatings, impregnations, etc. for a wide range of applications, and three Danish small-/medium-sized companies solely focusing on nanotechnology-based products. The Danish companies represent the majority of relevant products by number; however, they are mainly sold from internet-based shops. On the other hand, products from the international companies are available from retail stores.

Four of the identified companies were approached with a questionnaire. Two of the three Danish companies responded to the questionnaire, while none of the international companies are represented in the result. Both respondents specifies that none of the identified nanotechnology-based aerosol products contain materials that fall within the applied nanomaterial definition in this survey.

3.2 Impregnation

The Danish impregnation spray market consists of a very large number of importers/manufacturers. In the mapping, six companies were identified as marketing nanotechnology-based cleaning sprays; four international companies and two Danish small-/medium-sized companies. The international companies comprise four companies specialized in textile/shoe impregnation and one company specialized in car care products. The Danish companies comprise two Danish companies solely focusing on nanotechnology-based products for a wide range of applications including impregnation of textiles and building materials.

Company type	Contacts (approached/ responses)	Questionnaires (sent/response)	Marketing sprays w. nanomaterials
Danish	2/1	2/1	1
International	4/2	3/1	1

TABLE 2
OVERVIEW OF ANSWERS OBTAINED FROM QUESTIONNAIRES.

One of the respondents markets two nanotechnology-based aerosol products for coating car glass and car varnish. The respondent specifies that the glass coating spray contains a water-soluble polymer that forms a nanofilm with a thickness of approximately 1-2 nm. Consequently, the glass coating is not a focus product because of the absence of solid nanomaterial in the liquid suspension. On other hand, the respondent specifies that the varnish coating contains 5% silica particles (reaction product of a Stoeber process) with a size of approximately 6 nm. The varnish coating spray is solvent-based and carbon dioxide is used a propellant gas with a typical volume per application of 50 ml. The respondent, however, claims that no aerosol droplets are formed because the product is applied into a foam spray head. According to the respondent, the varnish coating represents a minor share (less than 5%) of the total market for varnish coating in Denmark.

Another respondent markets 12 nano-technology based aerosol products specifies that the most of the products contains nano-sized silica and a few products contains nano-sized titanium dioxide, without specify which of the products that contain silica or titanium dioxide. The respondent does not know the concentration or the particle size distribution of the nanomaterials. According to the respondent, 1/3 of the products are solvent-based and 2/3 of the products are water-based. The solvent-based products are applied on none-absorbent surfaces (e.g., glass, tiles) and the water-based on absorbent surfaces (e.g., textiles). The typical volume per square meter varies between 15-20 ml for the solvent-based and 60-80 for the water-based products. The respondent stresses that the nano-coating hold 6-9 months and that the market for nano-technology based aerosol products makes up less than 1% of the total market.

3.3 Paints and coatings

The Danish paints and coatings market consists of a very large number of importers/ manufacturers. In 2012, 35 companies were registered as manufacturers of paint, varnish and similar coatings, printing inks and mastics (NACE: 203000) and 37 companies were registered as wholesalers of varnish, paint, wallpaper and floor covering, etc. (NACE: 467320). The majority of these companies markets one or more spray paints; consequently, the number of spray paints on the Danish market is expected to be several hundred.

In the mapping, three companies were approached, being two Danish manufacturers of paints and coatings and one international company marketing several coating sprays.
One respondent specified that the company markets four different spray paints/primers for different surfaces, including metal and glass fibre. All four products contain combinations of titanium dioxide, iron oxide, iron hydroxide and carbon black with an average volume-based particle size of 0.2 µm, 0.17 µm, 0.2 µm and 0.03 µm, respectively. However, both titanium dioxide, iron oxide and iron hydroxide may be termed nanomaterials (<100 nm) if applying the number-based particle size distribution conditions according to 2011/696/EU (see textbox section 2.1). According to the respondent, the concentration (%w/w) of titanium dioxide, iron oxide, carbon black and iron hydroxide varies between 1.9-7.3%, 0.1-0.2%, 0.01-0.4% and 0.04-0.7%,

respectively. All four products are solvent-based, use a propellant gas and the typical volume per application vary between 150 and 250 ml.

3.4 Sunscreens

The Danish sunscreen market consists of more than 30 different brands, including large international brands, smaller brands targeted at narrow customer segments and purely Danish brands. Manufacturers most often produce a number of different brands (including private label), and, likewise, importers and retailers offer several brands. In the recent Environmental Project 1603, (2014), it was found that of Danish manufactures focus on sunscreen products with the Nordic Ecolabel 'Svanen', which (since 2011) does not allow nanomaterials. Consequently, none of the Danish manufacturers offer sunscreen with nanomaterials; therefore, three international manufactures of sunscreen spray products were approached with a questionnaire in the mapping. However, only one company responded to the questionnaire. The company is an international manufacturer with two product lines having six and 15 sun products, respectively, of which a total of six are aerosol products. Some of the non-spray products contain nano-sized titanium dioxide; however, according to the respondent the company does not market sunscreen spray products containing nanomaterials on the Nordic market.

3.5 Type of nanomaterials and user groups

In the mapping of aerosol products containing nanomaterials on the Danish market, only impregnation, paints and coatings were identified. These products are used infrequently (once/twice a year) and are mainly used by adults. Moreover, the types of nanomaterials in the identified products are limited to silica, titanium dioxide, iron oxide and iron hydroxide.

3.6 Summary

In the table below the survey findings for the main products types are presented.

Products	Types	Number of companies and products identified	Nanomaterial
Cleaning	Nanotechnology -based pump sprays	7/19	According to the respondents, the products do not contain nanomaterials
Impregnation	Nanotechnology -based pump and propellant sprays	14/52	According to the respondents, some of the products do contain nanomaterial (e.g. silica and titanium dioxide)
Paints and coatings	Regular propellant sprays	72/>100	According to the respondent and literature, pigments may be used in nano-size. 72 companies was registered as manufactures or wholesalers of varnish, paint and coatings (NACE: 203000 & 467320); consequently, the number of spray paints has been estimated to be several hundred.
Sunscreens	Regular pump sprays	>50/1*	Only one sunscreen spray containing nanomaterials has been identified on the Danish market.

* ACCORDING TO THE MANUFACTURES, THE PRODUCT IS NO LONGER MARKETED ON THE DANISH MARKET

TABLE 3

Summary of the survey findings.

4. Risk for consumers exposed to nanomaterials in aerosol products

The purpose of the following chapter is to evaluate whether exposure to aerosol spray products containing solid nanoparticles and available on the Danish market present a specific risk for consumers and to compare with products not containing nanoparticles.

As indicated by the results of the market survey, there seems to be few consumer aerosol products on the Danish market containing solid nanoparticles except in the form of pigments. The results of the marked survey indicated that there are even fewer aerosol products on the market containing propellant gas and a dispensing system that produces an aerosol mist of liquid particles. Some aerosol products are designed to dispense the product as a foam, and are not expected to emit inhalable aerosol. Others are available with manual pumps producing larger droplets than aerosols with pressurised liquids. However, little information is generally available to characterise parameters relevant for exposure estimation such as number of particles in the spray and surface area per mass unit, and aerosol or droplet velocity and size distribution in the spray plume. As larger droplets tend to deposit quickly, it is primarily the smaller aerosols that will be airborne in the breathing zone of the user.

4.1 Exposure to nanoparticles in consumer aerosol products

The aerosol dynamics during spraying with an aerosol product contributes to making exposure assessment a complicated affair. Many parameters describing both the content of the aerosol product, the nozzle / spray dispersing system, the dynamics (aggregation, agglomeration, evaporation, sedimentation, etc.) in the spray plume as well as how the aerosol product is applied need to be considered and sufficient information generally not available for a particular exposure scenario.

Furthermore it needs to be considered that whereas inhalation exposure to nanomaterials in the pure form has been investigated to some extent in animal studies, consumer products containing nanomaterials also contain several other ingredients – some of which may be associated with specific hazardous properties. In addition surface modification / coating of nanoparticles may have an impact on the toxicity and also on the absorption of the particles e.g. through changes in the surface charge. Exposure to particles contained in both nanotechnology based products and regular products will also be affected by the product composition and by the sprayer type. An important factor in relation to exposure assessment is the extent to which agglomeration and deagglomeration of particles in the product and in the aerosol may occur. Agglomerates may also be formed from association of nanoparticles with larger particles resulting in agglomerates that contain a combination of engineered nanoparticles and non-nanomaterials (Salem & Katz (ed.), 2014).

Nanosized aerosol particles may be generated during spraying, even from products not containing nanoparticles in the liquid, and exposure may therefore result from (1) engineered nanoparticles contained in the liquid, (2) nanosized composite particles of nano-objects with other product ingredients, (3) nanoparticles formed from liquid product ingredients in the process of spraying, (4) nanoparticles resulting from evaporation of water or organic solvents from larger droplets, and (5) formation of new nanoparticles from gas-phase chemicals (Salem & Katz (ed.), 2014) or any combination of these.

Another discussion in relation to exposure assessment involving inhalation of nanomaterials is the metrics to be used to express hazard and exposure. Currently there is no scientific agreement regarding the most appropriate dose metrics to be used for exposure and hazard assessment of airborne nanomaterials. Mass is the typical metric used to express toxicological effects and exposure. However, as mentioned by Michel et al. (2013), it is debated whether particle number or surface area should be added, as toxic effects such as inflammation, are likely to be related to the particle surface area. In the ECHA guidance for nanomaterials (ECHA, 2012a) it is also mentioned that metrics such as surface area concentration (cm^2/m^3) and number concentration ($number/m^3$) might be relevant to take into account for the dose/concentration-response characterisation. Particle displacement volume has also been discussed as the critical metric in relation to inhalation of insoluble spherical particulate matter. Overall, a single metric is not likely to be sufficient for characterisation and quantification of all types of nanomaterials. It therefore seems necessary to take the type of nanomaterial, the exposure route, the kinetics, and/or the toxicological / ecotoxicological endpoint into consideration when selecting the most appropriate dose metrics.

