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Supplementary Survey of Products on the Danish Market Containing Nanomaterials

Part of the "Better control of nano" initiative 2012-2015

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Supplementary Survey of Products on the Danish Market Containing Nanomaterials

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Foreword

The project *Supplementary survey of products on the Danish market containing nanomaterials* has been carried out from January 2013 to January 2014.

The report describes the project results within the product groups that will not be included in the coming Danish Nanoproduct Register[1]. These include food and feed, food packaging and food contact materials, cosmetics, pesticides, medical devices and water treatment systems. This includes a mapping of the prevalence of products within the selected groups containing possible nanomaterials on the Danish market, a literature survey identifying nanomaterials and products containing them within the product groups, use and users of the products as well as an assessment of the future use of nanomaterials in the selected product groups.

The project was initiated by identifying relevant nanomaterials and the products, in which they are used, according to literature, i.e. surveys, reports, scientific studies, etc. Subsequently, the mapping was initiated by identifying mainly relevant Danish companies and trade associations, followed by an interview with them on their possible use of nanomaterials. The knowledge gained has been assessed and outlined; however, it was acknowledged that the general knowledge of nanomaterials in the products was often limited. Eventually, the future use of nanomaterials in the respective product groups was evaluated based on responses from the mapping and current research focuses.

The project was carried out by Danish Technological Institute and has been headed by M.Arch. Kathe Tønning and MSc, PMP Gitte Sørensen as project manager and scientific manager, respectively, with significant contributions from MSc Christian Holst Fischer and MSc Henrik Vejen Kristensen.

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

Katrine Bom, the Danish EPA
Flemming Ingerslev, the Danish EPA
Vivi Johansen, the Danish EPA
Kathe Tønning, Danish Technological Institute
Gitte Sørensen, Danish Technological Institute

The project was financed by the Danish Finance Act, Agreement 2012-2015 on Better Control of Nanomaterials and their Safety ("Bedre styr på nano").

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[1] Draft Order on a register of mixtures and articles that contain nanomaterials as well as the requirement for manufacturers and importers to report to the register.
Issued pursuant to Article 42 of the Chemicals Act.

Summary

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 objective of the survey is to identify and map nanoproducts that are not included in the Danish Nanoproduct Register to gain knowledge of the prevalence, use and user groups as well as anticipated future prevalence of nanoproducts on the Danish market within the identified product groups. Exposure evaluations and risk assessments of the nanoproducts are not part of this survey.

The survey comprises the product groups: food and feed, food contact materials, cosmetics (colorants, UV filters and preservatives), pesticides, medical devices and water treatment systems. The mapping of the product groups available on the Danish market covers products containing materials that are defined as a nanomaterial according to the nanomaterial definition recommended by the European Commission. The literature review includes Danish, European and, when relevant, international occurrences of nanomaterials in products of each product group.

In this survey, a nanomaterial is defined according to the Recommendation of the EU Commission on the definition of nanomaterials (2011/696/EU), which may differ from the definitions used for specific product groups. Notably, it is important to recognize that the recommended definition includes particulate materials as nanomaterials when more than 50 % of the particles are in the nano range (1-100 nm) using the number-based particle size distribution: A volume- or mass-based size distribution is frequently used in other definitions. Also, aggregates and agglomerates of such particles are included in the definition used in this context. These parameters may mean that more materials than usually termed nanomaterials in the respective regulations are included in this survey. In addition, the mapping of the prevalence of products with nanomaterials on the Danish market includes materials that may or may not be nanomaterials, depending on e.g. the grades used or when the exact particle size distribution is not known. For this reason many of the listed products might, but do not necessarily contain nanomaterials.

Food and feed

The food and feed industries are uncertain whether they use nanomaterials in their products; mainly because of the lack of a generally accepted definition and the fact that they do not know the number-based particle size distribution. According to the Danish Veterinary and Food Administration, no food products containing nanomaterials have been approved for the Danish market. This is not necessarily contradictive to the overview of materials presented below. This can only be indicative and is dependent on the specific definition of a nanomaterial, and it includes a wider range of materials compared to the specific food-related EU-definition of a nanomaterial, which has recently been proposed by the EU-Commission and which states that traditionally used additives are excluded.

In the literature, a number of products containing potential nanomaterials have been identified, and the possible nanomaterials include silica, titanium dioxide, carbon black and other colour additives as well as carrier systems, which may be used in e.g. dairy, hot and cold drinks, confectionary, poultry as well as some may be used in feed products. The future use of nanomaterials, specifically new and/or engineered nanomaterials, in food and feed is highly dependent on legislation; however, if approved, the use is expected to slowly increase in the future.

For food, the identified additives are used as colour, carrier, etc. in a wide variety of products, including all processed food such as dairy, confectionary, baked goods, beverages and seasonings. The products contain in the range from insignificant amounts (<< 0.01 %) up to 1 % of the additive, and the products are part of a normal human diet for all age groups.

MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH FOOD INDUSTRY.

Material	Product(s)	Function(s)	Amount
Silicon compounds (e.g. silicon dioxide), silicates	Widely used (e.g. canned food and vegetables)	Anticaking, purifier, antifoaming, aroma carriers, thickener	N/A
Calcium carbonate	Widely used	Colour, stabiliser, anticaking	N/A
Natural colorants/ pigments (e.g. anthocyanins, beetroot, cochineal, chlorophyll, carotenoids)	Widely used (juice, beer, wine, meat, dairy, confectionary)	Colour	Varies
Titanium dioxide	Confectionary (e.g. gum, biscuits, chocolate)	Surface coating/colour	Approx. 0.01-5 µg/mg

Overall, the feed industry assumes that the feed contains no nanomaterials, primarily based on their focus on avoiding dust due to legislation on health and safety at work. However, their products may contain aggregates or agglomerates of nanoparticles and, thereby, formally be covered by the general nanomaterial definition. The identified additives illustrated below are used in feed products in general and are contained in concentrations from <<1 % to 4 %.

MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH FEED INDUSTRY.

Material	Product(s)	Function(s)	Amount
Silicon compounds, silicates	General livestock feed, including pressed feed flakes and pellets; premixtures	Carrier	Approx. 1 mass%
Calcium carbonate, calcium phosphate	General livestock feed; fish feed	Nutrient, carrier	Approx. 1-4 mass%
Metal salts and oxides (ferric oxide, trace elements: Cu, Zn, Mn, Co)	General livestock feed; fish feed	Nutrients	<< 1 mass%
Amino acid chelate of trace elements	General livestock feed	Nutritional additive	<< 1 mass%
Colorants/pigments (e.g. carotenes, astaxanthin)	General livestock feed (particularly for egg-laying hens); fish feed	Colour	<< 1 mass%

Food contact materials
Nanomaterial and nanotechnology applications for food contact materials are rapidly becoming a commercial reality, and in the literature, a number of products containing potential nanomaterials have been identified. However, in Europe, the introduction of nano-enabled food contact materials is slow due to legislative restrictions and slow consumer acceptance. Currently, only three materials with primary particles in the nano-size range (synthetic amorphous silicon dioxide, titanium nitride and carbon black) have been authorized for use in plastic materials and objects in contact with food on the European market.

Interviews with Danish producers of food packaging (including plastic containers, films and paper packaging) reveal no use of nanomaterials in food contact materials; nevertheless, some respondents from the industry note that there might be nanomaterials in pigments, glue, polymer and paper used for labelling and wrapping, but they cannot specify the type of materials included.

Kitchenware and various electronic devices (e.g. refrigerators, freezers and coffee machines) deliberately containing nanomaterials (nano silver) have been brought to market; however, at the time of the mapping, none of these products could be identified on the Danish market. This corresponds to findings in the interviews, showing that kitchenware and various electronic devices with nanomaterials have been withdrawn from the European market. It is considered to be very likely that pigments such as carbon black and titanium dioxide are used in plastic components and coatings/lacquers in kitchen appliances.

Cosmetics
Since nanomaterials used as colorants, UV filters or preservatives are exempted from part of article 16 in the regulation on cosmetic products, these have been the key focus in this survey on cosmetics. Numerous pigments used in cosmetics can be defined as nanomaterials, depending on the method of measurement for particle size and surface area. These pigments include (but are not limited to) iron oxides, carbon black and aluminium hydroxide. Carbon black (nano) is used in mascara and eyeliner in concentrations <3 % for coloring; titanium dioxide (anatase) is used in face powder, foundation and sunscreens as a UV filter in concentrations of <5 %, and both carbon black and titanium dioxide is used in nail polish for coloring purposes in concentrations of 2-3 %.

Interviews with Danish cosmetic producers indicate a decrease in the use of nanomaterials in cosmetic products; however, the use of nanomaterials as pigments, UV absorbers and preservatives is expected to continue, but is dependent on the authorisation of pigments, UV absorbers and preservatives in Annex IV-VI of (EC) 1223/2009.

MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH COSMETICS INDUSTRY.

Material	Product(s)	Function(s)	Amount
Titanium dioxide	Sunscreens; face powder; foundation; nail polish	UV filter	<5 %
Carbon black	Make-up; eyeliner; mascara; nail polish	Colorant	< 3 %
Iron oxides	Make-up	Colorant	N/A
Aluminium hydroxide	Make-up	Colorant	N/A

Pesticides
According to the definition applied in this survey, no commercial pesticides with nanomaterials have been identified on the Danish market; however, literature describes a number of potential applications of nanomaterials in pesticide products. The application of pesticide nano-formulations provides new (more) methods for protection against degradation, controlled release and increased solubility of the active ingredients. Nano-pesticides within the agrochemical sector are emerging, and many predict a rapid growth in the coming years. More than 3,000 patents dealing with nano-pesticides have been submitted during the last decade.

Medical devices
Many nanomaterials are emerging and used in medical devices, and some are identified in products on the Danish market, as is seen from the table below. The nanomaterials offer a number of effects that may be beneficial for the medical devices, and the literature gives examples like plaster and wound dressings, ostomy bags and catheters, dental fillings, glue and implants, composite polymers and glue as well as contrast agent. The products may contain e.g. silver compounds, zinc oxide or titanium dioxide for an antimicrobial effect, calcium alginate for moist absorption, silicates, zirconium dioxide, iron oxide or pigments. Most products are used by healthcare professionals for treatment of patients, where the medical devices are in direct contact with the patient's body. In the future, the use of the identified as well as several emerging and new nanomaterials is expected to increase significantly, if legislation will continue to allow it.

MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH MEDICAL DEVICE INDUSTRY.

Material	Product(s)	Function(s)	Amount*
Silicates	Dental fillings, glue and implants	Mechanical properties	10-20 %
Zirconium dioxide (zirconia)	Dental fillings, glue and implants	Mechanical properties	10-20 %
Silver	Wound dressings and plasters	Antibacterial	N/A
Calcium alginate	Wound dressings and plasters	Carrier and moist absorbent	N/A
Copper	Ostomy bags	Filter	<0.0001 %
Zinc oxide	Plasters, wound dressings, ostomy bags	Pigment and adhesion	0.1-20 %
Iron oxide	Polymer devices	Pigment	<0.2 %
Titanium dioxide (anatase)	Ostomy and incontinent devices , plasters	Pigment	0.001-0.5 %

* *Information was provided by producers as mass concentration of the entire device.*

Water treatment
On the Danish market, photocatalytic UV-irradiation systems with titanium dioxide nanoparticles as a catalyst have successfully been implemented in a small number of public swimming facilities, and large-scale systems for treating ballast water have been on the market for several years. Water-treatment products with nanosilver are marketed online and may be imported.

Solar photocatalytic water treatment plants are at a demonstration phase and pilot projects for drinking water purification in developing countries are being tested. Incorporation of nanomaterials in the membrane has been shown as a possible solution to the fouling challenges and is expected to be more prevalent in the near future. Adsorbents exploiting the large surface-to-mass ratio of nanomaterials are heavily explored, and, while some commercial products are already available, an increased use of nano-adsorbents in water treatment is expected.

MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH WATER TREATMENT INDUSTRY.

Material	Product(s)	Function(s)	Amount
Titanium dioxide	UV irradiation systems	Removal of pathogens and trace contaminants	N/A
Silver	Disinfection	Antimicrobial	N/A

Sammenfatning

Denne rapport indgår i rækken af projekter under indsatsen ”Bedre styr på nano”, som administreres af Miljøstyrelsen.

Formålet med kortlægningen er at identificere og kortlægge nanoprodukter, som ikke er en del af nanoproduktregisteret, så kendskab til nanoprodukters udbredelse, brug og brugere samt den formodede fremtidige udbredelse på det danske marked inden for de identificerede produktgrupper opnås. Eksponerings- og risikovurderinger af nanoprodukterne udgør ikke en del af denne undersøgelse.

Kortlægningen omfatter følgende produktgrupper: Fødevarer og foder, fødevarekontaktmaterialer, kosmetik (farvestoffer, UV-filtre og konserveringsmidler), pesticider, medicinsk udstyr og vandbehandlingssystemer. Kortlægningen af produktgrupper tilgængelige på det danske marked omfatter produkter indeholdende materialer, der er defineret som et nanomateriale ifølge Europa-Kommissionens anbefaling til definition af et nanomateriale. Litteraturgennemgangen omfatter danske, europæiske og, hvis relevant, internationale forekomster af nanomaterialer i produkter fra hver produktgruppe.

I denne undersøgelse defineres et nanomateriale i henhold til Europa-Kommissionens definition (2011/696/EU), som kan være forskellig fra specifikke produktgruppers definition. Det er især vigtigt at bemærke, at partikulært materiale indgår i definitionen af nanomateriale, når mere end 50 % af partiklerne er i nanostørrelse (1-100 nm) ved anvendelse af den antalsbaserede partikelstørrelsesfordeling. Dette til forskel fra andre definitioner, hvor den volumen- eller massebaserede partikelstørrelsesfordeling anvendes. Endvidere indgår aggregater og agglomerater af sådanne partikler i EU-definitionen. Dette kan betyde, at flere materialer end normalt omfattet af betegnelsen nanomaterialer i de respektive lovgivninger indgår i denne undersøgelse. Derudover omfatter kortlægningen af produkter med nanomaterialer på det danske marked materialer, som kun *muligvis* er nanomaterialer, afhængig af fx kvaliteten eller den nøjagtige partikelstørrelsesfordeling for den specifikke råvare. Derfor *kan* mange af de identificerede produkter indeholde nanomaterialer, men gør det ikke nødvendigvis.

Fødevarer og foder
Fødevare- og foderindustrien er usikre på, hvorvidt nanomaterialer bruges i produkter. Det skyldes især manglen på en generelt accepteret definition af nanomaterialer og at den antalsbaserede partikelstørrelsesfordeling ikke kendes. I henhold til Videncentret for Dyrevelfærd under Fødevarestyrelsen er ingen fødevarer indeholdende nanomaterialer blevet godkendt til det danske marked. Dette er ikke nødvendigvis i modstrid med oversigten over materialer nedenfor. Oversigten er kun vejledende og afhænger af den specifikke definition af et nanomateriale. Den indeholder et bredere udvalg af materialer sammenlignet med den specifikke EU-definition af et nanomateriale relateret til fødevarer, som er foreslået af EU-Kommissionen for nylig og som angiver, at traditionelle additiver er udeladt.

I litteraturen beskrives en række produkter, som indeholder mulige nanomaterialer, og disse inkluderer silika, titandioxid, carbon black og andre farvetilsætningsstoffer samt bærematerialer, som kan anvendes i fx mejeriprodukter, kolde og varme drikke, konfekture og fjerkræ samt nogle enkelte i foderprodukter. Den fremtidige brug af nanomaterialer (især nye og/eller industrielt fremstillede nanomaterialer i fødevarer og foder) afhænger meget af lovgivningen; hvis de godkendes, forventes en langsom stigning i deres fremtidige anvendelse.

I forbindelse med fødevarer bruges de identificerede tilsætningsstoffer som farvestoffer, bærematerialer osv. i mange forskellige produkter, herunder i alle industrielt behandlede fødevarer såsom mejeriprodukter, konfekture, bagte produkter, drikkevarer og krydderier. Tilsætningsstofferne findes i meget små koncentrationer (<< 0,01 %) og op til 1 %, og de indgår i den daglige kost for alle aldersgrupper.

MATERIALER (DER ANSES FOR AT VÆRE ET NANOMATERIALE) IDENTIFICEREDE I DEN DANSKE FØDEVAREINDUSTRI.

Materiale	Produkt(er)	Funktion(er)	Mængde
Siliciumforbindelser (fx siliciumdioxid), silikater	Meget udbredt (fx dåsemad og grøntsager)	Antiklumpning, renser, antiskummiddel, aromabærere, fortykker	N/A
Calciumkarbonat	Meget udbredt	Farve, stabilisator, antiklumpning	N/A
Naturlige farvestoffer/ pigmenter (fx antocyanin, rødbede, kochenille, klorofyl, carotenoider)	Meget udbredt (juice, øl, vin, kød, mejeriprodukter, konfekture)	Farve	Varierer
Titandioxid	Konfekture (fx tyggegummi, kiks, chokolade)	Overfladebehandling/ farve	Ca. 0,01-5 µg/mg

Generelt antager foderindustrien, at der ikke er nanomaterialer i foder, primært baseret på at de fokuserer på at undgå støv iht. arbejdsmiljølovgivningen. Deres produkter kan dog være aggregater eller agglomerater af nanopartikler og derfor formelt høre ind under den generelle definition af et nanomateriale. De identificerede tilsætningsstoffer vist nedenfor er almindeligt anvendt i foderprodukter og er tilsat i koncentrationer fra <<1 % til 4 %.

MATERIALER (DER ANSES FOR ET NANOMATERIALE) IDENTIFICEREDE I DEN DANSKE FODERINDUSTRI.

Materiale	Produkt(er)	Funktion(er)	Mængde
Siliciumforbindelser, silikater	Alm. husdyrfoder, inkl. foderflager og -piller; forblandinger	Bærestof	Ca. 1 masse %
Calciumkarbonat, calciumfosfat	Alm. husdyrfoder; fiskefoder	Næringsstof, bærestof	Ca. 1-4 masse %
Metalsalte og oxider (jern(III)oxid, sporelementer: Cu, Zn, Mn, Co)	Alm. husdyrfoder; fiskefoder	Næringsstof	<< 1 masse %
Aminosyrechelat af sporelementer	Alm. husdyrfoder	Tilsætningsstof (ernæringsstof)	<< 1 masse %
Farvestoffer/pigmenter (fx caroten, astaxanthin)	Alm. husdyrfoder (især til æglæggende høner); fiskefoder	Farve	<< 1 masse %

Fødevarekontaktmaterialer
Der kommer i disse år fødevarekontaktmaterialer med nanomaterialer eller baseret på nanoteknologi på det globale marked, og i faglitteraturen er identificeret en række produkter, der indeholder mulige nanomaterialer. I Europa sker introduktionen af fødevarekontaktmaterialer baseret på nanomaterialer meget langsomt pga. lovgivning og lav forbrugeraccept. I øjeblikket er kun tre materialer med primære partikler i nanostørrelse (syntetisk amorf siliciumdioxid, titannitrid og carbon black) tilladt til brug i plastmaterialer og beholdere, som kommer i kontakt med fødevarer, på det europæiske marked.

Interview af danske fødevareemballageproducenter (inkl. producenter af plastbeholdere, film og papirindpakning) viser ingen brug af nanomaterialer i fødevareemballage, men enkelte af de interviewede har bemærket, at der muligvis findes nanomaterialer i pigmenter, lim, polymer og papir, som bruges til labels, mærkning og indpakning. De kan dog ikke specificere, hvilke materialer det drejer sig om.

Køkkenudstyr og diverse elektronisk apparater (fx køleskabe, frysere og kaffemaskiner), som bevidst indeholder nanomaterialer (nano sølv), er tidligere blevet markedsført. På tidspunktet for kortlægningen fandtes dog ingen af produkterne på det danske marked. Dette er i overensstemmelse med oplysningerne fra de interviewede virksomheder, hvoraf det fremkom, at køkkenudstyr og andre elektroniske apparater, der indeholder nanomaterialer, er blevet fjernet fra det europæiske marked. Det vurderes dog som meget sandsynligt, at pigmenter som carbon black og titandioxid anvendes i plastkomponenter i og coatinger/lakker på køkkenudstyr og elektroniske apparater.

Kosmetik
Nanomaterialer brugt som farvestoffer, UV-filtre eller konserveringsmidler er fritaget fra en del af artikel 16 i forordningen om kosmetiske produkter og har derfor været i fokus i denne kortlægning af kosmetik. Adskillige pigmenter, der bruges i kosmetik, kan defineres som nanomaterialer, afhængig af hvordan partikelstørrelsen og overfladearealet bestemmes. Disse pigmenter omfatter (men er ikke begrænset til) jernoxider, carbon black og aluminiumhydroxid. Carbon black (nano) bruges i mascara og øjenblyanter i koncentrationer på <3 % som farve; titandioxid (anatase) bruges i pudder, pudderunderlag og solcremer som et UV-filter i koncentrationer på <5 %, og både carbon black og titandioxid bruges i neglelak som farvegiver i koncentrationer på 2-3 %.

Interview af danske kosmetikproducenter indikerer et fald i brugen af nanomaterialer i kosmetiske produkter; brugen af nanomaterialer såsom pigmenter, UV-filtre og konserveringsmidler forventes dog at fortsætte, men afhænger af godkendelsen af pigmenter, UV-filtre og konserveringsmidler i Annex IV-VI af (EC) 1223/2009.

MATERIALER (DER ANSES FOR AT VÆRE ET NANOMATERIALE) IDENTIFICEREDE I DEN DANSKE KOSMETIKINDUSTRI.

Materiale	Produkt(er)	Funktion(er)	Mængde
Titandioxid	Solcreme; pudder; pudderunderlag; neglelak	UV-filter	< 5 %
Carbon black	Makeup; øjenblyant; mascara; neglelak	Farvestof	< 3 %
Jernoxider	Makeup	Farvestof	N/A
Aluminiumhydroxid	Makeup	Farvestof	N/A

Pesticider
I henhold til definitionen anvendt i denne kortlægning er der ikke identificeret kommercielle pesticider med nanomaterialer på det danske marked. Litteraturen beskriver dog et antal mulige anvendelser af nanomaterialer i pesticider. Anvendelsen af nano-formuleringer af pesticider vil kunne bidrage med nye metoder til beskyttelse mod nedbrydning, kontrolleret frigivelse og øget opløselighed af aktivstofferne. Nano-pesticider i den agrokemiske branche er på vej frem, og mange spår dem en hurtig vækst i de kommende år. Mere end 3.000 patenter vedrørende nano-pesticider er blevet indsendt i løbet af de sidste 10 år.

Medicinsk udstyr
Mange forskellige nanomaterialer tages i disse år i brug i medicinsk udstyr, og nogle findes i produkter på det danske marked, som det ses af tabellen nedenfor. Nanomaterialer har en række gavnlige effekter i medicinsk udstyr, og i litteraturen findes eksempler som plastre og forbindinger, stomiposer og katetre, plomber, lim og implantater, kompositpolymerer og lim samt kontrastvæske. Produkterne kan indeholde sølvforbindelser, zinkoxid eller titandioxid for at opnå en antimikrobiel effekt; kalciumalginat til absorbering af fugt; silikater, zirkoniumdioxid, jernoxid eller pigmenter. De fleste produkter bruges af ansatte i sundhedssektoren til behandling af patienter, hvor det medicinske udstyr kommer i direkte kontakt med patientens krop. I fremtiden forventes en betydelig stigning i anvendelsen af både de identificerede samt nye nanomaterialer, hvis lovgivningen fortsat tillader det.

MATERIALER (DER ANSES FOR AT VÆRE ET NANOMATERIALE) IDENTIFICEREDE I DEN DANSKE INDUSTRI FOR MEDICINSK UDSTYR.

Materiale	Produkt(er)	Funktion(er)	Mængde*
Silikater	Plomber, lim og implantater	Mekaniske egenskaber	10-20 %
Zirkoniumdioxid (zirconia)	Plomber, lim og implantater	Mekaniske egenskaber	10-20 %
Sølv	Forbindinger og plastre	Antibakteriel	N/A
Kalciumalginat	Forbindinger og plastre	Bærer og fugtabsorbent	N/A
Kobber	Stomiposer	Filtre	< 0,0001 %
Zinkoxid	Plastre, forbindinger, stomiposer	Pigmenter og vedhæftning	0,1-20 %
Jernoxid	Polymermekanismer	Pigmenter	< 0,2 %
Titandioxid (anatase)	Stomi- og inkontinensartikler, plastre	Pigmenter	0,001-0,5 %

** Information blev givet af producenterne som massekoncentration af hele udstyret.*

Vandbehandling
På det danske marked er fotokatalytiske UV-bestrålingssystemer med titandioxid-nanopartikler som katalysator implementeret i nogle få offentlige svømmehaller med succes, og storskala-systemer til behandling af ballastvand har været på markedet i flere år. Vandbehandlingsprodukter med nanosølv sælges online og kan importeres.