Nazarenko et al. (2014) compared quantitative assessments of inhalation exposure for five regular and five nanotechnology-based pump aerosol products and used mass-based aerosol concentrations as an input for the mathematical model used for exposure assessment of cosmetics powder and calculated both the "inhalation exposure" and the "deposited dose", where inhalation exposure is the aerosol mass entering the human respiratory system during an exposure event and the deposited dose is the aerosol mass of all measured particle sizes deposited in the human respiratory system during an exposure event. The reason for using mass-based metrics was that the number-based or surface area-based metrics would not allow adequate representation of the nanomaterial content in the total aerosols where most nano-objects exist in the form of agglomerates. As the investigated consumer aerosol sprays were in non-pressurized containers and were sprayed using a pump-based mechanism, the de-agglomeration processes normally observed for the propellant-based aerosol products were not expected to occur to the same extent.

Dose metrics used for the exposure and risk characterisation of aerosolized particles will in this case be mass (g product) as exposure information on number of particles in the spray plume or surface area is not available for the selected exposure scenarios.

Aerosols in the nano-size range can as mentioned be generated both from aerosols containing nanomaterials, which are the subject of the present report, and by the propellant spray process from products not containing any nanomaterial. Different spray application methods typically produce different size distributions of the generated aerosols. This will have an effect on the particle transport into and through the breathing zone and in the respiratory system. The closer to the breathing zone the product is sprayed the higher inhalation exposure is likely to occur (Salem and Katz (ed.), 2014).

Bekker et al. (2014) have investigated whether personal exposure to manufactured nano-objects (silica particles in the size range 50-100 nm, as well as magnesium oxides, iron and iron oxides , and silica particles in the size range 100-200 nm) contained in the aerosol products can occur at a greater distance than the immediate proximity of the source, defined as > 1 m from the source, or at a period after emission of the spray, in order to identify possible "bystander" or "re-entry" exposure. Results showed that direct reading instruments did not differentiate between the manufactured nano-objects and other nano-sized aerosols and results was therefore influenced by nano-sized liquid aerosols emitted by the propellant gas spray process itself making interpretation difficult.

Overall it was however concluded that exposure could occur at a greater distance (> 1 m) from the source and at a period after emission, although the actual level of nano-objects could not be determined.

Overspray is the portion of the original mass sprayed by an aerosol product that does not stay on the treated surface. Overspray includes both the fraction that bounces back from the treated surface as well as the fraction that does not hit the surface to be treated. The airborne portion represents a risk of exposure to both the applicator and also other persons close to the spraying operation as well as the environment. Airborne overspray may result in inhalation and air-to-skin dermal exposure, and to a lesser degree exposure through ingestion if aerosols entering the throat are swallowed and/or in case of hand-to-mouth behaviour.

Solid aerosol particles are expected to have a higher tendency to bounce off solid surfaces and back into the air compared to liquid aerosols. In order to estimate the potential particulate exposure from overspray, information about e.g. particle size distribution is required (Jayjock, 2012).

An experimental scenario simulating human exposure to aerosol exposure (TiO_2 in propellant spray) released under realistic spraying conditions indicated that most droplets were coarse sizes (CMD=22 µm) immediately after spraying whereas the final aerosol contained primarily solid TiO_2 particles of nano size (75 nm). This is due to the fact that the large droplets deposit on the surface or dry rapidly as the propellant evaporates (Chen et al., 2010). In this connection it is mentioned that the physicochemical properties of the combined aerosol (particle and propellant droplets) can vary through evaporation, condensation, and coagulation as a function of temperature, air ventilation and humidity in the environment. Based on the results and an estimated worst case mass concentration of 3.4 mg/m^3 in the breathing zone (equivalent to a number concentration of 1.6×10^{-5} particles/cm^3), the authors suggest that consumers can be exposed to a significant concentration of airborne TiO_2 nanoparticles when using products containing TiO_2 in an aerosol spray application. The nanoparticle fraction of the aerosol amounted to 170 µg/m^3. It is assumed that the worst case mass concentration was primarily contributed by dry TiO_2 particles.

Aerosols are produced from both pump sprays and propellant sprays, with larger fractions of respirable droplets/particles in the spray from propellant sprays compared to pump sprays. Results from analyses have also shown that a higher propellant volume results in a significantly smaller particle size distribution and in particular an increase in the percentage volume smaller than 10 µm. Droplet size was also shown to change depending on the valve used (Virden, 2014).

Rothe et al. (2011) note that propellant gas sprays typically may produce proportionate respirable particles or droplets <10 µm particle size, whereas pump sprays emit larger droplets in a non-respirable range >10 µm particle size. Industry data suggest that the mean diameter of primary droplets of a pump spray is in the range of 70 µm diameter while <1% is in the respirable range (Rothe et al., 2011). It is not mentioned if the percentage is by weight or by number. Typically the larger particles with aerodynamic diameter >10 µm will deposit in the nose or throat and will not penetrate deeper into the lung. Smaller particles that are not captured in the naso-pharyngial region (>5 µm) will be deposited in the tracheobronchial region, and may be further absorbed or removed by mucociliary clearance. Particles removed from the airways by mucociliary clearance may end up being swallowed, and inhalation exposure to aerosols may therefore also result in oral exposure. The sub-micron particles (<1 µm) and the nanoparticles (< 100 nm) are able to penetrate deep into the alveolar region that does not have the same removal mechanisms as the upper airways (Bakand et al., 2012). Particles may relocate from the lung surface into the pulmonary tissue, where they become accessible to lymphatic drainage and may translocate to the blood stream and subsequently end up in secondary organs (Geiser and Kreyling, 2010). Part of the air and airborne particles will be exhaled without substance retention and the actual dose will therefore depend on this factor.

This factor may vary between 1 % and 100 % but in EU the regulatory default is 75 % by mass. For a worst case scenario the retention is set to 100 %.

4.2 Hazard and risk from nanoparticles in consumer aerosol products

Once in the lungs, the fate of the particles and nano-particles will depend on the physico-chemical properties and other characteristics.

4.2.1 Physicochemical characteristics

It is well known that properties such as size, specific surface area, shape and crystallinity play an important role in the toxicity of nanomaterials together with a number of other characteristics. Important physicochemical parameters for characterisation of nanomaterials are e.g. listed in the SCCS Guidance on the safety assessment of nanomaterials in cosmetics (SCCS, 2012a) and include among others the following:

- Chemical identity (e.g. molecular structure)
- Purity and nature of impurities
- Coatings, surface moieties, doping material, processing chemicals, etc.
- Particle size, particle number size distribution and particle mass size distribution
- Morphology: Physical form and crystalline phase/shape
- Surface characteristics such as surface charge, interfacial tension, reactive sites and surface reactivity
- Solubility
- Surface area
- Catalytic activity
- Density/porosity of granular materials and pour density
- Redox potential
- pH, viscosity, and stability

Other important characteristics related to the spray from aerosolised products with nanomaterials include information on:

- Agglomeration
- Concentration (particle number concentration)
- Size distribution (spatial and temporal profile of aerosol)
- Distance from aerosol source to target

4.2.2 Hazard characteristics

Particles may have an irritative potential, exert systemic toxicity following inhalation, inflammation resulting in cancer and cardiovascular effects, produce respiratory sensitisation, or produce local toxicity in the lower respiratory tract, which is usually associated with insoluble particles.

The lungs have defence mechanisms in the form of macrophages, which are able to take up and initialise breakdown of the poorly soluble particles by phagocytosis as far as the relatively limited capacity allows. Exposure to very high concentrations of particulate matter may result in lung overload, which can lead to chronic inflammation, fibrosis, and eventually be involved in lung tumour formation following long-term exposure (Rothe et al., 2011). In risk assessment the general assumption is that humans are more sensitive than animals, which is reflected in the selection of assessment factors for calculation of human no-effect levels. However, in the case of e.g. poorly soluble, low toxicity dusts, animal species such as rats appear to be more sensitivity to lung overload. Lung inflammation and/or cancer resulting from lung overload may therefore require a lower assessment factor than the generally applied default value due to the relative sensitivities of rats and humans (European Commission, 2010).

Saber et al. (2014) have demonstrated that inhalation of nanoparticles induces a pulmonary acute phase response in mice. The acute phase response generates increased levels of acute phase proteins in blood which are risk factors in the pathogenesis of cardiovascular disease. The acute phase response is in general believed to be beneficial except if the inflammation and the acute phase response becomes chronic. It is defined as the systemic changes in plasma proteins, the so-called acute phase proteins (e.g. serum amyloid A (SAA) and C-reactive protein (CRP)) induced by cytokines released from inflamed areas but also other acute phase phenomena. In spite of the name it accompanies both acute and chronic inflammation. Findings suggesting this association are supported by controlled human exposure studies as well as by epidemiological studies. The authors also provide evidence "that pulmonary inflammation, as measured by the neutrophil influx, is a predictor of the acute phase response and that the total surface area of deposited particles correlates with the pulmonary acute phase response" (Saber et al., 2014).

With regard to particles in a matrix, Smulders et al. (2014) demonstrated that even though direct exposure to engineered nanoparticles (ENP) induced some toxic effects through inhalation exposure in mice, they showed little or no adverse toxicological effect when incorporated in a complex paint matrix. The results were obtained in a study with BALB/c mice investigating the toxic effects and biodistribution of three pristine ENPs (TiO2, Ag, and SiO2) and three aged paints containing ENPs (TiO2, Ag, and SiO2) along with control paints without ENPs, included for comparison. Mice were aspirated in the oropharyngeal region (behind the oral cavity) with ENPs or paint particles (20 µg/aspiration) once a week for 5 weeks and sacrificed either 2 or 28 days post final aspiration treatment. Bronchoalveolar lavage fluid (BALF) was obtained from the animals and systemic blood toxicity was evaluated to ascertain cell counts, induction of inflammatory cytokines, and key blood parameters. In addition, metal concentrations were determined in the lung, liver, kidney, spleen, and heart.