Fotokatalytiske vandbehandlingsanlæg er i demonstrationsfasen, og pilotprojekter til drikkevandsrensning i udviklingslandene er under afprøvning. Indarbejdning af nanomaterialer i membranen er en mulig løsning på udfordringerne med fouling og forventes at blive mere udbredt i den nærmeste fremtid. Adsorberende stoffer, der udnytter nanomaterialers store overfladeareal pr. volumen, undersøges grundigt, og mens nogle kommercielle produkter allerede er til rådighed, forventes en stigning i anvendelsen af nano-adsorberende stoffer inden for vandbehandling.

MATERIALER (DER ANSES FOR AT VÆRE ET NANOMATERIALE) IDENTIFICEREDE I DEN DANSKE VANDBEHANDLINGSINDUSTRI.

Materiale	Produkt(er)	Funktion(er)	Mængde
Titandioxid	UV-bestrålingssystemer	Fjernelse af patogener og spor af forurenende stoffer	N/A
Sølv	Desinfektion	Antimikrobiel	N/A

1. Introduction to the Survey

In recent years, a number of products containing nanomaterials (nanoproducts) have been introduced on the Danish market, and – due to the technological development – that trend is expected to continue. An agreement under the Danish Finance Act of 2012 proposed an increased effort from 2012-2015 in relation to nanomaterials, and a decision was made to establish a Danish Nanoproduct Register. This register will however, not include products covered by regulation remit to other ministries and/or already covered by registration obligation due to EU regulation, the Danish Environmental Protection Agency has initiated a supplementary survey of these nanoproducts (available on the Danish market).

1.1 Objective of the survey

The objective of the survey is to identify and map nanoproducts that are not included in the Danish Nanoproduct Register to gain knowledge of the prevalence, use and user groups as well as the future trend of nanoproducts on the Danish market within the identified product groups as given below. Exposure evaluations and risk assessments of the nanoproducts are not part of this survey.

1.2 Delimitation

The survey solely comprises products available on the Danish market and the relevant product groups of the survey have been defined as:

- Food and feed
- Food contact materials
- Cosmetics (limited to nanomaterials used as colorant, UV filter or preservative)
- Pesticides
- Medical devices
- Water treatment.

1.3 Survey methods

The preliminary screening is based on previous surveys of nanoproducts, recent scientific literature/reviews on present and future use of nanomaterials and roadmaps from European Technology Platforms. Moreover, a number of Danish resource persons from various trade and industry organisations and governmental institutions have contributed.

To survey the prevalence of and anticipated future trends for products containing nanomaterials on the Danish market, relevant Danish producers, importers, retailers and trade organisations have been interviewed using a questionnaire developed for the specific purpose. The interviewees have generally answered the survey based on current knowledge of the raw materials used/contained as well as their properties. The experience from the interviews implies that the industry's physico-chemical knowledge on the relevant materials is, in many cases, limited, and vague and/or diverse nanomaterial definitions are applied in various industries – many different from the definition applied in this survey. Therefore, it may be uncertain whether the materials identified in the interviews actually are considered to be nanomaterials. When possible, numbers or estimates of the amounts or concentrations of identified (nano-) materials in the products are supplied.

The future trends are a summary of the present work and forecasts in the literature and the opinions of resource persons, experts, industry and industry organisations that have been part of the screening and survey.

1.4 Structure of the report

The present report is structured to give an evaluation of each product group individually, meaning that a chapter is designated for each. In most chapters, the specific product group will be described with regard to:

1. The prevalence of the nanomaterials in products on the Danish market from the perspective of the Danish industry and industry organisations (based on interviews of Danish producers, importers, retailers, industry associations, etc.).
2. The preliminary screening to identify nanomaterials used in the product group at international level (based on a review of literature, surveys, databases and other available sources).
3. Use and user groups (based on literature, surveys and general knowledge).
4. Anticipated future trends of applying nanomaterials in the specific product group (based primarily on literature and supplemented by input from the interviewees).

2. Nanoproducts and Nanomaterials

The decision on, whether a product is a nanoproduct or not, depends on the definitions, which currently are neither legally nor scientifically described, and various definitions applied may be ambiguous. The basic aspect of a nanoproduct is that the product is or contains a nanomaterial. The general definition applied in this survey is described below.

2.1 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 Organisation for Economic Co-operation and development (OECD) as recommended by the European Commission. This heterogeneity severely 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).

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."

The interpretation of 2011/696/EU applied in this survey is adapted from the European Commission staff working paper (Commission (b) 2012) and will cover the materials described in the text below and in Table 1:

- *Powders of nano-objects*
  Nano-powders may consist of individual nano-objects in the nano-scale or agglomerates/ aggregates thereof.

- *Nano-suspensions*
  A nano-suspension consists of solid nano-objects suspended or dispersed in a liquid phase.
- *Nano-aerosols of solid nano-objects*
  Nano-aerosols are materials which consist of a gaseous phase containing freely moving solid nano-objects.
- *Composite materials with nano-objects*
  Nano-composite materials (or nano-composites) consist of at least two different phases, at least one of which has nano-scale features.

The following materials will not be included in the nanomaterial interpretation applied in this survey:

- *Nano-emulsions*
  Nano-emulsions consist of liquid nano-objects suspended or dispersed in a liquid phase. They are not covered by 2011/696/EU as the term particle – as defined in 2011/696/EU – only covers solid nano-objects (defined and rigid shape).
- *Nanostructured materials*
  Surfaces or objects with an engineered internal or external nanostructure (if objects are larger than 100 nm).
- *Solid/liquid nano-foams and nanoporous materials*
  A nano-foam consists of nano-scale gas bubbles surrounded by liquid or solid struts. They are not covered by 2011/696/EU as the term particle – as defined in 2011/696/EU – only covers solid nano-objects (defined and rigid shape), thus excluding gas bubbles.

TABLE 1
OVERVIEW OF INCLUDED AND EXCLUDED TYPES OF NANOMATERIALS ACCORDING TO THE NANOMATERIAL DEFINITION APPLIED IN THE PRESENT SURVEY.

Included	Excluded
Powders of nano-objects (nanoparticles, nano-plates, nano-fibres) and aggregates/agglomerates hereof	Nano-emulsions
Nano-suspensions	Nanostructured materials
Nano-aerosols of solid nano-objects	Solid/liquid nano-foams and nanoporous materials
Composite materials with nano-objects	

2.2 The nanoproduct definition applied in the survey

At present, an unambiguous definition of a nanoproduct has not been described scientifically or legally. In this survey, a product containing nanomaterial, according to the above definition, is designated as a nanoproduct. For some products, very little information exists on the use of nanomaterials, making it challenging to determine whether or not a product is covered by the definition. In case of ambiguity, products are included in the survey. For these reasons, the applied definition is extensive, implying that a wide range and a large number of products are included in the survey and, notably, that products identified and included in this survey may not all be defined a nanoproduct if looking further into the details of the materials used. Thereby, products and materials included in this survey may prove to not be genuine nanoproducts or nanomaterials.

In this survey the attempt has been to use a definition that is as similar as possible to the definition applied for the Danish Nanoproduct Register; however, no exemptions are applied in this survey, and the comparability to the terms of the Danish Nanoproduct Register Act is limited.

3. Food and Feed

In the literature, food and feed are often addressed together, since the basic aspects such as applications and potential impacts are expected to be similar (Nanotechnology 2008; Committee 2011). This is also the case in this survey.

In the food and feed industry, there are many potential applications of nanotechnology, ranging from minor modifications of natural food ingredients in order to enhance taste, palatability, texture, stability, etc., to significant modifications leading to e.g. increased nutrient bioavailability. However, it should be noted that nano-scale objects are already naturally present in food and feed, as many ingredients are comprised of biopolymers, being endogenous proteins, carbohydrates and fats, with particle or droplet sizes extending down to nano-scale.

“Natural” nano-scale components present as emulsions (homogenized milk, mayonnaise, etc.), components, structure (lipid, protein, carbohydrate) and delivery vehicles based on vesicular delivery systems (e.g. liposomes, emulsions) used to encapsulate bioactive ingredients are abundant in food products. However, they do not fall within the nanomaterial definition used in this survey and will, therefore, not be covered. Further, the majority of these “natural” nano-scale components are abundant components that have existed for decades or even centuries in food products.

The European food and feed industry must comply with the General Principles and requirements of the Food Law (the general food law; Regulation (EC) 178/2002). It is generally considered that potential use of nanotechnology in the food and feed area will be covered by Regulation (EC) 178/2002 or by specific approval processes, including Regulation (EC) 1333/2008 on food additives (Nanotechnology 2008) and Regulation 258/97/EC on novel foods. In Regulation (EC) 1333/2008, it is specifically stated that if a nano-form of an already permitted food additive were to be developed, then it would be considered a new additive and would need a pre-marketing approval. All existing food additives are currently being re-evaluated by the European Food Safety Authority (EFSA) and, among other things, the particle size distribution is being evaluated. Some evaluations are already completed, and all re-evaluations must be finished by 31 December 2015. A new proposal for revising the novel food regulation is expected from the EU Commission by the end of 2013. The aim is, among others, to clarify that foods and food ingredients containing new intentionally manufactured nanomaterials are covered by the novel food Regulation. This is already the case with the existing Regulation, although it is not specifically mentioned in the text. So far, the Danish Veterinary and Food Administration has not received any inquiries from companies requesting authorisation of new products containing nanomaterials.

3.1 Identified Danish prevalence of nanomaterials in food and feed

Interviews with representatives from the Danish food industry support the findings in the literature that the identified food additives with a potential size distribution in the nano-scale are used in food products and sold on the Danish market. However, many are not considered a nanomaterial in the industry and are not defined as one using traditional mass-based particle size distributions, whereas they may be termed nanomaterials if applying the number-based particle size distribution conditions according to 2011/696/EU.

Respondents to the survey have noted that, as with food additives, a number of food ingredients may potentially contain and be characterised as nanomaterials. Examples of these mentioned in the interviews include natural colorants/pigments (e.g. anthocyanins E163) and dust from flour or sugar.

However, none of the respondents have been able to give precise information on the size distribution of food ingredients and additives due to the following aspects:

- The interviewees point to the fact that many of the used additives may be borderline examples of known materials that may or may not fall under the regulatory definition of a nanomaterial. A definition of a nanomaterial in food regulation is expected to be settled by March 2014 by the European Commission in relation to the Novel Food Regulation.
- Interviews show that companies are presently unsure if their products will be covered by the definition in the the future regulation and/or are reluctant to characterize their ingredients and additives as nanomaterials until regulation is in place.
- Many producers buy mixes of numerous food additives that are in compliance with the food regulation, and, therefore, they do not have full information on the specific additives.

As already mentioned, no inquiries from companies requesting to market food products containing nanomaterials have been registered by the Danish Veterinary and Food Administration. To this it must be added that no responses have indicated that they use or sell products that base their function on nano-size-related properties.

Applying the Recommendation of the EU Commission on the definition of nanomaterials (2011/696/EU) strictly, a broad range of food products containing well-known ingredients and additives may be characterized as containing nanomaterials. On the other hand, if nanomaterials are viewed as novel food and defined within a revised Novel Food Regulation, little evidence of nanomaterials in Danish food products is present, as this regulation specifically applies to *"foods and food ingredients which have not hitherto [before 15 May 1997] been used for human consumption to a significant degree"* (Regulation (EC) 258/97 on novel foods and novel food ingredients).

Therefore, the overview of findings presented in Table 2 can only be indicative and dependent on the specific definition of a nanomaterial, which for the purpose of this survey has been set as described in Chapter 2. This means that the definition is identical throughout the survey, but may differ from the food-related definition of a nanomaterial, which was not fully settled at the time of the interviews. Subsequently, a food-related definition of nanomaterials has been sent to hearing, defining that only engineered nanomaterials will be covered by the definition. This entails that traditionally used additives are excluded from the food definition (amendment to Regulation (EU) 1169/2011) and that many of the materials identified in the interviews are thereby not a nanomaterial according to the food-related definition, although it may be characterised a nanomaterial according to the general definition described in Chapter 2.

TABLE 2
MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH FOOD INDUSTRY.

Material	Product(s)	Function(s)	Amount
Silicon compounds (e.g. silicon dioxide), silicates	Widely used (e.g. canned food and vegetables)	Anticaking, purifier, antifoaming, aroma carriers, thickener	N/A
Calcium carbonate	Widely used	Colour, stabiliser, anticaking	N/A
Natural colorants/ pigments (e.g. anthocyanins, beetroot, cochineal, chlorophyll, carotenoids)	Widely used (juice, beer, wine, meat, dairy, confectionary)	Colour	Varies
Titanium dioxide	Confectionary (e.g. gum, biscuits, chocolate)	Surface coating/colour	Approx. 0.01-5 µg/mg

The interview results on nanomaterials in feed from the Danish feed industry displays a number of clear trends:

- They only use additives approved for feed use.
- To date, there has been very little focus and debate on the use of nanomaterials in feed (except for the point of workplace exposure). Therefore, the knowledge of nanoparticles or nanomaterials in the feed is marginal.
- None of the interviewees expect their products to contain nanomaterials as defined in this project; however, they most often do not have particle size documentation for the feed material or additives.

Feed is most often pelletized or pressed into feed flakes from powders in the size range of 0.25-1 mm or for some nutrients, e.g. some vitamins and minerals, the minimum sizes are expected to be in the microscale. For livestock, premixtures are supplied as powders consisting of either a mix of several vitamins and minerals or as vitamins and/or minerals mixed with a carrier (such as silica or calcium compounds), which may be in the nano-scale. In order to comply with legislation on health and safety at work (to avoid dust), the powders are significantly larger than nano-scale, but may possibly be aggregates or agglomerates of primary particles in the nano-scale . Similarly for fish feed, a general optimal particle size of ingredients is 0.5-1.75 mm, i.e. much larger than nano-scale, and the feed products may be extruded. Specifically, vitamin and mineral ingredients for some fish products are defined as being 95 % smaller than 500 µm or 350 µm; however, they are expected to be significantly larger than nano-scale.

A number of the feed materials or additives identified in the screening phase, that may be considered nanomaterials, were registered as being used in feed products and their function/use is summarized in Table 3. Notably, the interviewees do not expect the ingredients to be nanomaterials as defined in this survey, but the particle size data are unknown. All materials listed in the table have been used in feed in the Danish industry for decades, except the chelates, which were introduced 5-7 years ago.

TABLE 3
MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH FEED INDUSTRY.

Material	Product(s)	Function(s)	Amount
Silicon compounds, silicates	General livestock feed, including pressed feed flakes and pellets; premixtures	Carrier	Approx. 1 mass%
Calcium carbonate, calcium phosphate	General livestock feed; fish feed	Nutrient, carrier	Approx. 1-4 mass%
Metal salts and oxides (ferric oxide, trace elements: Cu, Zn, Mn, Co)	General livestock feed; fish feed	Nutrients	<< 1 mass%
Amino acid chelate of trace elements	General livestock feed	Nutritional additive	<< 1 mass%
Colorants/pigments (e.g. carotenes, astaxanthin)	General livestock feed, including egg-laying hens ; fish feed	Colour	<< 1 mass%

3.2 Literature survey on nanomaterials in food and feed

Until recently, the literature on nanomaterials and nanotechnology in the food and feed industries has been very limited; however, since 2010 a few surveys and reviews have outlined known and/or anticipated applications. An overview of nanomaterials in food and feed applications is given in Table 4.

Silicon dioxide/silica (E551) and **silicates** are used in a number of variations as a food additive and in feed (Commission (b) 2012). It is debated, if they should be considered a nanomaterial when in food and feed products, as the smaller particles may aggregate strongly to larger colloids (ELC 2009). Amorphous silicon dioxide has been used in powdery foods, such as seasonings and coffee creamer, as a separating agent, flow aid, thickening and anti-caking agent. The silica concentration of selected powdery foods was found to be 0.05-0.6 % and with 5-19 (w)% in nano-form[2] (Dekkers, Krystek et al. 2011). The number-based content of nano-sized silica is not known from this study, but it cannot be precluded that more than 50 % (number-based) of the silica is in the nano range and that it is therefore defined as a nanomaterial. Based on the findings, Dekkers and co-workers estimated an average daily intake of nanosilica of 124 mg (high numbers of portions per day of products containing the highest amounts of nanosilica per portion). Moreover, colloidal silica is used as a clarifying agent in beverages such as wine and fruit juice, and pyrogenic silica is used as an anti-foam agent in coffee and tea (Commission (b) 2012). The European Food Safety Authority (EFSA) has stated that a re-evaluation of silicon dioxide must be completed at the latest by 2016.

Titanium dioxide (E171) is a common additive as a pigment. It is debated, whether it is to be considered a nanomaterial when in food products, since the smaller particles may aggregate strongly to larger colloids (ELC 2009). Titanium dioxide is present in concentrations varying between 0.0005 % and 0.04 %, as determined in a number of products. Moreover, it has been found that the mean size of food grade titanium dioxide is 110 nm and that 36 % of the particles by number are smaller than 100 nm. As for silica, it cannot be precluded that the number-based size distribution exceeds 50 % and thereby may be termed it as a nanomaterial. Titanium dioxide is used

[2] An upper size limit of 200 nm was used in this study.

in e.g. dairy products, candy, gums, baked goods, seasonings and beverages (Weir, Westerhoff et al. 2012). Weir and co-workers estimated an average daily intake of titanium dioxide (food grade) for the US population of 1-2 mg/kg_{bw} for children under the age of 10 years and approximately 0.2-0.7 mg/kg_{bw} for the other consumer groups.

Calcium carbonate (E170) is used as a nutrient, anti-caking agent, acidity regulator, colour, salt substitute and hardening agent in a broad range of products including beverages, dairy, confectionery, cereal and fine bakery products. The typical average particle size of food grade calcium carbonate is stated by the industry to be 5 µm, with less than 1 % of the particles having a diameter below 100 nm (EFSA 2011), meaning that it may not be defined as a nanomaterial. In feed products, calcium carbonate is used as feed material and technical additive.

Iron, calcium and **silver** and oxides hereof are being marketed as health supplements, but are not approved as food additives and therefore not covered for food in this report. In feed, metal oxides and metal salts are trace elements used as nutritional additives. The feed additives are typically in the micrometer size range and are presumably not termed nanomaterials.

Carbon black (E153) from vegetable origin is used as a colorant in various food products, such as confectionary and sweets (Miranda-Bermudez, Belai et al. 2011). In 2012, the European Food Safety Authority stated that the presence of nanoparticles in vegetable carbon products on the market could be excluded (EFSA 2012).

Non-water-soluble compounds such as some **vitamins, antioxidants, flavourings** and **fats** and **natural colour additives** (e.g. carotenoids) are used as compounds with nutritional value and colorants, respectively, in food, food supplements and feed (e.g. dairy, confectionary, meat products, beverages and fish feed). The non-water-soluble compounds may be very small, and it is not unlikely that they will fall in the nano-size range. An expert in the food colour additive confirmed an industrial development in reducing particle size of colour additives towards the nano-size range. Natural colour additives constitute an alternative to synthetic colour additives, and the use of natural colour additives, flavouring and oil often requires a manipulation (carrier system) to render a compound readily dispersible in water, often referred to as (nano-)entrapment or (nano-)encapsulation (ELC 2009; Chaudhry, Watkins et al. 2010). Carbohydrates (e.g. starch), gelatin, beta-cyclodextrin and calcium alginate are frequent examples of nanocarriers, and numerous companies manufacture and sell such products (Möller, Eberle et al. 2009). Emulsified non-water-soluble compounds are potentially in the nano-range; however, the size of the carrier system may be larger (Möller, Eberle et al. 2009).

TABLE 4
TYPE OF POSSIBLE NANOMATERIAL USED FOR FOOD AND FEED PRODUCTS (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THE PRODUCT TYPE.

	Titanium dioxide	Silicon dioxide	Silicates	Calcium carbonate	Natural colour additives	Nanocarrier systems
Covered by the definition*?	X	X	X	(X)	X	X
Seasoning, coffee creamer, etc. (powdery foods)	X	X	X			
Wine, fruit juice, etc. (beverages)	X	X	X	X		
Coffee, tea		X	X			
Dairy products	X			X		
Confectionary, chewing gum	X			X	X	
Baked goods	X			X		X
Sauce	X					
Poultry, sea food		X				
Cereal				X		
Feed		X	X	X	X	

** Is the material assumed to be considered a nanomaterial according to the definition applied in the present survey?*

3.3 Use and user groups

Many of the identified additives have several properties and may be added to food or feed to obtain one or more of these in the product. A non-exhaustive list of the properties is given in Table 5.

TABLE 5
TYPE OF POSSIBLE NANOMATERIAL USED FOR FOOD AND FEED PRODUCTS (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THEIR FUNCTIONAL PROPERTY EXERTED IN THE PRODUCT.

Effect	Titanium dioxide	Silicon dioxide	Silicates	Calcium carbonate	Iron, calcium, silver	Natural colour additives	Nanocarrier systems
Flow agent		X	X				
Separating agent		X	X	X			
Anti-foam agent		X	X				
Colour additive	X					X	X
Health supplement					X		X

As demonstrated in the above tables, the identified materials are added to a wide range of food products, meaning that they are part of everyday intake in a normal diet for all groups, from babies to the elderly.

Feed products are primarily used professionally to feed livestock, while a minor amount is used by consumers for pets and private privately kept domestic animals.

3.4 Future trends

Interviews of the food industry from the survey indicate no special interest in nanomaterials, and, in general, they have limited expectations of near-future innovations relating to the use of nanomaterials in food. Similar conclusions from the interviews of the feed industry have been obtained; up to now, there has been no focus on the nano ingredients for feed and the industry does not recognize significant advantages of nanomaterials in feed (except for the possibly improved bioavailability of nutrients). Therefore the general opinion in the feed industry is that the ingredients as well as the particle size of the ingredients will not change and become nano-scale in the future.

Both literature and the industries state a currently limited prevalence of nanomaterials (excluding the naturally occurring biopolymers) in the food and feed market and that a significant use of nanomaterials and nanotechnology in the industries is unlikely in the short- to medium-term; in particular due to cost implications and specifically pronounced for feed applications. The majority of identified nanotechnology applications for food and feed are currently at R&D or near-market stage, indicating that an increased use of nanomaterials might occur in food and feed in the future (Nanotechnology 2008; EFSA 2009).

Certain food applications identified in the global market are likely to enter the Danish and the rest of the European market over time, if approved by Regulation (EC) 178/2002. These include, but are not limited to sensory improvements (flavour/colour enhancement, texture modification), increased absorption and targeted delivery of nutrients and bioactive compounds, and stabilisation of active ingredients such as nutraceuticals in food matrices. Specifically, nanomaterials (such as proteins, nanofibres/nanofibrils, dispersions of calcium carbonate) to obtain enhanced product stability and texture have a potential in the near future, as these are considered to require only minor modifications of natural ingredients, and some are available on the international market. Conversely, the present research and development focus on targeted delivery of nano-encapsulated food ingredients or nutrients may result in applications in the longer term, due to cost implications. Such systems may improve bioavailability of nutrients or mask taste, odour or appearance, and they may be constituted by lipids, natural polymers or synthetic polymers. Additionally, research explores interactive foods using encapsulated ingredients or additives (for example flavour modifier or vitamins) that are released by stimuli added by the consumer in order to modify the characteristics of the food (Nanotechnology 2008).

All future food and feed products must comply with Regulation (EC) 178/2002 or specific approval processes, and the introduction of new nanomaterials in the food and feed product market in Denmark will therefore be recognized by the Danish Veterinary and Food Administration.

Food and feed highlights

A number of the ingredients may not be considered a nanomaterial, and due to the lack of a final definition, both food and feed industry are currently uncertain whether they use nanomaterials in their products or not. According to the Danish Veterinary and Food Administration, no food products containing nanomaterials have been approved for the Danish market. Literature and surveys have, though, identified a number of relevant products and potential nanomaterials on the European and global food and feed markets.

Significant potential product types

- All processed food, for example dairy, confectionary, baked goods, beverages, seasoning, etc.
- Feed is assumed to contain no nanomaterials, but contain many of the same materials as food products.

Significant potential nanomaterials

- Silicon dioxide/silica, titanium dioxide, pigments, nanocarrier systems.
- All are additives and typically constitute low amounts of the final food/feed product; from <<0.01 % to 1 % in food and from <<1 mass% to 4 mass% in feed.

Use and users

- Food potentially containing the significant materials is part of a normal human diet for all age groups.
- Feed potentially containing the significant materials is part of the daily intake for livestock, domestic animals and bred fish.

The use of nanomaterials in food and feed is dependent on legislation; however, if allowed, the use of nanomaterials is expected to increase in the future in spite of slow uptake and hesitation in the industry.

4. Food Contact Materials

Food contact materials are materials and articles intended to come into contact with food such as packaging materials, cutlery and dishes, processing machines and containers. Food-packaging applications form the largest share of the current and short-term predicted nano-enabled products in the food sector (Bradley, Castle et al. 2011). In 2008, the global nano-enabled food and beverage packaging represented $4bn and was forecasted to hit $7bn by 2014 (Duncan 2011).