Information and evaluation of dermal penetration and absorption is available for some particulate nanomaterials. Substances such as titanium dioxide, carbon black and zinc oxide which are used in cosmetics in the nano-form have been evaluated by the Scientific Committee on Consumer Safety (SCCS) with the overall conclusion that there is no indication of any skin absorption (SCCS, 2014a; SCCS, 2014b; SCCS, 2012). Silica in nano-form is in the process of being evaluated by SCCS. Studies on skin absorption of metallic nanomaterials such as iron oxide based materials are limited. Baroli et al. (2007) have investigated the penetration ability of iron oxide and iron-based rigid spherical nanoparticles using human full-thickness skin. The results showed that the nanoparticles were able to passively penetrate through the stratum corneum (SC) lipidic matrix and hair follicle orifices and reach the deepest layers of the SC, at the stratum-granulosum-SC interface, and hair follicles. In exceptional cases the particles were found in the viable epidermis. This finding could however be correlated with the surfactant-rich dispersion vehicle and the authors also emphasize that the results should be carefully evaluated and take into account the experimental conditions which could lead to a false positive. No particles were identified in receptor fluids and it was concluded that the nanoparticles were not able to permeate the skin.

There is in general a need for a better understanding of nanoparticle skin absorption through both healthy and damaged skin. However for the nanomaterials mentioned above, no available investigations have been identified demonstrating dermal penetration and systemic absorption of the solid nanoparticles.

Environmental exposure to nanoparticles in aerosol products used outdoors and emitted during the spray process may occur when the aerosols are deposited on soil or enter water courses.

Environmental exposure from the actual spraying process is in general considered to be limited and less of a concern compared to potential human exposure. Secondary exposures from release of nanoparticles during disposal of spray cans containing residues or from the treated products or persons in the case of sunscreens are not considered within the context of the present project.

In a background paper for a coming workshop to discuss regulatory challenges in risk assessment of nanomaterials, ECHA states that there is still a need to determine if and under which circumstances nanomaterials accumulate in the environment and in environmental species (ECHA, 2014).

4.3 Selection of products for exposure and risk evaluation

Based on the results and the information received as part of the survey two products and scenarios were selected to illustrate the risk for the consumers from exposure to aerosols containing nanoparticles from a paint product and an impregnation product:

- Paints and coatings: Indoor/outdoor spray application of a solvent-based paint product to be applied on smaller irregular surfaces from an aerosol can. The paint contains nanosized titanium dioxide, iron oxide, iron oxide hydroxide and zinc oxide. Possible inhalation, dermal and environmental exposure from overspray.
- Impregnation: Indoor spray application of a solvent-based impregnation aerosol product containing nanosized silica and intended for application on non-absorbent surfaces such as glass and tiles. Possible inhalation and dermal exposure from overspray.

Sunscreen products are not considered as no particular information regarding presence of aerosol sprays on the Danish market was identified as part of the survey. It was rather concluded that Danish suppliers tend to avoid spray products, which is also in line with the opinion from the Scientific Committee on Consumer Safety regarding use of nanotitanium dioxide (SCCS, 2014a), the caution suggested by SCCS regarding ZnO nanoparticles in spray applications (SCCS, 2012), and the recommendation in the Opinion on Carbon Black (nano-form) (SCCS, 2014a) to avoid these substances in sprayable cosmetic products.

4.4 Selected toxicity parameters of nanoparticles

Toxicity parameters relevant for the selected exposure scenarios and for the nanoparticles contained in the selected products as identified in the review literature are shown in **Fejl! Henvisningskilde ikke fundet.**.

TABLE 4
RELEVANT TOXICITY PARAMETERS FOR THE SELECTED NANOPARTICLES

Substance (nano)	NOAEC/NOAEL	Comments	Source
Titanium dioxide	Inhal.: 0.5 mg·m^{-3}	Coated material Short term value based on exposure of rats to aerosols for five days at 0.5, 2.0 or 10.0 mg·m^{-3}	Landsiedel, 2014
	Dermal: ND	No dermal penetration has been determined.	SCCS, 2014a
	Oral: 62.5 mg·kg$_{bw}$$^{-1}$·d^{-1}	Mice, intragastric administration, every orther day for 30 days, 0, 62.5, 125 and 250 mg·kg$_{bw}$$^{-1}$·d^{-1} Low acute oral toxicity	SCCS, 2014a
Carbon black	Inhal: 1 mg·m^{-3}	Subchronic studies in rats, mice and hamsters	SCCS, 2014b
	Dermal: ND	Dermal exposure is considered of little concern	SCCS, 2014b
	Oral: >10,000 mg·kg$_{bw}$$^{-1}$	Oral toxicity unlikeluy to be of concern.	SCCS, 2014b

Substance (nano)	NOAEC/NOAEL	Comments	Source
Iron oxide	All routes: ND	No NOAEC/NOAELs have been identified	
Iron oxide hydroxide	All routes: ND	No NOAEC/NOAELs have been identified	
Silica	Inhal: 0.5-10 $mg \cdot m^{-3}$	Rodents. Pulmonary inflammation	ECETOC, 2006
	Dermal: ND	-	-
	Oral: 1500 $mg \cdot kg_{bw}^{-1} \cdot d^{-1}$	Liver effects	Dekkers et al., 2011

ND= no data identified

In Table 5 occupational exposure limits are presented for the selected substances where such values are identified. It should be noted that most of the values are not specific to the nano-form.

TABLE 5
EXAMPLES OF OCCUPATIONAL EXPOSURE LIMITS FOR THE SELECTED NANOPARTICLES

Substance (nano)	Titanium dioxide	Carbon black	Iron oxide	Iron oxide hydroxide	Silica (amorphous)
OEL	REL: 0.3 $mg \cdot m^{-3}$	3.5 $mg \cdot m^{-3}$	3.5 $mg \cdot m^{-3}$	1) ND 2) The DK OEL is 5 $mg \cdot m^{-3}$ for respirable, inert mineral dust	1) 2.0 $mg \cdot m^{-3}$ 2) 1.5 $mg \cdot m^{-3}$ (resp. fraction)
Comment	The recommended exposure limit (REL) is established for worker exposure as a time-weighted average (TWA) concentration for up to 10 hours per day during a 40-hour work week, representing the level that over a working lifetime is estimated to reduce the risk of lung cancer to below 1 in 1000	Not specific to the nano-form	Not specific to the nano-form Calculated as Fe	2) Not specific to the nano-form	Not specific to the nano-form 1) For cas: 1343-98-2 (silicic acid, amorphous, respirable 2) TLV, Norway
Source	1) NIOSH, 2011 2) Danish Working Environment Authority, 2011	Danish Working Environment Authority, 2011	Danish Working Environment Authority, 2011	Danish Working Environment Authority, 2011	1) Danish Working Environment Authority, 2011 2) Norwegian labour inspection, 2011

ND= no data identified

Derived DNEL values for inhalation exposure identified from in the ECHA dissemination tool on the ECHA homepage and not specifically for the nano-form are shown in Table 6. Where more registration dossiers are available, the lowest value is shown. DNEL values have not been identified for the nanoparticles in the reviewed literature.

TABLE 6
IDENTIFIED DNEL VALUES FOR THE BULK FORM OF SELECTED PARTICLES (NOT SPECIFIC TO THE NANO-FORM)

Substance (nano)	Titanium dioxide	Carbon black	Iron oxide	Iron oxide hydroxide	Silica (amorphous)
DNEL (inhal)	10 $mg{\cdot}m^{-3}$ (not specific to nano)	2 $mg{\cdot}m^{-3}$ (not specific to nano) (lowest)	10 $mg{\cdot}m^{-3}$ (not specific to nano)	1) ND 2) Reported as 3 mg/m3 for the pigment grade	4 $mg{\cdot}m^{-3}$ (not specific to nano)
Source	ECHA, 2014	ECHA, 2014	ECHA, 2014	1) Only preregistered under REACH 2) Safety data sheet identified on the Internet (EUCHEMY, 2012)	ECHA, 2014

ND= no data identified

Aschberger and Christensen (2011) suggested an INEL (Indicative No-effect Level) of 17 $\mu g/m^3$ for nano-TiO_2 (21 nm particles) for occupational inhalation exposure based on a NOAEC of 0.5 mg/m^3 obtained from a 13-week inhalation study including assessment of pulmonary responses up to 52 weeks post-exposure. This value is approximately 18 times lower than the REL recommended by NIOSH but is not developed for regulatory purposes.

For the risk evaluation of the two selected exposure scenarios the DNELs presented in Table 7 are suggested.

TABLE 7
SUGGESTED DNEL (INHALATION) VALUES FOR THE NANOPARTICLES TO BE USED IN THE RISK EVALUATION

Substance (nano)	Titanium dioxide	Carbon black	Iron oxide	Iron oxide hydroxide	Silica (amorphous)
DNEL	0.3 $mg{\cdot}m^{-3}$	2 $mg{\cdot}m^{-3}$	10 $mg{\cdot}m^{-3}$	3 $mg{\cdot}m^{-3}$	1.5 $mg{\cdot}m^{-3}$
Comment	The REL for occupational exposure established by NIOSH in 2011 is selected as the most recent value from an authority. This value is based on potential carcinogenic effects.	The identified value reported with the REACH registration dossier for carbon black (CC) is selected. The average primary particle diameter of CC range from 10 to 100 nm.	Iron oxide is reported to have a mass median diameter of approx. 1 µm in the REACH registration dossier. Although the DNEL is not expected to be based on the nano-form it is used in the risk evaluation.	Value for pigment grade identified in the SDS is selected.	The OEL established by Norway is selected as it is lower than the DNEL suggested in the REACH registration dossier.

Penetration of nanoparticles into the outer layers of the stratum corneum, the hair follicles and sweat glands have been observed for some nanoparticles, but no dermal absorption has been demonstrated yet for the nanomaterials mentioned in Table 7. Although no conclusive evidence is available at present, the current understanding is the no significant absorption is expected. Dermal DNEL values for the substances have also not been identified.