In Europe, the introduction of industrial applications of nano-enabled food-packaging applications is slow due to legislative restrictions and slow consumer acceptance (Silvestre, Duraccio et al. 2011). Food packaging must comply with Regulation (EC) 1935/2004 on materials and articles in contact with food and those that might reasonably be expected to be in contact with food or to transfer their constituents to food. Currently, only three materials with primary particle in the nano-size range (synthetic amorphous silicon dioxide[3], titanium nitride[4] and carbon black[5]) have been authorized for use in plastic materials and objects in contact with food on the European market (Commission (a) 2012). The effective particle size of the aggregates and agglomerates of silicon dioxide, titanium nitride and carbon black in the product are significant larger; however, they fall within the applied nanomaterial definition in this study. Safety evaluations of titanium nitride nanoparticles and of a nano-scale silicon dioxide coating (less than 100 nm) for plastic packaging in food contact materials have been published by EFSA in 2012 and 2007, respectively (EFSA 2007; EFSA 2012).

In addition to food packaging materials, a range of kitchen appliances deliberately containing nanomaterials have been brought to market with improved properties such as antibacterial, odour-eliminating and self-cleaning surface. These products include food storage, cocking equipment, kitchenware and various electronic devices (e.g. refrigerators, freezers and coffee machines); however, less than 15 products are listed in the databases "The Project of Emerging Nanotechnologies" and "The Nanodatabase" by The Danish Consumer Council.

4.1 Identified Danish prevalence of nanomaterials in food contact materials

Interviews with Danish producers of food packaging (including plastic containers, films and paper packaging) reveal no use of nanomaterials in food contact materials. Research projects have explored the potential of nanomaterials (e.g. nano-clay), but the research has not lead to commercial applications so far.

Some respondents from the industry note that there might be nanomaterials in pigments, glue, polymer and paper used for labelling and wrapping, but they cannot specify the type of materials included. One respondent, producing a wide range of kitchen equipment and food storage, specifies that the use of nanomaterials are frequently examined within the company. Consequently, the respondent states that nanomaterials are not used for any of their products.

[3] For synthetic amorphous silicon dioxide: primary particles of 1–100 nm which are aggregated to a size of 0,1–1 µm which may form agglomerates within the size distribution of 0,3 µm to the mm size. (Substance no. 504)

[4] For titanium nitride: Only to be used in PET bottles up to 20 mg/kg. In the PET, the agglomerates have a diameter of 100–500 nm consisting of primary titanium nitride nano-particles; primary particles have a diameter of approximately 20 nm. (Substance no. 807)

[5] For carbon black: primary particles of 10–300 nm which are aggregated to a size of 100–1200 nm which may form agglomerates within the size distribution of 300 nm–mm. (Substance no. 411)

Interviews in the pigment industry showed that many (up to 100) of the currently available pigments for offset and print are sized near the range of the nano-scale and may be defined as nanomaterials according to the EU recommendation (EC 2011/696/EU), depending on the applied technique for measuring particle size and specific surface area. That has been noted in recent REACH dossiers by the producer, and, following, examples of pigments within the nano-scale size have been mentioned, including Lithol Rubine (PR57:1), Permanent Maroon Medium (PR15) and Toluidine Maroon (PR13).

The responses from two large international companies, producing a wide range of kitchen appliances and domestic appliances, show that they have both withdrawn products containing nanosilver from the European market as a consequence of increasing concerns about the toxicity of nanomaterials to environmental systems and human health. These findings support the literature and indicate a general decrease in the use of nanomaterials in kitchen appliances. The respondents claim that none of their products contain nanomaterials according to the definition used for their industry; however, it is highly likely that e.g. pigments such as carbon black and titanium dioxide, that may be defined as according to EC 2011/696/EU, are used in plastic components and coatings/lacquers in kitchen appliances.

4.2 Literature survey on nanomaterials in food contact materials

Nanomaterial and nanotechnology applications for food packaging – both food-contact materials and food non-contact materials – are rapidly becoming a commercial reality, and the use of nanomaterials is significantly larger within the food packaging industry compared to food and feed (Chaudhry and Castle 2011). Currently, there appears to be no direct use of complex inorganic nanoparticles such as carbon nanotubes in foods, whereas simple inorganic molecules like titanium dioxide and clay particles are being used in packaging (Nanotechnology 2008). The material functionalities of food contact materials can be subdivided into five categories: pigments, improved packaging properties, active packaging material and intelligent food packaging, antibacterial and self-cleaning kitchenware, though some nanomaterials may improve more than one of these functionalities. An overview of nanomaterials in food contact materials is given in Table 6.

Pigments

In food contact materials, organic and inorganic pigments including **carbon black** and **titanium dioxide** are commonly found in colour concentrates for plastics, paperboard, can-end cement and sealants for the packaging of food (Environment Canada 2011).

Improved packaging properties

Nanocomposite materials – containing low levels (2-5 %) of nano-objects within the plastic matrix – show several advantages over conventional food packaging materials, for example improved mechanical characteristics, reduced gas and liquid permeability, reduced weight and increased flame resistance. Nanocomposite materials primarily improve properties in bottles and films and, in some cases, they provide as coatings for other materials.

In particular, various **organo-clays** have gained increasing interest and account for nearly 70 % of the global nano-enabled food and beverage market volume (Möller, Eberle et al. 2009). Many composite materials have been successfully commercialized in Asia and America, e.g. polyethylene (PET) bottles for beverage (juice, beer and soft drinks) to minimize the loss of CO_2 from the drink and the ingress of O_2 (Nanotechnology 2008; Duncan 2011).

The low cost of clay has led to the development of nano-clay-polymer composites for use in a variety of food-packaging applications for products such as meat, cheese and cereals; for extrusion coating of packaging for fruit juice and dairy products; and co-extrusion processes for the manufacturing of bottles for carbonated drinks (Hatzigrigoriou and Papaspyrides 2011).

A number of different nanomaterials can be added to the pure polymer or the nano-composite to provide an additional barrier or functional properties for food packaging purposes. For instance, **titanium nitride** for improved rigidity and strength of the material (Chaudhry and Castle 2011).

Literature states that **titanium dioxide** nanoparticles can be added to the film to block UV light (Chaudhry and Castle 2011) while preserving transparency of the material, and **acrylic nanoparticles** can be added to strengthen polylactic acid films (Robinson and Morrison 2010). Further, the two nanomaterials are commercially available for the mentioned purposes.

Vacuum deposition of nanoparticles, e.g. **silicon dioxide**, onto a film, is used to increase the shelf-life of carbonated drinks and snacks, confectioneries and coffee (Silvestre, Duraccio et al. 2011).

Active packaging material and intelligent food packaging
Active materials and articles mean materials and articles that are intended to extend the shelf-life or to maintain or improve the condition of packaged food; they are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food. Specifically, for active packaging on the European market, the active packaging systems must be adequately labelled to allow identification by the consumer of non-edible parts, and new active or intelligent substances must be approved by the European Food Safety Authority (EFSA)[6]. Polymer composites containing **zinc oxide**, **silver**, **calcium phosphate** or **silver zeolite** nanoparticles, adding antimicrobial properties to the material, have been commercialized (Robinson and Morrison 2009).

Nanosensors made from **gold** and **titanium dioxide** nanoparticles can monitor and report the condition of the food when incorporated in food packaging. The nanosensors are in the early stages of development, and in Europe, only a few products are on the market, mainly for showing whether or not a product is likely to be palatable (Robinson and Morrison 2010).

Antibacterial and self-cleaning kitchenware
Several companies are marketing refrigerators, freezers and coffee machines in which nano-sized **silver** and **titanium dioxide** is incorporated in various inner surfaces in an apparent attempt to prevent microbial growth and maintain a clean and hygienic environment in the product. Similarly, antibacterial kitchenware coated with nano-sized silver (e.g. cutlery, pans, cutting boards, food containers and salad bowls) have been commercialized (Miller, Lowrey et al. 2008). None of these products have been identified on the Danish market; however, the products can readily be purchased online.

Within the last decade, several manufacturers have been marketing refrigerators, freezers and washing machines with antibacterial properties using nano-sized silver. However, the majority of these products are no longer to be found on the market. In 2005, one large manufacturer of kitchen appliances lunched a product line of antibacterial products, but had these products temporarily withdrawn from the market as a consequence of public backlash and pressure from NGOs. (El-Badawy, Feldhake et al. 2010).

[6] Regulation (EC 450/2009) lays out an authorisation process for the use of new active or intelligent substances in food contact materials. The legislation foresees that manufacturers requesting such an authorisation must first submit an application for the assessment of the safety of the relevant substance(s) to EFSA.

TABLE 6
TYPE OF POSSIBLE NANOMATERIAL USED INTERNATIONALLY FOR FOOD CONTACT MATERIALS (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THEIR FUNCTIONAL PROPERTY IN THE PRODUCT.

	Organo-clay	Titanium dioxide	Titanium nitride	Acrylic nanoparticles	Zinc oxide	Silver nanoparticles/ calcium phosphates	Silver zeolites	Silicon dioxide	Gold nanoparticles	Carbon black
Covered by the definition*?	X	X	X	X	X	X	X	X	X	X
Plastic (film, containers)	X	X	X	X	X	X	X	X	X	X
Plastic bottles	X	X	X					X		
Paperboard/ carton, paper										X
Cans (metal, glass)										X
Refrigerators, coffee machines,		X				X				
Cutlery, pans, cutting boards, food containers, salad bowls						X				

** Is the material assumed to be considered a nanomaterial according to the definition applied in the present survey?*

4.3 Use and user groups

The above-mentioned nanomaterials are mainly incorporated into or onto the polymeric materials used for food contact materials. Therefore, the general public, i.e. all age groups, are in contact with the materials.

TABLE 7
TYPE OF POSSIBLE NANOMATERIAL USED FOR FOOD PACKAGING (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THEIR FUNCTIONAL PROPERTY IN THE PRODUCT.

Effect	Organo-clay	Titanium dioxide	Titanium nitride	Acrylic nanoparticles	Zinc oxide	Silver nanoparticles/ calcium phosphates	Silver zeolites	Silicon dioxide	Gold nanoparticles	Carbon black
UV blockers		X			X					
Material and barrier properties	X			X				X		
Antimicrobials					X	X	X			
Nanosensors		X							X	
Pigments		X								X

4.4 Future trends

Much research has been and is being carried out on the incorporation of nanomaterials and nanotechnology in food packaging to obtain improved properties. The work is carried out on a national, European as well as a global level, for instance, in projects such as NanoPack (funded by The Danish Council for Strategic Research), the GoodFood project (FP6) and Natural Antimicrobials for Innovative Safe Packaging (FP7).

The predominant food-related area for short-term future exploitability of nanotechnology is food packaging (Nanotechnology 2008), and many of the world's largest food-packaging companies are actively exploring the potential of nanotechnology in order to develop new food-packaging materials with improved properties. These may include mechanical, barrier and antimicrobial properties as well as tracing and monitoring the conditions of food during storage and transport for e.g. food safety applications and precision processing (Nanotechnology 2008). A number of nano-improved packaging applications on the global, European and/or Danish markets are listed above, and even more are currently in the pipeline and being researched and developed.

Much R&D focus is currently given to nanocomposites, including specifically materials with nanoclay particulates; however, metal and metal oxide nanoparticles, nanofibres and nanotubes are also added to nanocomposites to alter barrier/functional properties. In addition, further functionalisation is added by including e.g. antimicrobial activities, visual indicators of food freshness, monitoring and tracking devices etc. A widespread use of biosensor technologies have to be significantly developed before they can be applied in food-packaging material (Robinson and Morrison 2009).

Additionally, active and intelligent food packaging are areas where nanotechnology is expected to have a large impact on food packaging with e.g. the development of RFID tags, temperature and gas sensors based on nanomaterials (Robinson and Morrison 2009). Current research focuses on the incorporation of nanosensors into food-packaging materials for tracking, safety and biosecurity purposes and on the development of rapid biosensors for the detection of chemical contaminants, viruses or pathogenic bacteria in food. The sensors include particles, engineered at nano-scale, to attach to pathogens or other contaminants which are then selectively identified by fluorescence or magnetic devices (Nanotechnology 2008).

For active packaging, the development of controlled release packaging, which can release nano-scale antimicrobials, antioxidants and/or flavours to increase shelf-life and sensory characteristics, has been on-going since 2005 (LaCoste, Schaich et al. 2005). A patent has been granted on nanocapsules releasing chlorine dioxide upon moisture exposure or nanoparticles (e.g. titanium dioxide) to photo-catalyse the production of gases for inhibition of microbial growth (US patent 5922776 A). Today, nanosilver and zinc oxide are used to obtain an antimicrobial effect by incorporation in e.g. plastic packaging materials, and an increased use of nanosilver in composite materials for food packaging is expected. However, in Denmark and Europe that is also dependent on the legislative approval of the application (Robinson and Morrison 2009).