4.5 Exposure scenarios

4.5.1 Exposure scenario 1: Paints containing solid nanoparticles

The selected paint product is supplied in an aerosol spray can with a volume of 250 ml containing four different nanoparticles and intended to be used during one event. The product can be used both indoors and outdoors.

In a Tier 1 approach it is assumed that all nanoparticles are is released as airborne particulate into a standard room. This may be due to direct release or to evaporation from a liquid or a solid matrix

The exposure scenario is described as follows:

Activity: Indoors spray painting of propeller and outdrive from a leisure boat.
Location: Small shed of 20 m^3. It is assumed that the propeller and outdrive is removed from the boat while painted.
Approach: Tier 1 screening approach, as a more refined assessment would require information about e.g. the particle size distribution.

4.5.2 Exposure scenario 2: Impregnation product containing solid nanoparticles

The selected impregnation product is supplied in an aerosol spray can with a volume of 300 ml containing one type of nanoparticles and intended to be used indoors.

The exposure scenario is described as follows:
Activity: Indoors spraying of tiles in a bathroom
Location: Bathroom volume of 20 m^3
Approach: Tier 1 screening approach, as a more refined assessment would require information about e.g. the particle size distribution.

4.5.3 Exposure assessment

In appendix 2 the product related parameters relevant for the two exposure scenarios are shown. The table structure is based on the structure developed in relation to the ongoing Danish EPA project regarding "Consumer exposure and risk assessment of nanomaterials in products on the Danish market" and slightly modified to reflect the needs of the present project. Not all parameters as shown are included in the Tier 1 screening assessment.

For scenario 1, data for one of the four aerosol paint products identified through the survey has been added as an example as shown in appendix 3. Information was received as part of the survey or was found in a product data sheet (PDS) or safety data sheet (SDS) available on the Internet.

With regard to the information received from the supplier, only data describing the nanomaterials contained in the aerosol can is available. As no specific data to describe the aerosol generated during use are available, the exposure assessment will be based on a simplified approach using default data and data identified in the literature.

For scenario 2 very little market data are available and input data are therefore estimated, e.g. based on information for paints.

More realistic estimates may be achieved if an exposure assessment is carried out using the ConsExpo 4.0 spray module or the SprayExpo 2.01 which is also available in an MS Excel® worksheet. The SprayExpo worksheet[5] requires the following main input parameters: "the released droplet spectrum, the release rate, the concentration of the active substance, the spatial and temporal pattern of the release process, the vapour pressure of the liquid, the size of the room and the ventilation rate". In the description it is also stated that the path of the sprayer can be explicitly included into the model, and for surface treatment by spraying, a droplet deposition module is incorporated in the program package. This module calculates the fraction of non-impacting droplets (overspray / droplets not reaching the target), which are relevant for human exposure. The SprayExpo worksheet also contains a paint scenario based on use of a pneumatic spray gun. The SprayExpo is especially suited for large room volumes and may therefore be less representative for consumer use. BAuA (Federal institute of Occupational Safety and Health in Germany) who is responsible for the development of the model also notes that SprayExpo underestimates dermal exposure in the majority of cases, but is more representative in the case of room spraying.

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[5] SprayExpo MS Excel ® worksheet: http://www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/SprayExpo.html

However, also regarding input parameters for use of the SprayExpo model the data-availability is limited.

In the NANEX project (Nanex, 2010), the ConsExpo Model has been evaluated using e.g. exposure values for nano–titanium dioxide in sunscreens. Exposures were calculated for sunscreen cream/lotion, sunscreen sprays and sunscreen on lips. Regarding sprays it was concluded that "Based on conservative assumptions, the application of the spray module in ConsExpo indicated that potential very high peak indoor concentrations can occur. This needs further research, as does other spray applications with nanomaterials containing products. It should be noted that existing spray models do not properly account for agglomeration effects."

In appendix 3 an overview of the data describing the two selected scenarios involving a paint and an impregnation spray is presented. Parameters are selected to characterise the worst case exposure situation and the exposed group. Due to limited data availability regarding the aerosols and particles in the spray plume, data from the literature are presented where relevant.

Table 7 provides an overview of the algorithms used to calculate the inhaled concentration and the daily dose resulting from consumer exposure to an aerosol paint or an aerosol impregnation product. As indicated by the description of available data major assumptions need to be made in order to carry out an exposure assessment, and the result must be seen in view of these limitations. However, as a worst case scenario it is assumed that all available particles in the product will remain as nano-sized particulates in the spray plume and that the majority of the airborne overspray will be inhaled. This will greatly overestimate the exposure from the nanoparticles present in the product. It should be stressed that in addition to the nanoparticles contained in the product, the user will be exposed to nanosized aerosols generated during spray application, larger aerosols in the respirable range as well as solvents evaporating from the aerosols and the treated object.

The table also includes the algorithms for risk characterisation as recommended by ECHA. Due to the many uncertainties regarding the actual exposure, the risk calculation can only be considered indicative and not specifically to address the potential problems related to nanomaterials. A more robust estimation would as indicated earlier in this chapter involve information to characterise e.g. the exposure based on particle size distribution, inhalable fraction, mass generation rate, airborne fraction, and weight fraction of the ingredient.

TABLE 8
OVERVIEW OF ALGORITHS USED FOR ESPOSURE AND RISK ASSESSMENT

Parameter	Algorithm	Comment	Source
Exposure and risk estimation, inhalation			
Conc. of nanomaterial in room air/breathing zone (C_{inh})	$C_{inh} = \frac{Q_{prod} \cdot Fc_{prod} \cdot Fo}{V_{room}} \cdot 1000$ [mg·m^{-3}] Q_{prod}: Amount product used per application [g] Fc_{prod}: Weight fraction of product ingredient [g·g^{-1}] V_{room}: Room volume [m^3] Fo: Overspray factor [-]	Tier 1 It is assumed that all nanoparticles in the overspray are evenly distributed in the spray plume.	ECHA (2012b)
Daily inhalatory dose per body weight (D_{inh})	$D_{inh} = \frac{F_{resp} \cdot C_{inh} \cdot IH_{air} \cdot T_{contact}}{BW} \cdot n$ [mg·kg$_{bw}^{-1}$·d^{-1}] F_{resp}: Respirable fraction (default = 1) [-] IH_{air}: ventilation rate of person [m^3·d^{-1}] $T_{contact}$: Duration of contact per event [d] n: mean number of event per day [d^{-1}] BW: Body weight [kg]	Tier 1 Assuming that all nanomaterials are in the respirable fraction.	ECHA (2012b)
Risk characterisation	$RCR = \frac{D_{inh}}{DNEL}$ [-]		ECHA (2012b)

Parameter	Algorithm	Comment	Source
ratio (RCR)			
DNEL if RCR≥1	$DNEL \geq \frac{D_{inh}}{RCR}$ [mg·kg$_{bw}^{-1}$·d^{-1}]	Appropriate DNELs are not available, and therefore the risk is illustrated by the values of the DNEL that, if exceeded, would result in a risk characterisation ration larger than 1.	
Exposure and risk estimation, dermal			
Dermal overspray exposure	No applicable model available		
Dermal load (L_{der})	The external dermal load (L_{der}) and dose (D_{der}) (direct contact) according to Equation R.15-5, and 15-6: $C_{der} = \frac{C_{prod} \cdot 1000}{D}$ [mg·cm^{-2}] $L_{der} = C_{der} \cdot TH_{der}$ [mg·cm^{-2}] C_{der}: Dermal concentration of substance on skin [mg·cm^{-3}] C_{prod}: Concentration of substance in product before dilution [g·cm^{-3}] D: Dilution factor [1 if not diluted] L_{der}: Amount of substance on skin per event [mg·cm^{-2}] TH_{der}: Thickness of product on layer (assumed 0.001 cm) n: Mean number of events per day		ECHA (2012b)
External dermal dose (D_{der})	The external dermal dose (D_{der}) (direct contact) the procedure according to Equation R.15-7: $D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{BW}$ [mg·kg$_{bw}^{-1}$·d^{-1}] D_{der}: Dermal dose [mg·kg$_{bw}^{-1}$·d^{-1}] A_{skin}: Surface of exposed skin (cm^2) BW: Body weight (kg) [60 kg] n: Mean number of events per day		ECHA (2012b)
Risk characterisation ratio (RCR)	$RCR = \frac{D_{der,ext}}{DNEL}$ [-]		ECHA (2012b)
DNEL if RCR≥1	$DNEL \geq \frac{D_{der,ext}}{RCR}$ [mg·kg$_{bw}^{-1}$·d^{-1}]	Appropriate DNELs are not available, and therefore the risk is illustrated by the values of the DNEL that, if exceeded, would result in a risk characterisation ration larger than 1.	

Inhalation exposure:
Calculation of the inhalation exposure at a screening level based on the available data is associated with high uncertainty as no specific information is available regarding the emission characteristics.

However, the daily inhalatory dose is estimated using data presented in appendix 3, the algorithms presented in Table 7, and the following assumptions:

- All nanoparticles are evenly distributed in the overspray, which remain airborne during the exposure period,
- The nanoparticles will immediately be distributed to the room air volume and remain airborne during the exposure time (no deposition),

- All inhaled particles are respirable.

The calculated inhalatory concentrations and doses for nanoparticles included in **scenario 1** are:

Titanium dioxide: $C_{inh} = 170.5\ mg \cdot m^{-3}$ $D_{inh} = 2.3\ mg \cdot kg_{bw}^{-1}\ d^{-1}$

Carbon black: $C_{inh} = 22\ mg \cdot m^{-3}$ $D_{inh} = 0.3\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Iron oxide hydroxide**:** $C_{inh} = 38.5\ mg \cdot m^{-3}$ $D_{inh} = 0.5\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Iron oxide: $C_{inh} = 11\ mg \cdot m^{-3}$ $D_{inh} = 0.15\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

The calculated inhalatory dose for nano-silica included in **scenario 2** is:

Silica: $C_{inh} = 80\ mg \cdot m^{-3}$ $D_{inh} = 0.53\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Detailed calculations are presented in **Fejl! Henvisningskilde ikke fundet.**

Dermal exposure:
Calculation of the external dermal exposure at a screening level based on the available data will be also associated with high uncertainty due to lack of data regarding the emission characteristics.

However, the external daily dermal load was estimated using data presented in appendix 3, the algorithms presented in Table 7, and the following assumption:

- All nanoparticles are evenly distributed in the overspray
- Deposition of a layer of 1 mm thickness on the skin
- Concentration of the nanoparticles are the same in the spray as in the liquid
- The nanoparticles will immediately be distributed to the room air volume and be available for deposition on the skin
- Layer of thickness of aerosol product is 1 mm
- 50 % of hand surface is exposed
- 50 % of head area is exposed

The calculated external dermal doses for nanoparticles included in **scenario 1** are:

Titanium dioxide: $D_{der} = 5\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Carbon black: $D_{der} = 0.64\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Iron oxide hydroxide**:** $D_{der} = 1.1\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Iron oxide: $D_{der} = 0.32\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

The calculated dermal dose for nano-silica included in **scenario 2** is:

Amorphous silica: $D_{der} = 7.3\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Detailed calculations are presented in appendix 4.

4.5.4 Human health risk evaluation

Inhalation exposure

No DNELs specific for the nano-form of the substances were identified in the literature. In order to calculate a risk characterisation ratio relevant for the selected worst case scenarios, industry suggested DNEL values established for workers for the inhalation route have been identified from the information available in the REACH registration dossiers on the ECHA homepage for all substances addressed in the exposure scenarios except iron oxide hydroxide which is only preregistered. These DNEL values are not established specifically for the nano-form of the materials. For carbon black the reported primary particle size is however in the nano-range. For iron oxide hydroxide a DNEL was identified in a safety data sheet for a pigment grade of the substance likely to contain particles with a diameter in the nano range.

In addition to the DNELs, binding or recommended occupational exposure limits have been used as reference values for consumer protection to calculate an alternative risk ratio. For titanium dioxide the recommended exposure limit (REL) suggested by NIOSH for nanoscale TiO2 has been used. For synthetic amorphous silica the Norwegian TLV for respirable amorphous silica has been used as the lowest identified.

The registered carbon black is informed to have a mass median diameter of 12-13 µm.

In Table 9 the calculated risk characterisation values are shown.

TABLE 9
RISK CHARACTERISATION RATIO (INHALATION EXPOSURE)

Titanium dioxide	Carbon black	Iron oxide	Iron oxide hydroxide	Silica
RCR based on DNEL values suggested by industry in the REACH registration dossiers (not specific to the nano-form)				
$RCR = \frac{C_{inh}}{DNEL} = \frac{170.5}{10}$ $\boldsymbol{RCR = 17}$	$\boldsymbol{RCR = \frac{C_{inh}}{DNEL} = \frac{22}{2}}$ $\boldsymbol{RCR = 11}$	$RCR = \frac{C_{inh}}{DNEL} = \frac{11}{10}$ $\boldsymbol{RCR = 1.1}$	$RCR = \frac{C_{inh}}{DNEL^{*)}} = \frac{38.5}{3}$ $\boldsymbol{RCR = 12.8}$	$\boldsymbol{RCR = \frac{C_{inh}}{DNEL} = \frac{80}{4}}$ $\boldsymbol{RCR = 20}$
RCR based on Recommended Exposure levels/OELs for occupational exposure				
$RCR = \frac{C_{inh}}{REL} = \frac{170.5}{0.3}$ $\boldsymbol{RCR = 568}$	$RCR = \frac{C_{inh}}{OEL_{DK}} = \frac{22}{2}$ $\boldsymbol{RCR = 11}$	$RCR = \frac{C_{inh}}{OEL_{DK}} = \frac{11}{5}$ $\boldsymbol{RCR = 2.2}$	$RCR = \frac{C_{inh}}{OEL_{DK}} = \frac{38.5}{5}$ $\boldsymbol{RCR = 7.7}$	$\boldsymbol{RCR = \frac{C_{inh}}{OEL_{NO}} = \frac{80}{1.5}}$ $\boldsymbol{RCR = 53.3}$

*) DNEL for pigment grade

The RCR values calculated for the substances indicate an unacceptable risk for the consumer based on this worst case calculations using both the DNEL values suggested for workers by industry and exposure limits established for occupational exposure. For titanium dioxide it is important to consider that the REL from NIOSH in the calculation is based on an average exposure of up to 10 hours per day during a 40-hour work week over a working lifetime, and that it is established to reduce risks of lung cancer to below 1 in 1,000. Consumer exposure to the type of paint addressed in the exposure scenario 1 is expected to involve maximum 2 - 4 exposure events per year lasting approximately 1 - 2 hours. The risk of chronic effects is therefore considerably reduced. If the DNEL of 10 mg/m^3 established by industry for TiO2 (not specific to the nano-form) is used in the calculation instead of the REL of 0.3 mg/m^3 the resulting RCR is 17.

SINCE THE REFERENCE VALUES USED FOR THE CALCULATION ARE NOT SPECIFIC FOR THE NANO-FORM OF THE SUBSTANCES, THE CONCLUSIONS REGARDING THE RISK FOR THE CONSUMER WOULD BE THE SAME FOR AEROSOL SPRAY PRODUCTS CONTAINING THE NON-NANO FORM OF THE SUBSTANCES. WHEN EVALUATING THE CALCULATED EXPOSURES IT SHOULD BE EMPHASIZED THAT THESE FIGURES REPRESENTING EXPOSURE TO THE PARTICLES CONTAINED IN THE PRODUCT ARE EXPECTED TO BE HIGHLY OVERESTIMATED DUE TO THE ASSUMPTIONS THAT ALL PARTICLES RELEASED FROM THE PRODUCT AND NOT REACHING THE OBJECT TO BE

TREATED, ARE AIRBORNE AND INHALABLE. WITHOUT FURTHER INFORMATION TO CHARACTERISE E.G. THE SPRAY RELEASED FROM THE PRODUCTS AND THE DEPOSITION OF PARTICLES, FURTHER REALISTIC REFINEMENT OF THE CALCULATIONS HAS NOT BEEN CONSIDERED POSSIBLE. A REALISTIC EVALUATION OF THE TOTAL EXPOSURE TO NANOPARTICLES IN THE RELEASED SPRAY SHOULD ALSO CONSIDER THAT AEROSOLS IN THE NANO-RANGE MAY BE GENERATED FROM PRODUCTS NOT CONTAINING SOLID NANOPARTICLES.

However, when drawing this conclusion it should be considered that traditional risk assessment methodologies based on mass metrics show limitations when applied to nanomaterials – and that there is a need for further characterisation of the actual exposure. The main conclusion from the evaluation of the risk related to the specific scenarios involving exposure of the aerosol products investigated in this study is that these products not expected to present a significant risk to the consumer, but that more frequent use may present a risk if the products are used indoors in poorly ventilated room. This would also be the case with similar products containing the substances in non-nano-form. As no specific data were available to characterise the aerosol spray released from the products, it was not possible to address a possible risk related specifically to the nano-properties such as e.g. particle size distribution and surface area of the particles and also not to account for agglomeration/deagglomeration, aggregation and combination of nanoparticles with larger molecules.

Dermal exposure

As no information on dermal absorption is available and no dermal DNEL values have been identified a calculation to estimate the risk is not carried out. In a recent report prepared for Danish EPA on "Occurrence and effects of nanosized titanium dioxide in consumer products" (expected to be published in 2014) an RCR was calculated for a worst case scenario involving daily application of two times 36 g sunscreen lotion containing the maximum allowed amount of nano anatase TiO_2. Based on this result the dermal absorption that would lead to an RCR of 1 was calculated. The DNEL used for the calculation was based on an oral NOAEL value and application assessment factors to account for the various uncertainties. Based on the calculation it was concluded at which level of human dermal absorption an unacceptable risk could occur. The external dermal dose estimated in this worst case scenario with a sunscreen product was almost 60 times the estimated dose in the present paint scenario.

4.5.5 Environmental considerations

The environmental risks associated with nanosized particles in spray paints are linked to the release nanoparticles from overspray into the atmosphere and then onto soil and into water bodies, or in some cases direct exposure to soil or water.

In the selected scenario where the aerosol paint is applied indoors, environmental exposure is considered insignificant.

4.5.6 Uncertainties

Without proper characterisation of the released spray from the aerosol can, the estimated exposure as calculated for the two scenarios is highly uncertain and most likely largely overestimated. Factors that contribute to uncertainty in the calculation are:

- Information on particle size, distribution, aggregation, and agglomeration in the spray cloud is not available
- Characterisation of particles is not available including information about coating and doping of particles
- Airborne exposure concentrations are very conservative as it is assumed that the overspray will be airborne during the exposure period of 1 hour, although effective spraying is estimated to last for 10 minutes.
- It is estimated that all nanomaterials are available at the same concentration as in the liquid

- Poor correlation between the presence of nanosized particles in liquid of consumer aerosol products and the inhalation exposure of the nanosized aerosol fraction
- Experiments with hand spraying have shown that spraying technique has an impact on the concentration and size distribution of the released particles (Nazarenko et al., 2011).

4.6 Human exposure and risk from nanoparticle-based vs. regular aerosol products

In general the application of chemicals by the use of aerosol products should be considered with additional care due to the increased inhalation risk in comparison with other methods of bringing chemicals into use. This is also why it is generally recommended not to use aerosol products in closed rooms without ventilation (Danish EPA homepage).

In order to estimate and compare the exposure and risk from nanoparticle-based and regular consumer sprays, information on a number of factors depending on the composition of the aerosol product, the application method, and the resulting spray plume is required. In addition the metrics to be used to describe the dose must be determined.

Relevant information about the nanoparticles, the aerosols and the spray plume to be obtained include e. g.:

- Composition
- Concentration (particle number concentration)
- Shape
- Size distribution (spatial and temporal profile of aerosol)
- Crystallinity
- Surface area
- Functionalization
- Aggregation/agglomeration
- Evaporation/condensations in the aerosols
- Distance from aerosol source to target
- Etc.