Long-term applications of nanomaterials and nanotechnology in food packaging, i.e. requiring intense research and development, include self-healing composites, extreme condition packaging, nano-coding of plastics and paper materials for identification purposes as well as trade mark and fraud protection. These technologies are expected to emerge as the technologies advance, the corresponding costs are reduced, the use for food applications is considered safe and the industrial needs are increased (Nanotechnology 2008; Robinson and Morrison 2009).

Food contact material highlights

Silicon dioxide, titanium nitride and carbon black are the only three nanomaterials authorized for food packaging by the current European legislation, but many other possible materials exist in the global market and in research. With exemption to pigments (organic/inorganic), no nanomaterials have been identified in the Danish packaging industry. Kitchenware and various electronic devices (e.g. refrigerators, freezers and coffee machines), deliberately containing nanomaterials, have been brought to the market; however, at the time of the mapping none of these products could be identified at the Danish market.

Significant potential product types

- Plastic films and plastic containers.

Significant potential nanomaterials

- Carbon black, silicon dioxide, titanium nitride, nanocomposites (from nanoclay, metal and metal oxide nanoparticles; 2-5 mass%).

Use and users

- Potentially as pigments and to improve mechanical and barrier properties of traditional food packaging and to add functionalities such as sensoring/monitoring or release compounds/nanomaterials to food to achieve e.g. antimicrobial properties.

The use of nanomaterials in food packaging is dependent on legislation. If allowed, the use of nanomaterials is expected to increase in the future in spite of slow uptake and modesty in the industry especially for improved mechanical properties and within intelligent food packaging.

5. Cosmetics

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. A number of the delivery vehicles are based on vesicular delivery systems (liposomes, transferosomes) (ObservatoryNANO (b) 2010) that do not fall within the nanomaterial definition applied in this report and will, therefore, not be covered. Likewise, the abundant use of nano-emulsions is not included in the nanomaterial definition and will not be covered.

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). If the Commission has concerns regarding the safety of a nanomaterial, they can request an opinion from the Scientific Committee on Consumer Safety (SCCS). If the SCCS cannot assess the safety on the basis of existing data, the Commission will ask industry for necessary data within a given time limit. New regulation of a given ingredient in nano-scale can be introduced by the Commission on the basis of the SCCS opinion, if there is a potential risk or if data is inadequate.

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) will be made by the Commission at the latest in January 2014, indicating the categories of cosmetic products and the reasonably foreseeable exposure conditions.

All cosmetic products must be safety assessed before being introduced to the market according to article 10. The requirements to the safety report are further elaborated on in annex I to the regulation. Here it is stated that special attention needs to be given to the potential impact of particle size, on the toxicological profile of each ingredient in the product.

As nanomaterials used as colorants, UV filters or preservatives are exempted from part of article 16 in the regulation on cosmetic products, these will be the key focus in this survey on cosmetics.

5.1 Identified Danish prevalence of nanomaterials in cosmetics

Interviews with Danish cosmetic producers indicate a decrease in the use of nanomaterials in cosmetic products. Most Danish cosmetic producers offer a range of products in compliance with the ecolabel ‘Svanemærket’ which does not allow the use of nanomaterials with a few exceptions.

Most notably, this has led to a substitution of the former widespread use of titanium dioxide for the benefit of chemical UV filters in sunscreen.

From an interview with the Danish Consumer Council – regarding their 2013 survey covering 17 sunscreens, including five Danish products – it was noted, that none of the Danish products contained nano-titanium dioxide. The same was found for four other products. Out of the 17 sunscreens, nano-titanium dioxide was found in seven products. In the ingredient list, one brand specified that they use titanium dioxide in a nanoform. Zinc oxide[7] was identified in one product, but the producer has informed that it was not a nanozinc oxide.

In an interview with a Danish cosmetic producer, two nanomaterials were identified in five cosmetic products: carbon black (nano) is used in mascara and eyeliner in concentrations <3 % for colouring, titanium dioxide (anatase) is used in face powder and foundation as a UV filter in concentrations of <5 %, and both carbon black and titanium dioxide are used in nail polish for colouring purposes in concentrations of 2-3 %. According to the interview, nanomaterials (according to the number-based definition applied in this survey rather than a nanomaterial as often defined, based on mass) have been used in nail polish for several years, while the use of nanomaterials in mascara, eyeliner, face powder and foundation has been introduced within the last year. For all product types it was noted that nanomaterials were used in a relative small number of products – from 1/6 to 2/6 of each product type.

Zinc oxide, ferric oxide and aluminium hydroxides were identified in some products, but they were considered to be micron-sized materials, according to the respondent.

From interviews with cosmetic retail representatives it was quoted that until their cosmetic suppliers label products containing nanomaterials (in compliance with (EC) 1223/2009) they cannot provide specific information on the products, nanomaterials and concentrations used in cosmetics, but they expect to see an unspecified number of products from their existing product catalogue being labelled with 'nano' in the near future.

From interviews with chemical suppliers to the cosmetic industry it was learned that numerous pigments used in cosmetics can be defined as 'nanomaterials' depending on the method of measurement for particle size and surface area. These pigments include (but are not limited to) iron oxides, carbon black and aluminium hydroxide.

TABLE 8
MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH COSMETICS INDUSTRY.

Material	Product(s)	Function(s)	Amount
Titanium dioxide	Sunscreens; face powder; foundation; nail polish	UV filter	< 5 %
Carbon black	Make-up; eyeliner; mascara; nail polish	Colorant	< 3 %
Iron oxides	Make-up	Colorant	N/A
Aluminium hydroxide	Make-up	Colorant	N/A

[7] Whether the zinc oxide was used as a UV filter is not known.

5.2 Literature survey on nanomaterials in cosmetic product types

Nanomaterials applied in cosmetic products are estimated to a value of 100 m € and the main nanomaterials are synthetic amorphous silica, titanium dioxide and zinc oxide (Commission (b) 2012). An overview of the nanomaterials used in cosmetic applications is reproduced in Image 1 and given in Table 9. In general, cosmetic manufacturers use nano-scale versions of ingredients to provide better UV protection, deeper skin penetration, long-lasting effects, increased colour and finish quality, etc. (Raj, Shorna et al. 2012).

In many cases, the specific cosmetic use (i.e. the product type) of a given nanomaterial is not specified in literature, often since the material is used in several product types. When this is the case, the general term ‘cosmetics’ is used.

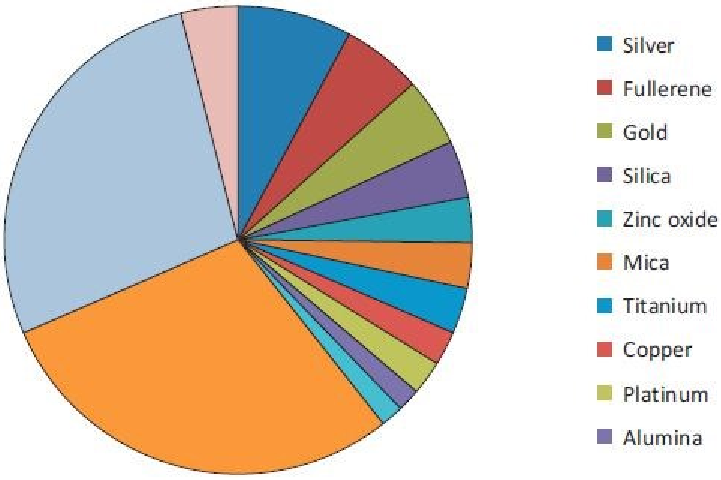

IMAGE 1
PRINCIPLE NANOMATERIALS USED IN COSMETICS. GRAPH FROM (RAJ, SHORNA ET AL. 2012).

Silica is used in a number of variations and may be used for example as an opacifying agent in cosmetics. Precipitated silica (amorphous silica, SiO_2) is used as carrier silica for liquids and semi-liquids and as anti-caking agent in toothpaste and other cosmetics, while silica gels, which are cross-linked silica network formed from the polymerisation of fine colloidal silica, are used in e.g. face powders, as flow conditioner and for oil absorption. Fumed silica is applied in toothpaste and cosmetics and as a carrier material for active ingredients (Commission (b) 2012), e.g. as silica nanocapsules (ObservatoryNANO (b) 2010).

Titanium dioxide is abundant in cosmetics: 5000 tonnes/year are used in the personal care industry, of which around 430 tonnes are applied for UV protection in sunscreens (Weir, Westerhoff et al. 2012). Titanium dioxide effectively reflects UV by physically blocking the UV radiation and the nano-form (around 20-50 nm) is transparent, which provides an aesthetic advantage for use in sunscreens (mostly rutile) (Commission (b) 2012; Raj, Shorna et al. 2012). The maximum concentration of titanium dioxide allowed in cosmetics according to (EC) 1223/2009 is 25 % whether nano- or macroscale particles are applied, and typical concentrations are in the range from 2 % to 15 % according to product labels (EPA 2009). The Scientific Committee on Consumer Safety (SCCS) has recently published an opinion based on the risk assessment of nano-sized titanium dioxide used as UV filter in sunscreen. Conclusions in the opinion state that “*considering the absence of a systemic exposure, the SCCS considers that the use of nano TiO_2 in dermally applied cosmetic products should not pose any significant risk to the consumer*” and that “*the SCCS does not recommend the use of nano TiO_2 in sprayable applications*” due to uncertain overall safety (SCCS 2013).

Nano-form **zinc oxide** in the size range of approx. 20 nm may be used in cosmetics as efficient physical UV filters (Raj, Shorna et al. 2012); however, it is not approved as a UV filter in the EU and Denmark according to (EC) 1223/2009. Zinc oxide in pigmentary form is, however, authorized as a cosmetic colorant. Many sunscreens and moisturisers using nano-form zinc oxide and titanium dioxide are available (presumably outside Denmark and/or not used as UV filter), and new modified systems with e.g. **carnauba wax nanoparticles** are being marketed (ObservatoryNANO (b) 2010). Zinc oxide is currently under investigation and may be approved as a UV filter. The SCCS has recently published an opinion based on the risk assessment of nano-sized zinc oxide used as UV filter in sunscreen. Conclusions in the opinion state that "*there is no indication for penetration of ZnO nanoparticles through the skin*" and that "*the use of nano ZnO in cosmetic products should not pose a risk to the consumer in the absence of a significant systemic exposure*." This leads to the overall opinion that "*the use of ZnO nanoparticles with the characteristics as indicated below, at a concentration up to 25% as a UV filter in sunscreens, can be considered not to pose a risk of adverse effects in humans after dermal application"* (SCCS 2012).

The use of **aluminium hydroxides** (colorants) is reported in toothpaste and cosmetics, while nano-form **ferric oxide** particles are used in cosmetics, offering both shade control and UV protection (Commission (b) 2012). There is a small market for **fullerenes** and its derivatives in cosmetics, where these compounds are used as dark colour and in anti-aging skin creams (ObservatoryNANO (b) 2010; Commission (b) 2012; Raj, Shorna et al. 2012).

The colorant **carbon black** is used in e.g. mascara and eyeliner and it is approved by the FDA for use in eyeliner, brush-on-brow, eye shadow, mascara, lipstick, blushers and rouge, make-up and foundation and nail enamel (Commission (b) 2012). In the EU, carbon black is approved as a colorant for all types of cosmetic products.

Nano-crystals, being aggregates (typically ranging from 10-400 nm) of compounds such as rutin, hesperidin, resveratrol or ascorbyl palmitate, are used in cosmetics, and, likewise, **silicone**, **copper**, **silver** and **gold nanoparticles**, as well as **nanoclay** have been reported in cosmetics (ObservatoryNANO (b) 2010; Commission (b) 2012). Examples include the use of nano-silver for its antimicrobial activities in deodorants and nano-gold in toothpaste as disinfectant (Raj, Shorna et al. 2012).

Further, nanocapsules for delivery of ingredients include various **polymer nanocapsules**, for example cyclodextrins and calcium alginate, applied in cosmetics. **Solid lipid nanoparticles** (SLPs) are used for skin care and sunscreens as delivery systems and skin penetration enhancers, and for delayed release of perfume, but for wide application of SLPs, the production process needs optimisation (ObservatoryNANO (b) 2010; Raj, Shorna et al. 2012).

TABLE 9
TYPE OF POSSIBLE NANOMATERIAL USED FOR COSMETICS (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THE PRODUCT TYPE.