Losert et al. (2014) point out that the experimental setup for measuring release of substances from regular aerosol products cannot directly be used for manufactured Nano-Objects, and their Agglomerates and Aggregates (mNOAA) -containing sprays, because of different measurement methodologies and analytical instrumentations. For regular products, the mass is the analytical focus. For mNOAAs the mass is of less interest, because nanoparticles show high activity even if their contribution to mass is very small and therefore Losert et al. (2104) have focussed on particle size and number in their investigations.

Nazareko et al. (2011) examined five different nanotechnology-based consumer aerosol products along with analogous products, not identified as nanotechnology-based products and termed regular products. The results showed that nano-sized (1-100 nm) particles were present in both the nanotechnology-based products and the regular products. Analysis of the aerosols formed during simulated product application also showed that nano-sized particles were generated from both nanotechnology-based and regular products. The results showed a wide size distribution of aerosolized nanoparticles in the range of 14 nm – 20 μm. The large particles are expected also to include agglomerated nanoparticles. These particles have the potential to be inhaled and deposit in all regions of the respiratory system.

As part of the study it was also shown that different nebulizers produced different concentrations and size distribution of the released particles. Overall the authors concluded that "the data suggest that the use of the investigated nanotechnology-based as well as regular consumer sprays would result in inhalation exposures to single nano-sized particles and multi-sized agglomerates, including complex nanoparticle-containing composites" (Nazarenko et al., 2011)

4.7 Summary

As indicated by the results of the survey, the market share for the products containing nanomaterials addressed in the exposure scenarios is relatively limited, if aerosol products containing pigments are excluded. Thus they could not be expected to present a frequent hazard and possible risk to consumers.

The roughly estimated risk evaluation for the inhalation route demonstrates that there may be an unacceptable risk for the consumer from the exposure calculated for the two selected product types and exposure scenarios. Based on the available information it is not possible to differentiate between products containing solid nanoparticles and products not containing nanoparticles when calculating the risk. Taking the uncertainties into consideration the results indicate that both aerosol spray products containing nanoparticles and aerosol spray products not containing nanoparticles in the formulation could present a risk from inhalation in certain situations where aerosol products are used indoors on surfaces or objects in small rooms with lacking ventilation. It is therefore important to follow the usual recommendations of ensuring ventilation when such products are used.

With the current methodology it is not possible to distinguish between the nano-form and the non-nano-form of the product. Based on the complex dynamics of a spray, interaction between the ingredients and generation of nanoparticles during the spray application process may level out the difference in hazard potential between aerosols containing small amounts on solid nanoparticles and products without nanoparticles in the liquid. There could however be an additional risk associated with other possibly hazardous ingredients contained in the products and nanoparticles generated during use. The complexity of the exposure pattern from aerosol products therefore makes a more reliable risk assessment difficult without a better characterisation of the actual content of the spray plume.

The exposure to nanoparticles in consumer products also adds to the general exposure of the public to ultrafine particles resulting from natural sources of nanoparticles (photochemical reactions, volcanic eruptions, forest fires, erosion, etc.), air pollution from e.g. combustion processes and also particles generated in the indoor climate from candle burning and wood stoves. The exposure to nanoparticles from consumer products covered by the present survey is expected to be low both in terms of frequency and load over the year compared to other sources of nanoparticle exposure.

References

Aschberger K. and Christensen F.M. (2011). Approaches for establishing human health no effect levels for engineered nanomaterials. Nanosafe2010: International Conference on Safe Production and Use of Nanomaterials. Journal of Physics: Conference Series 304 (2011).

Baroli, B. M. G. Ennas, F. Loffredo, M. Isola, R. Pinna and M. Arturo López-Quintela (2007). Penetration of Metallic Nanoparticles in Human Full-Thickness Skin. Journal of Investigative Dermatology (2007) 127, 1701–1712.

Bekker, C., D. H. Brouwer, et al. (2014). "Airborne manufactured nano-objects released from commercially available spray products: temporal and spatial influences." Journal of Exposure Science and Environmental Epidemiology **24**(1): 74-81.

Chen, B. T., A. Afshari, et al. (2010). "Nanoparticles-containing spray can aerosol: characterization, exposure assessment, and generator design." Inhalation toxicology **22**(13): 1072-1082.

Danish EPA homepage. http://mst.dk/groenne-tips/hjemmet/spraymaling/spraymaling---baggrund/ and http://mst.dk/groenne-tips/hjemmet/impraegneringsmidler-paa-spray/

Danish Working Environment Authority (2011). Executive Order no. 507 of 17/05/2011 on Limit Values for Substances and Materials (as amended). (In Danish: Bekendtgørelse om grænseværdier for stoffer og materialer, BEK nr. 507 af 17/05/2011)

Dekkers S, Krystek P, Peters RJ, Lankveld DP, Bokkers BG, van Hoeven-Arentzen PH, Bouwmeester H & Oomen AG. Presence and risks of nanosilica in food products. Nanotoxicology. 2011;5(3):393-405

ECHA (2012a). Guidance on information requirements and chemical safety assessment. Appendix R8-15 Recommendations for nanomaterials applicable to Chapter R-8 Characterisation of dose [concentration] - response for human health.

ECHA (2012b). Guidance on information requirements and chemical safety assessment. Chapter R.15: Consumer exposure estimation Version 2.1 2012.

ECHA (2014). Topical Ccientific Workshop. Regulatory Challenges in Risk Assessment of Nanomaterials 23-14 October 2014. Background paper for the five topics. http://echa.europa.eu/documents/10162/5399565/bp_ws_risk_assessment_nanomaterials_en.pdf

EUCHEMY (2012). Safety Data Sheet for Iron Oxide Yellow. Issue date: 2012-09-01. http://www.euchemy.com/Public/Uploads/MSDS--YELLOW.pdf.

European Commission (2010). 6th meeting of the Competent Authorities Subgroup on Nanomaterials. 14-16 December 2010. Enterprise and Industry Directorate-General.

Geiser M. and Kreying W.G. (2010). Deposition and biokinetics of inhaled nanoparticles. Particle and Fibre Toxicology 2010, 7:2.

Hagendorfer, H., C. Lorenz, et al. (2009). "Size-fractionated characterization and quantification of nanoparticle release rates from a consumer spray product containing engineered nanoparticles." Journal of Nanoparticle Research **12**(7): 2481-2494.

Hernández Battez, A., R. González, et al. (2008). "CuO, ZrO2 and ZnO nanoparticles as antiwear additive in oil lubricants." Wear **265**(3–4): 422-428.

Lambourne, R. and T. Strivens (1999). Paint and surface coatings: theory and practice, Elsevier.

Larsen, S. T., C. Dallot, et al. (2014). "Mechanism of Action of Lung Damage Caused by a Nanofilm Spray Product." Toxicological Sciences.

Lorenz, C., H. Hagendorfer, et al. (2011). "Nanosized aerosols from consumer sprays: experimental analysis and exposure modeling for four commercial products." Journal of Nanoparticle Research **13**(8): 3377-3391.

Michel, K., J. Scheel, et al. (2013). "Risk assessment of amorphous silicon dioxide nanoparticles in a glass cleaner formulation." Nanotoxicology **7**(5): 974-988.

Nanex (2010). Micheletti C., R. Gerritsen et el. Development of Exposure scenarios for Manufactured Nanomaterials. Work package 4. Consumer Exposure Scenarios. Final Report, December 2010.

Nazarenko, Y., T. W. Han, et al. (2011). "Potential for exposure to engineered nanoparticles from nanotechnology-based consumer spray products." Journal of Exposure Science and Environmental Epidemiology **21**(5): 515-528.

Nørgaard, A. W., K. A. Jensen, et al. (2009). "Release of VOCs and Particles During Use of Nanofilm Spray Products." Environmental Science & Technology **43**(20): 7824-7830.

Norwegian Labour Inspection Authority (2011). Regulation on exposure limits for physical and chemical factors in the working environment and infection risk groups for biological agents. (In Norwegian: Forskrift om tiltaksverdier og grenseverdier for fysiske og kjemiske faktorer i arbeidsmiljøet samt smitterisikogrupper for biologiske faktorer. Fastsatt 6. desember 2011 nr. 1358. Sist endret ved forskrift 30. desember 2013 nr.1718.)NIOSH (online). NIOSH Pocket Guide to Chemical hazards. http://www.cdc.gov/niosh/npg/npgd0552.html

ObservatoryNANO (b) (2010). Nanotechnology in Cosmetics.

Osterwalder, U., M. Sohn, et al. (2014). "Global state of sunscreens." Photodermatology, Photoimmunology & Photomedicine **30**(2-3): 62-80.

Quadros, M. E. and L. C. Marr (2011). "Silver nanoparticles and total aerosols emitted by nanotechnology-related consumer spray products." Environmental Science & Technology **45**(24): 10713-10719.

Saber, A.T., N.R. Jacobsen, P. Jackson, S.S. Poulsen, Z.O. Kyjovska, S. Halappanavar, C.L. Yauk, H. Wallin U. Vogel. Particle-induced pulmonary acute phase response may be the causal link between particle inhalation and cardiovascular disease. Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology 2014

SCCS (Scientific Committee on Consumer Safety) (2012) OPINION ON Zinc Oxide (nano-form). Revision of 11 December 2012.

SCCS (Scientific Committee on Consumer Safety) (2012a) Guidance on the safety assessment of nanomaterials in cosmetics. June 2012

SCCS (Scientific Committee on Consumer Safety) (2014a) OPINION ON Titanium Dioxide (nano-form). Revision of 22 April 2014.

SCCS (Scientific Committee on Consumer Safety) (2014b). OPINION ON Carbon Black (nano-form). Revision of 27 March 2014.

Smulders S., Luyts K., Brabants G., Landuyt K.V., Kirschhock C., Smolders E., Golanski L., Vanoirbeek J., Hoet P. HM. (2014): "Toxicity of Nanoparticles Embedded in Paints Compared with Pristine Nanoparticles in Mice." Toxicological Sciences 2014. Advance Access publication June 13, 2014.

Virden A. (2014). The importance of particle size to spray hazard analysis. Regulatory testing for aerosol devices. Spray Technology and Marketing. May 2014-

Appendix 1: Questionnaire

Spray products containing nanomaterials

The questions deal alone with the products ??.

On behalf of the Danish EPA, Danish Technological Institute in collaboration with COWI A/S are carrying out a survey of the Danish market for spray products containing nanomaterials.

The above mentioned products have been identified because the products in name and/or marketing material indicates a content of nanomaterials or use of nanotechnology. In this context, we're asking you to answer, if the given products contain nanomaterials; and, if yes, we ask that you'll answer a few questions on the nanomaterial in your products as best possible.

Should you have any questions please feel free to contact us

We will appreciate that you answer as soon as possible. If we haven't heard from you by 28 April, we'll allow us to contact you again. Please return the questionnaire to: chfi@teknologisk.dk

Definition of a nanomaterial

"a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm."

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Question 1	Yes	No
Are any of the given products (??) containing nanomaterials?		
Question 2		
Which of the given products contain nanomaterials?		

The remaining questions must only be answered for the products listed in question 2. If your answer to question 1 is no, we don't need you to continue to answer the remaining questions.

Question 3
Which type of nanomaterial is used in each of the given products? You may use give trade names and producer of the nanomaterial, if this is relevant/easier.
Question 4
What is the particle size/size distribution of the nanomaterial in each of the given products?
Question 5
In which concentrations are the nanomaterials included in each of the given products?

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Question 6
For each given product, list if the products are water-based or solvent-based?

Question 7
For each of the given products, list if a manual pump of propellant gas is used?

Question 8
How much product is typical used per application of each of the given products (mass or volume)? What is the application time for each of the given products?

Question 9
What is the size of the aerosols/droplets in each of the given products?

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Question 10
How large a marked share would you estimate that each of the given products represent on the Danish marked?

Appendix 2: Product-related data for exposure assessment

Scenario 1: Aerosol spray paint

Parameter	Specified data	Estimated data	Source / comments
General information			
Type of product	Aerosol spray paint		Survey
Physical matrix	Liquid paint, solvent-based with propellant gas		Survey
Name and CAS no. of nanomaterial(s)	TiO2 (13463-67-7) Carbon black (1333-86-4) Iron hydroxide oxide (20344-49-4) Iron oxide (1309-37-1)		Survey
Propellant gas	Dimethylether: 50-75 %		SDS Dimethylether also functions as a solvent and therefore the product in the spray can is not a dispersion (RIVM, 2007).
Particle size of nanomaterials, volume based	TiO2: 0.2 µm Carbon black: 0.03 µm Iron hydroxide oxide: 0.2 µm Iron oxide: 0.17 µm	Number based particle size estimated at < 100 µm	Survey : Average volume-based particle size.
Location of nanomaterial eg. free/ matrix-bound	In liquid matrix		Survey
Primary exposure route(s)	Inhalation, dermal, environmental		Direct contact with unprotected skin without use of PPE – primarily direct, dermal contact with hands and aerosol deposition of overspray. (Exposure to the treated object can also occur, but is not considered further.)
Generation of nanomaterial during use		Aerosols in nano-size may be generated by the spray dispensing system	
Indoor/ outdoor use	Indoor/outdoor		Survey / SDS
Direct/ indirect exposure	Direct and indirect – human and environmental	Direct inhalation and dermal exposure. Indirect from overspray.	
Forseeable misuse	-	Yes	Indoor use without PPE recommended in the SDS and low ventilation. Spraying at a wrong distance from the object increasing overspray.
Release to the environment		Overspray deposited on soil or released to the aquatic environment	If spraying occurs in a closed shed with flooring or on a paved area the environmental exposure from overspray is expected to be limited.
Data used to calculate the external exposure			
Mass concentration of nanomaterials	TiO2: 3.1 % Carbon black: 0.4 % Iron hydroxide oxide: 0.7 % Iron oxide: 0.2 %		Survey Number concentration not available
Package design, volume	250 ml aerosol spray can		Survey (SDS: VOC-content: 829.2 g/l: propellant: 0.373 m^3/l)

Parameter	Specified data	Estimated data	Source / comments
Spreading rate	0.7 m²/500 ml		PDS Theoretical
Specific target group (children, teenagers etc.)		Adults	SDS: The product must not be used professionally by young people below the age of 18
Concentration in air / volume of product released to air		0.5 $g{\cdot}s^{-1}$ 250 ml/10 min (275 g/10 min based on d=1.1 g/cm3)	It is assumed that aerosol can is emptied in 10 minutes. (Typical value for paints: 0.8 $g{\cdot}s^{-1}$ in Steiling et al. (2014));
Duration of application		10 minutes	
Use per application	250 ml		Survey
Duration of exposure	1-2 hours		Survey Actual spraying time is expected to be 10 minutes for a 250 ml spray can
Frequency of exposure	2-4 times yearly		Survey
Overspray		0.4 (worst case)	(EPA, 1987) Overspray is a function of the pressure exerted by the contents of the container, the nozzle diameter, the size and shape of the target, and the size of the particles

Scanario 2: Aerosol impregnation spray

Parameter	Specified data	Estimated data	Source / comments
		General information	
Type of product	Aerosol impregnation spray		Survey
Physical matrix	Liquid, solvent-based with propellant gas		Survey
Name and CAS no. of nanomaterial(s)	Silica (7631-86-9)		Survey (Cas no. not indicated in survey)
Propellant gas		Propane/butane	
Particle size of nanomaterials, volume based	ND	Number based particle size estimated at < 100 µm	
Location of nanomaterial eg. free/ matrix-bound	In liquid matrix		Survey
Primary exposure route(s)	Inhalation, dermal		Direct contact with unprotected skin without use of PPE – primarily direct, dermal contact with hands and aerosol deposition of overspray. (Exposure to the treated tiles can also occur, but is not considered further.)
Generation of nanomaterial during use		Aerosols in nano-size may be generated by the spray dispensing system	
Indoor/ outdoor use	Indoor		Survey
Direct/ indirect exposure	Direct and indirect – human and environmental	Direct inhalation and dermal exposure. Indirect from overspray.	

Parameter	Specified data	Estimated data	Source / comments
Forseeable misuse	-	Yes	Indoor use without PPE recommended in the SDS and low ventilation. Spraying at a wrong distance from the target increasing overspray.
Release to the environment		No direct exposure To water treatment plan when washed off the surface	
Data used to calculate the external exposure			
Mass concentration of nanomaterials		Silica: ≤5%	Survey (estimated from concentration in varnish coating)
Package design, volume		300 ml aerosol spray can	
Spreading rate	15-20 ml/m²		Survey
Specific target group (children, teenagers etc.)		Adults	
Concentration in air / volume of product released to air		0.5 $g \cdot s^{-1}$ 300 ml/10 min (300 g/10 min based on d=1.0 g/cm3)	It is assumed that aerosol can is emptied in 10 minutes. (Typical value for paints: 0.8 $g \cdot s^{-1}$ in Steiling et al. (2014));
Duration of application		10 minutes	
Use per application	4 m² (bathroom), 20 ml/m² 80 ml		Survey
Duration of exposure		0.5 hours	Survey Actual spraying time is expected to be 30 minutes
Frequency of exposure		1 time weekly	
Overspray		0.4 (worst case)	(EPA, 1987) Overspray is a function of the pressure exerted by the contents of the container, the nozzle diameter, the size and shape of the target, and the size of the particles

Appendix 3: Overview of data describing the selected scenarios

Scenario 1: Aerosol spray paint

Physiological parameter	Specified data	Estimated data	Source / comments
Body weight (BW)		60 kg (female)	Nordic Council of Ministers (2011) (According to the SDS the product must not be used professionally by young people below the age of 18)
Ventilation rate (IH_{air})		20 m3/d (light activity)	ECHA (2012)
Amount of product used (Q)		275 g/event	Survey / PDS
Weight fraction of nanomaterial ingredient in product (F_{Cprod})	TiO_2: 0.031 g/g product Carbon black: 0.004 g/g product Iron hydroxide oxide: 0.007 g/g product Iron oxide: 0.002 g/g product		Survey
Room volume (V_{room})/		20 m^3	Indoor scenario: propellant and outdrive detached from the boat and painted indoors. (Worst case: small shed 2×4×2.5 m, own estimation)
Room ventilation		1 h^{-1}	ECHA (2012) Conservative default is 0.2 h^{-1}. However for a shed a conservative estimate is expected to be 1 h^{-1}.
Respirable conc. in breathing zone (C_{resp})	-	mg/m^3	No measurements available. Worst case: all nanoparticles in the product are available in respirable form.
Respirable fraction in breathing zone (F_{resp})		1	ECHA (2012) Conservative default
Conc. of nanomaterial in room air/breathing zone (C_{inh})		mg/m^3	1st tier: Weight of ingredient in released spray formulation divided by room volume
Overspray factor (Fo)		0.4	
Exposure time ($T_{contact}$)	1 hour		Survey (1-2 hours)
Frequency (FQ)		2-4 events/year	Survey
Lung retention		1	As worst case it is assumed that all inhaled particles will stay in the lungs
Skin surface in contact with product		50% of hands and face surface area	ECHA (2012): Mean surface area (Mean surface area in cm^2 according to Nordic Council of Ministers, 2011) **Hands:** ♂: 840 cm^2 (1070) ♀: 731 cm^2 (890) **Head (face):** ♂: 1180 cm^2 (1360) ♀: 1028 cm^2 (1140) **Total:**

Physiological parameter	Specified data	Estimated data	Source / comments
			♂: 2020 cm² (2430) ♀: 1759 cm² (2030)