Product type	Titanium dioxide	Silver	Gold	Carbon black	Fullerene	Iron oxide	Copper	Silica	Aluminium hydroxide
Covered by the definition*?	X	X	X	X	X	X	X	X	X
"Cosmetic"		X		X		X	X	X	X
Shampoo	X								
Sun screen	X					X		X	
Skin care/face cream					X				
Foundation/concealer	X			X		X			
Face powder				X				X	
Mascara				X		X			
Lipstick				X					
Eyeliner				X		X			
Nail enamel				X					
Deodorant	X	X							
Facial masks		X							
Toothpaste	X		X						X

** Is the material assumed to be considered a nanomaterial according to the definition applied in the present survey?*

5.3 Use and user groups

Cosmetics cover a wide range of care products that are overall distinguished by leave-on/leave-in products and rinse-off products, and the possible effects of nanomaterials are to a high extent dependent on this. The identified product types containing nanomaterials are listed below with elaborated descriptions of use and user groups. A comprehensive safety evaluation, including dosage (frequency and duration), of cosmetic products have recently been conducted by the Scientific Committee on Consumer Safety (SCCS 2012).

- Shampoo/conditioner: Wash-off products for hair care used by all age groups.
- Soap/body wash: Wash-off products for skin cleaning used by all age groups.
- Sunscreen: Leave-on product for UV protection applied to facial and body skin by all age groups.
- Skin care/face cream: Leave-on skin cream for face and/or body used by all age groups. Foundation/concealer: Leave-on facial products used mainly by female young and adult women.
- Face powder: Leave-on facial product used mainly by female young and adult women.
- Mascara: Leave-on product for eye lashes with little skin contact.
- Lipstick: Leave-on product for lips. Used by young and adult women.
- Eye liner: Leave-on product for skin around the eyes. Used by young and adult women.

- Nail enamel: Leave-on product for nails. Used by young and adult women.
- Deodorant: Leave-on product for armpits used by adolescents, young adults and adults once or more a day.
- Perfume: Leave-on product for facial/upper body use. Typically used by young adults and adults.
- Facial masks: Product applied to facial skin and rinsed off after a short time to cleanse and rejuvenate. Typically used by young adults and adults (primarily women).
- Toothpaste: Oral hygiene product used by all age groups, in general twice daily.

5.4 Future trends

Interviews in the cosmetics industry indicate a decrease in the industry's interest and use of nanomaterials in cosmetics. That is due to both fear of consumer responses to labelling standards and future EU regulation and environmental labelling that apply to most Danish producers.

However, ultrafine milling of pigments to (near-) nano-scale is according to the industry still an important development as it improves the colouring effect of most pigments. Whether these pigments will fall under the definition of a nanomaterial depends on measuring techniques and specification of the definition.

Much focus regarding nanomaterials in cosmetics is directed towards safety, and that is also evident in research on toxicity of nanomaterials, in general and for cosmetic applications. A general reluctance to talk about the use and possibilities of nanomaterials and nanotechnology in cosmetics is observed from industry and many industrial organisations, which is probably a result of the safety and toxicity focus and new regulation, bans and moratoriums (ObservatoryNANO (b) 2010).

As it appears from the literature review above, nanomaterials are prevalent in the cosmetics industry and have been for many years; however, just a few technologies are broadly employed, including liposomes, nanoemulsions and metal oxide nanoparticles – of which only the latter is included in this survey. Yet, controlled release functions of liposomes, nanoemulsions, polymer nanocapsules and SLNs are present on the market, and much current research directs attention to the improvement of existing encapsulation techniques and trigger-release mechanisms as well as technology transfer from newer drug delivery research for delivery purposes with specific consideration to reliable, cost-effective release triggers. Also, for example SLNs and nanocapsules require increased loading capability and storage stability, i.e. inhibition of the untimely release of ingredients, and the formation of objects need closer studies for full control and sufficiently cost-efficient production and application (ObservatoryNANO (b) 2010). The release systems may be relevant for a number of ingredients, including preservatives and colorants. The uses of silver, copper and silica nanoparticles in cosmetics are expected to continue, and research and improvement on e.g. their incorporation, antimicrobial/preserving effects and safety may be further studied.

Cosmetics highlights

Nanomaterials in cosmetics are abundant and many of the nanomaterials are used for a wide range of product types. Nanomaterials in cosmetics are labelled on the list of ingredients and catalogued by the European Commission. Nanomaterials must be notified to the Commission except for colorants, UV filters and preservatives.

Significant potential product types

- Sunscreen, face powders, foundation, eyeliner, nail polish, toothpaste; generally applied in a wide range of cosmetic products.

Significant potential nanomaterials

- Carbon black, silica, titanium dioxide, aluminium hydroxides and zinc oxide.

Use and users

- Primarily dermal and to some extent oral exposure of leave-on products for all age groups, and especially for sunscreen, children are exposed more than adults.

The use of possible nanomaterials such as pigments, UV absorbers and preservatives is expected to continue, but is dependent on the authorisation of pigments, UV absorbers and preservatives in Annex IV-VI of (EC) 1223/2009. The regulation provisions on nanomaterials will be revised as more knowledge of toxicity and safety of the nanomaterials is obtained.

6. Pesticides

Nano-pesticides within the agrochemical sector are just emerging, and many predict a rapid growth in the coming years. In the last decade, more than 3,000 patent applications dealing with nano-pesticides have been submitted (Kah, Beulke et al. 2012). Nevertheless, the only major agrochemical company having announced to manufacture products containing nanomaterials – being nano-emulsions – is Syngenta (ObservatoryNANO (a) 2010). According to the definition applied in this survey, no commercial pesticides with nanomaterials have been identified. This corresponds well with the Danish EPA who states that no pesticide nano-formulation is marketed in Denmark. In the below section, present and near-to-market applications of nano-pesticides are described.

It has been estimated that a large percentage of conventional pesticides are lost to the air during application, as run-off or by decomposing (depending on the environmental conditions), which affects both the environment and costs for the farmer negatively (ObservatoryNANO (a) 2010; Gogos, Knauer et al. 2012). Moreover, recent amendments to the EU regulation covering the use of pesticides (Regulation (EC) 1107/2009) may decrease the number of pesticides available (15 % of the 300 accepted chemicals have been estimated by the UK government's Pesticides Safety Directorate) (ObservatoryNANO (a) 2010; Kah, Beulke et al. 2012).

The agrochemical industry is aiming to address these challenges by targeting the pests more effectively and by controlled release of small (but sufficient) amounts of pesticide over a period of time. Nanomaterials with high surface area and appropriate release kinetics are explored for minimizing losses by reducing run-off and decreasing release kinetics. Specifically designed nanoparticles could be used for protecting the active ingredients and enhance uptake into the leaves and other parts of the plant. As active ingredients, nanomaterials have the potential to reduce the dosage through their enhanced reactivity (Gogos, Knauer et al. 2012).

The term nano-pesticide covers a wide variety of products. Most nano-formulations combine several objects in the nanometer size range, for example polymers, surfactants and metal nanoparticles with the active ingredient

6.1 Future potential use of nanomaterials in pesticides

The application of pesticide nano-formulations provides new (more) methods to obtain the desired properties of pesticides, these being (*i)* increased solubility of poorly soluble active ingredients, (*ii*) release of the active ingredient in a controlled/targeted manner and (*iii*) protection of the active ingredient against premature degradation (Kah, Beulke et al. 2012).

Formulations aiming to increase the solubility of poorly water-soluble compounds
The most common pesticides are based on poorly water-soluble active ingredients which are formulated as stabilised emulsions with droplet sizes ranging from 500 nm to 10 µm. In 2007, emulsifiable concentrates represented 28 % of the total number of formulations listed in the Pesticide Manual (U.S. Environmental Protection Agency) (Kah, Beulke et al. 2012).

Nano-emulsions and microemulsions are formulations consisting of an active ingredient dissolved in oil, surfactant solubilisers, co-surfactants and water (Knowles 2004). Information collected by the ObservatoryNANO from industrial representatives suggests that micro-emulsions are likely to be more prevalent than nano-emulsions (Kah, Beulke et al. 2012). Nano-emulsions are systems that are metastable. The challenge is to stabilize them against crystallisation, agglomeration and sedimentation. The development of economically viable preparation and stabilisation methods remains the subject of intensive research (ObservatoryNANO (a) 2010; Kah, Beulke et al. 2012).

Dispersions of nano-sized crystalline or amorphous active ingredients in liquid media lead to the formation of **nano-suspensions,** having similar properties to solutions. The approach aims to maximize the surface area to increase dissolution rate and solubility saturation of poorly water-soluble active ingredients (Kah, Beulke et al. 2012). Challenges remain in the processing of nano-dispersions and in maintaining stability (ObservatoryNANO (a) 2010).

Nano-formulations for controlled/targeted release, protection from premature degradation
For the last decade, hundreds of studies have explored the possibility of releasing the active ingredient in a controlled manner. As a carrier system, **polymer-based** formulations, **solid-lipid nanoparticles**, **silica nanoparticles** and **nanoclays** have been studied (Kah, Beulke et al. 2012). In addition, the carrier system can be used to protect the active ingredient from premature degradation. Currently, no nano-carrier formulation has been commercialized (Kah, Beulke et al. 2012.

TABLE 10
TYPE OF POSSIBLE NANOMATERIAL USED FOR PESTICIDE PRODUCTS (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THEIR FUNCTIONAL PROPERTY EXERTED IN THE PRODUCT.

Effect	Nano-emulsions	Nano-dsipersions	Polymer-based formulations	Solid-lipid nanoparticles	Silica	Nanoclay
Solubility	X	X				
Controlled release			X	X	X	X

6.2 Use and user groups

Pesticides are used in the agricultural sector and mainly by professionals; however, some products are marketed for consumers as well. Most of the products are marketed as liquid and granule products for pest protection/treatment of crops.

Pesticides highlights

According to the definition applied in this survey, no commercial pesticides with nanomaterials have been identified on the Danish market; however, literature describes a number of potential applications of nanomaterials in pesticide products. The application of pesticide nano-formulations provides new (more) methods for protection against degradation, controlled release and increased solubility of the active ingredients.

Significant potential product types

- Nano-emulsions and nano-dispersions
- Targeted and controlled release.

Significant potential materials

- Nanocarrier systems: Nanoclay, silica and polymer nanoparticles, solid-lipid nanoparticles.

Use and user groups

- Most products sold as liquids and granules
- Mainly used by professionals.

Nano-pesticides within the agrochemical sector are emerging and many predict a rapid growth in the coming years. More than 3,000 patents dealing with nano-pesticides have been submitted during the last decade.

7. Medical Devices

Medical devices as defined in the European Medical Device Directive include devices to be used specifically for:

- Diagnosis, prevention, monitoring, treatment or alleviation of disease.
- Diagnosis, monitoring, treatment, alleviation of or compensation for an injury or handicap.
- Investigation, replacement or modification of the anatomy or of a physiological process.
- Control of conception (Council Directive 93/42/EEC).

In practice, this includes various types of medical devices such as diagnostic imaging equipment, x-ray machines and magnetic resonance imaging (MRI) scanners, pacemakers and cochlear ear implants and other implantable devices, prostheses and dentures, mechanical contraceptives such as spirals, pathology tests and diagnostic devices such as in vitro diagnostic test kits, aids for disabled such as walking sticks and equipment produced for a particular patient (custom-made medical devices) (see also EC 2009).

In the field of medical devices, the following product categories of alleged use of nanomaterials have been identified by Notified Bodies[8]:

- Carbon nanotubes in bone cement
- Nano-paste hydroxyapatite powder for bone void filling
- Polymer-setting material with nanoparticles in dental cement
- Polycrystalline nano-ceramics in dental restorative materials
- Nano-silver or other nanomaterials used as coatings on implants and catheters
- Nano-silver used as an antibacterial agent, for example in wound dressings.

A number of surgical blades (cutting edge diameter in the nano- to microregion), nano-needles (external diameter 200-300 nm) and nano-tweezers (surgical tools) have been developed and marketed. These products do not fall within the nanomaterial definition applied in this survey as they are considered a nanostructured surface and will, therefore, not be covered.

7.1 Identified Danish prevalence of nanomaterials in medical devices

Interviews with Danish medical device companies and sales offices give support to the literature and indicate a number of predominant uses of nanomaterials.

Dental treatment

Nano Resin ceramics are widespread in the dental applications market and they are found in dental filling, adhesives and implant products. Both **silane-treated silicate** and **zirconium dioxide nanoparticles** are used to create strong and flexible nano-composites with concentrations of up to 1 % zirconia and 10-20 % silicates.