Scenario 2: Aerosol impregnation spray

Scenario: Aerosol spray paint			
Physiological parameter	**Specified data**	**Estimated data**	**Source / comments**
Body weight (BW)		60 kg (female)7	Nordic Council of Ministers (2011) (According to the SDS the product must not be used professionally by young people below the age of 18)
Ventilation rate (IH_{air})		20 m3/d (light activity)	ECHA (2012)
Amount of product used (Q)		275 g/event	Survey / PDS
Weight fraction of nanomaterial ingredient in product (F_{Cprod})	Silica: 0.05 g/g product		Survey
Room volume (V_{room})/		10 m³	Indoor scenario: treatment of tiles (Bathroom 2×2×2.5 m, own estimation)
Room ventilation		0.2 h⁻¹	ECHA (2012) Conservative default is 0.2 h⁻¹.
Respirable conc. in breathing zone (C_{resp})	-	mg/m³	No measurements available. Worst case: all nanoparticles in the product are available in respirable form.
Respirable fraction in breathing zone (F_{resp})		1	ECHA (2012) Conservative default
Conc. of nanomaterial in room air/breathing zone (C_{inh})		mg/m³	1st tier: Weight of ingredient in released spray formulation divided by room volume
Overspray factor (Fo)		0.4	
Exposure time ($T_{contact}$)		0.5 hour	Survey (1-2 hours)
Frequency (FQ)		1 event/week	
Lung retention		1	As worst case it is assumed that all inhaled particles will stay in the lungs
Skin surface in contact with product		50% of hands and face surface area	ECHA (2012): Mean surface area (Mean surface area in cm² according to Nordic Council of Ministers, 2011) **Hands:** ♂: 840 cm² (1070) ♀: 731 cm² (890) **Head (face):** ♂: 1180 cm² (1360) ♀: 1028 cm² (1140) **Total:** ♂: 2020 cm² (2430) ♀: 1759 cm² (2030)

Appendix 4: Exposure calculations

Scenario 1: Aerosol spray paint
Inhalation

Titanium dioxide:

$$C_{inh} = \frac{Fo \cdot Q_{prod} \cdot Fc_{prod}}{V_{room}} \cdot 1000\ [mg \cdot m^{-3}] = \frac{0.4 \cdot 275 \cdot 0.031}{20} \cdot 1000 = 170.5\ mg \cdot m^{-3}$$

$$D_{inh} = \frac{F_{resp} \cdot C_{inh} \cdot IH_{air} \cdot T_{contact}}{BW} \cdot n\ [mg \cdot kg_{bw}^{-1} \cdot d^{-1}] = \frac{1 \cdot 170.5 \cdot 20 \cdot 0.04}{60} \cdot 1 = 2.3\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$$

Carbon black:

$$C_{inh} = \frac{Fo \cdot Q_{prod} \cdot Fc_{prod}}{V_{room}} \cdot 1000\ [mg \cdot m^{-3}] = \frac{0.4 \cdot 275 \cdot 0.004}{20} \cdot 1000 = 22\ mg \cdot m^{-3}$$

$$D_{inh} = \frac{F_{resp} \cdot C_{inh} \cdot IH_{air} \cdot T_{contact}}{BW} \cdot n\ [mg \cdot kg_{bw}^{-1} \cdot d^{-1}] = \frac{1 \cdot 22 \cdot 20 \cdot 0.04}{60} \cdot 1 = 0.3\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$$

Iron oxide hydroxide**:**

$$C_{inh} = \frac{Fo \cdot Q_{prod} \cdot Fc_{prod}}{V_{room}} \cdot 1000\ [mg \cdot m^{-3}] = \frac{0.4 \cdot 275 \cdot 0.007}{20} \cdot 1000 = 38.5\ mg \cdot m^{-3}$$

$$D_{inh} = \frac{F_{resp} \cdot C_{inh} \cdot IH_{air} \cdot T_{contact}}{BW} \cdot n\ [mg \cdot kg_{bw}^{-1} \cdot d^{-1}] = \frac{1 \cdot 38.5 \cdot 20 \cdot 0.04}{60} \cdot 1 = 0.5\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$$

Iron oxide:

$$C_{inh} = \frac{Fo \cdot Q_{prod} \cdot Fc_{prod}}{V_{room}} \cdot 1000\ [mg \cdot m^{-3}] = \frac{0.4 \cdot 275 \cdot 0.002}{20} \cdot 1000 = 11\ mg \cdot m^{-3}$$

$$D_{inh} = \frac{F_{resp} \cdot C_{inh} \cdot IH_{air} \cdot T_{contact}}{BW} \cdot n\ [mg \cdot kg_{bw}^{-1} \cdot d^{-1}] = \frac{1 \cdot 11 \cdot 20 \cdot 0.04}{60} \cdot 1 = 0.15\ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$$

Dermal

Titanium dioxide:

$$C_{der} = \frac{C_{prod} \cdot 1000}{\mathrm{D}}\ [\mathrm{mg \cdot cm^{-3}}] = \frac{0.034 \cdot 1000}{1} = 34\ \mathrm{mg \cdot cm^{-3}}$$

$$L_{der} = C_{der} \cdot TH_{der}\ [\mathrm{mg \cdot cm^{-2}}] = 34 \cdot 0.01 = 0.34\ \mathrm{mg \cdot cm^{-2}}$$

$$D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{\mathrm{BW}}\ [\mathrm{mg \cdot kg_{bw}^{-1} \cdot d^{-1}}] = \frac{0.34 \cdot 1759 \cdot 0.5 \cdot 1}{60} = 5\ \mathrm{mg \cdot kg_{bw}^{-1} \cdot d^{-1}}$$

Carbon black:

$$C_{der} = \frac{C_{prod} \cdot 1000}{\mathrm{D}}\ [\mathrm{mg \cdot cm^{-3}}] = \frac{0.0044 \cdot 1000}{1} = 4.4\ \mathrm{mg \cdot cm^{-3}}$$

$$L_{der} = C_{der} \cdot TH_{der}\ [\mathrm{mg \cdot cm^{-2}}] = 4.4 \cdot 0.01 = 0.044\ \mathrm{mg \cdot cm^{-2}}$$

$$D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{\mathrm{BW}}\ [\mathrm{mg \cdot kg_{bw}^{-1} \cdot d^{-1}}] = \frac{0.044 \cdot 1759 \cdot 0.5 \cdot 1}{60} = 0.64\ \mathrm{mg \cdot kg_{bw}^{-1} \cdot d^{-1}}$$

Iron oxide hydroxide:

$C_{der} = \frac{C_{prod} \cdot 1000}{D}$ [mg·cm-3] = $\frac{0.0077 \cdot 1000}{1} = 7.7$ mg·cm-3

$L_{der} = C_{der} \cdot TH_{der}$ [mg·cm-2] = $7.7 \cdot 0.01 = 0.077$ mg·cm-2

$D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{BW}$ [$mg \cdot kg_{bw}^{-1} \cdot d^{-1}$] = $\frac{0.077 \cdot 1759 \cdot 0.5 \cdot 1}{60} = 1.1$ $mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Iron oxide:

$C_{der} = \frac{C_{prod} \cdot 1000}{D}$ [mg·cm-3] = $\frac{0.0022 \cdot 1000}{1} = 2.2$ mg·cm-3

$L_{der} = C_{der} \cdot TH_{der}$ [mg·cm-2] = $2.2 \cdot 0.01 = 0.022$ mg·cm-2

$D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{BW}$ [$mg \cdot kg_{bw}^{-1} \cdot d^{-1}$] = $\frac{0.022 \cdot 1759 \cdot 0.5 \cdot 1}{60} = 0.32$ $mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Scenario 2: Impregnation spray
Inhalation

$$C_{inh} = \frac{Fo \cdot Q_{prod} \cdot Fc_{prod}}{V_{room}} \cdot 1000 \ [mg \cdot m^{-3}] = \frac{0.4 \cdot 80 \cdot 0.05}{20} \cdot 1000 = 80 \ mg \cdot m^{-3}$$

$$D_{inh} = \frac{F_{resp} \cdot C_{inh} \cdot IH_{air} \cdot T_{contact}}{BW} \cdot n \ [mg \cdot kg_{bw}^{-1} \cdot d^{-1}] = \frac{1 \cdot 80 \cdot 20 \cdot 0.02}{60} \cdot 1 = 0.53 \ mg \cdot kg_{bw}^{-1} \cdot d^{-1}$$

Dermal

Amorphous silica:

$C_{der} = \frac{C_{prod} \cdot 1000}{D}$ [mg·cm-3] = $\frac{0.05 \cdot 1000}{1} = 50$ mg·cm-3

$L_{der} = C_{der} \cdot TH_{der}$ [mg·cm-2] = $50 \cdot 0.01 = 0.50$ mg·cm-2

$D_{der} = \frac{L_{der} \cdot A_{skin} \cdot n}{BW}$ [$mg \cdot kg_{bw}^{-1} \cdot d^{-1}$] = $\frac{0.5 \cdot 1759 \cdot 0.5 \cdot 1}{60} = 7.3$ $mg \cdot kg_{bw}^{-1} \cdot d^{-1}$

Nanomaterials in Commercial Aerosol Products on the Danish Market

Rapporten undersøger udbredelsen af aerosol-produkter, hvor nanomaterialer indgår i den væske, som bringes på sprayform. Der er fundet meget få aerosolprodukter med nano på det danske marked. Man har dog har fundet nogle rengøringsprodukter, imprægneringsprodukter og maling. Mange produkters nanoindhold er i form af almindelige pigmenter, som er i nanostørrelse. En simpel risikoevaluering tyder på, den samme risiko for aerosolprodukter med og uden nano. Begge kan udgøre en risiko, hvis de anvendes indendørs i uventilerede rum. Derfor gælder det generelt om at undgå spray-produkter og om nødvendigt kun at bruge sprays udendørs, eller lufte kraftigt ud.

The report examines the use of aerosol products where nanomaterials are part of the liquid to be brought in spray form. Very few aerosol products with nano are found on the Danish market. The identified products were: cleaning products, waterproofing products and paint. The nano content in many of the products is in the form of ordinary pigments which are nano-sized. A simple risk assessment suggests the same risk profile of aerosol products with and without nano. Both can pose a hazard if used indoors in unventilated spaces. Hence, the use of spray products should in general be used outdoors or in ventilated rooms.

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