Wound dressings and plasters

[8] A Notified Body is an organization appointed by the national accreditation authorities and "notified" to the European Commission to approve products covered by the Medical Devices Directive

Silver nanoparticles for antibacterial effects are used in wound dressings and plasters in concentrations of approx. 1-5 % while **calcium alginate** is found to be used as a nanocarrier system for antibacterial agents (e.g. as alginated silver) and to absorb moist around wounds. Both silver and calcium alginate have been on the market for more than 10 years and are widely used by healthcare professionals. The use of silver in these types of products is widespread all-though, in some cases, it is expected that manufacturers use silver particles of a bigger size.

Ostomy bags
Copper is used for filtration in ostomy bags in concentrations of <0.0001 % of the device. It is encapsulated in foam or foils that are in direct contact with the skin or ostomy system of patients.

Pigmentation of medical devices
Several pigments in near-nanosize are used in different applications for dying and UV protection. Nanomaterial examples from the interviews include **iron oxide**, **titanium dioxide** and **zinc oxide** used in applications ranging from plasters, wound dressings and ostomy devices in concentrations of approx. 0.1-20%.

Nano-sized zinc oxide works as an antibacterial agent and can enhance the antibacterial effect of other biocides. However, none of the interviews point to a use of zinc oxide as an antibacterial agent, but rather for pigmentation and adhesive properties.

TABLE 11
MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH MEDICAL DEVICE INDUSTRY.

Material	Product(s)	Function(s)	Amount*
Silicates	Dental fillings, glue and implants	Mechanical properties	10-20 %
Zirconium dioxide (zirconia)	Dental fillings, glue and implants	Mechanical properties	10-20 %
Silver	Wound dressings and plasters	Antibacterial	N/A
Calcium alginate	Wound dressings and plasters	Carrier and moist absorbent	N/A
Copper	Ostomy bags	Filter	<0.0001 %
Zinc oxide	Plasters, wound dressings, ostomy bags	Pigment and adhesion	0.1-20 %
Iron oxide	Polymer devices	Pigment	<0.2 %
Titanium dioxide (anatase)	Ostomy and incontinent devices , plasters	Pigment	0.001-0.5 %

** Information was provided by producers as mass concentration of the entire device.*

It has not been possible to gather information on application of biomedical imaging, bone cement and fillings in Denmark.

7.2 Literature survey on nanomaterials in medical devices

Research on nanomaterials in medical devices covers a range of applications. Four areas have reached a level of development to yield commercial applications – hard tissue engineering, dental restorative materials, antimicrobial surface treatments and medical diagnostics. An overview of nanomaterials in medical device applications is given in table 12.

Bone cement, bone filling, dental restorative materials

In hard tissue engineering, the addition of fibres and/or particles, such as **carbon nanotubes**, to bone cement has been shown to improve fatigue performance. Several companies market injectable bone void filling products and ceramic implants containing ***beta*-tri-calcium phosphates**, **hydroxyapatite (calcium phosphates)** and **zirconium dioxide** nanoparticles for orthopaedic and dental applications (Alves Cardoso, Jansen et al. 2012; Ventola 2012).

Antimicrobial materials and coatings

In 2011, approx. 320 tonnes of **nano-silver** was produced and used worldwide, and the predicted use of nano-silver in 2015 is 1,120 tonnes for all product categories (Lem, Choudhury et al. 2012). Potential medical device applications of nano-silver include surgical instruments, face masks, bone cement and wound dressings. In hospital settings, nano-silver is used extensively for wound management, particularly for the treatment of burns, various ulcers, for healing of donor sites and meshed skin grafts (Silver, Phung et al. 2006).

Titanium dioxide nanoparticles coated with silver are applied for coating operation tables and surgical equipment to prevent or reduce the presence of pathogenic bacteria, vira and fungi. Moreover, **copper** and **zinc oxide** can be used for antimicrobial materials and coatings, but the prevalence of these materials in medical devices are at present time unknown.

Medical diagnostics

The use of nanomaterials and nanoparticles for biomarker detection and diagnostic imaging is considered one of the most significant and promising nano-medical applications. Paramagnetic and superparamagnetic **iron oxide** nanoparticles are used as contrast agents for biomedical imaging (Ventola 2012).

TABLE 12
TYPE OF POSSIBLE NANOMATERIAL USED FOR MEDICAL DEVICES (NON-EXHAUSTIVE TABLE). THE NANOMATERIALS ARE ASSIGNED TO THE PRODUCT TYPE.

	Beta-tri-calcium phosphates	Hydroxyapatite	Zirconium dioxide	Silver	Titanium dioxide	Copper	Zinc oxide	Iron oxide
Covered by the definition*?	(X)	X	X	X	X	X	X	X
Bone void filling products	X	X	X					
Ceramic implants	X	X	X					
Surgical instruments				X	X			
Bone cement				X	X			
Wound dressings				X				
Antimicrobial coatings				X	X	X	X	

** Is the material assumed to be considered a nanomaterial according to the definition applied in the present survey?*

7.3 Use and user groups

Medical devices cover a wide range of products (see table 12), most of which are used in healthcare, psychiatry, elderly care or dental settings. The identified product types containing nanomaterials are listed below with descriptions of use and user groups:

- Bone cement, bone filling materials, implants and dental restorative materials are used for orthopaedic and dental surgery. These products are used by professional healthcare staff only, but are used and incorporated inside the body. Nanomaterials are bound in a resin matrix and exposure to consumers is assessed to be limited to release from mechanical wearing and accidental oral intake (in the case of dental fillings).
- Antimicrobial wound dressings are used for wound treatment. The products are applied to the skin and wounds for a temporary time period by both professional healthcare staff and patients. Plasters with nano-silver are in some cases sold directly to consumers.
- Antimicrobial face masks, gloves, etc. are used daily by hospital and home-care staff. The products are in contact with the skin and airways.
- Antimicrobial catheters, etc. are used in invasive surgery by healthcare professionals. Release of nanomaterials to flesh and skin is expected to be minimal.
- Contrast agents are used intravenously for medical diagnostics and are, thereby, exposed directly inside the body.
- Various medical devices from composite materials containing nano-sized pigments are applied on the skin, mucous membrane or wounds, but dermal exposure is minimal due to the matrix entrapment.

TABLE 13
TYPE OF POSSIBLE NANOMATERIAL USED FOR MEDICAL DEVICES (NON-EXHAUSTIVE TABLE).

Effect	*Beta*-tri-calcium phosphates	Hydroxyapatite	Zirconium dioxide	Silver	Titanium dioxide	Copper	Zinc oxide	Iron oxide
Bone filling and cement	X	X	X					
Dental restorative materials	X	X	X					
Antimicrobial catheters, wound dressing, and surface treatments				X	X	X	X	
Biomedical imaging and biomarkers								X

7.4 Future trends

Interviews point to a growing market for the products mentioned above, with a marketing of new products containing nanomaterials at the same (moderate) level as today. However, the future use of nanomaterials in medical devices is strongly dependent on the regulation in the EU (Medical Device Directive, the Biocide Directive and REACH) and the US (US Food and Drug Administration).

One of the most argued and researched areas of application of nanomaterials are products with antimicrobial effects. Although several applications can be identified, chemical and biocidal producers have been reluctant to target innovation into this direction (Schut 2011), primarily due to restrictive and costly regulation and, secondly, due to a trade-off of costs and efficiency between nano- and micro-sized materials. Yet, looking at the list of biocides under evaluation for approval under the Biocide Directive product type 2 (DG-EVN 2013), several applications of biocidal products based on titanium dioxide, zirconium and silver/ copper/zinc compounds for metallic ion-release are identified. None of the products are labelled as a nanomaterial-based product in the inventory.

The battle against multi-resistant bacteria and hospital-acquired infections is a prime concern in the global health sector and may push the development of new antibacterial systems on medical devices based on nanomaterials. At the same time, there are several examples of national regulatory authorities (incl. the Danish Serum Institute (2013)) that do not advocate the use of biocides (incl. nanomaterials) in the healthcare sector due to epidemiological concerns of antibiotic resistance (Tvenstrup 2013). Based on the given considerations, a moderate development of antibacterial solutions for medical device applications is expected.

Tissue engineering using nanomaterials is another field of significant research and innovation that may yield new medical device products within a time range of five years. Nanomaterials mimic the constituent properties of natural tissues better than macro-sized materials. Scientists work to utilize carbon-based nanomaterials (carbon nanotubes, nanofibres, fullerenes, grapheme, etc.) and synthetic polymeric nanomaterials for soft tissue (vascular, cardiac, cartilage, ligament and neural) as well as for hard tissue (bone, craniofacial and dental) (Gaharwar, Sant et al. 2013). As seen today, hard-tissue applications on market to a large degree utilize ceramic and mineralised nanomaterials for biomimicking natural structures like nacre and bone structures (Parratt and Yao 2013).

Imaging diagnostics is another profound research area with new applications using metallic nanomaterials (for example gold, silver and silica) and polymeric nanomaterials (for example chitosan, dextran, PEG and PLGA). The field is to some extent merging with drug delivery, where inherent photo-capabilities and carrier functions may be combined for diagnostic and therapeutic purposes (Menon, Jadeja et al. 2013).

Medical devices highlights

Several nanomaterials are used in medical devices and some are identified in Danish companies and products.

Significant potential product types

- Plaster and wound dressings; ostomy bags and catheters; dental fillings, glue and implants; composite polymers and glue; contrast agent.

Significant potential materials

- Antibacterial agents: alginate silver, silver, zinc oxide, titanium dioxide (anatase)
- Moist absorbent: calcium alginate
- Mechanical properties: zirconium dioxide and silicates
- Colour: iron oxide and other pigments.

Use and users

- All products (except wound plasters and ostomy bags) are used by healthcare professionals for treatment of patients.
- The identified products are in direct contact and exposed to skin, tissue or mucous membrane.
- Typical medical devices use nanomaterials as additives in composite materials.
- Nanomaterials in liquid dispersions, glue and pastes are used in dental care applications and wound treatment.

Imaging, diagnostics and tissue engineering represent promising research and innovation fields expected to yield new applications based on carbon, synthetic polymeric, metallic and ceramic nanomaterials. R&D investments and regulatory trends point to a moderate introduction of new solutions to the marked.

8. Water Treatment

It is widely recognized that nanotechnology and applications thereof hold the promise to resolve issues relating to water shortage and water quality. Considerable efforts are underway to explore the use of nanomaterials in applications such as adsorption, catalysis and membrane separation. The first commercial products have recently been displayed on the market and nanotechnology in water treatment is expected to see a rapid growth in the coming years.

8.1 Identified Danish prevalence of nanomaterials in water treatment

Interviews with representatives from the Danish industry support the findings in literature that the applications of nanomaterials for water purification and waste-water treatment are just emerging. On the Danish market, photocatalytic UV irradiation systems have successfully been implemented in a very limited number of public swimming facilities, and large-scale systems for treating ballast water have been on the market for several years. Water-treatment products with nanosilver are marketed online and may be imported.

TABLE 14
MATERIALS (THAT MAY BE CONSIDERED A NANOMATERIAL) IDENTIFIED IN THE DANISH WATER TREATMENT INDUSTRY.

Material	Product(s)	Function(s)	Amount
Titanium dioxide	UV irradiation systems	Removal of pathogens and trace contaminants	N/A
Silver	Disinfection	Antimicrobial	N/A

The UV irradiation systems are treated with a thin coating layer of titanium dioxide, meaning that the amount of titanium dioxide is negligible compared to the total system, and due to the deposition technique, no or insignificant amounts of nanomaterial is expected to be released to the water. For silver-treated systems, the amount of silver is minor, but no exact figures are given. To excert an antimicrobial effect, silver ions must be released from the surface, causing a risk of exposure.

8.2 Literature survey on nanomaterials in water treatment

Adsorption is commonly used as a polishing step to remove organic and inorganic contaminants. Nano-adsorbents offer significant improvement compared to micro-sized adsorbents because of their high surface area (Qu, Alvarez et al. 2013). Carbon-based nano-adsorbents, metal-based nano-adsorbents and polymeric nano-adsorbents have all been intensively studied (Mohmood, Lopes et al. 2013), yet only metal-based nano-adsorbents, including **titanium dioxide, zero-valent iron** and **iron oxide,** are commercially available. These are marketed for removal of metallic pollutants such as Cr(VI), Cu(II), Co(II), As(V/III) and Hg(II) from industrial effluents (Sharma, Srivastava et al. 2009). To overcome additional separation steps in the water treatment, the nano-adsorbents are commonly used in fixed or fluidized adsorbers in the form of pellets/beads or porous granules loaded with nano-adsorbents (Qu, Alvarez et al. 2013).

In particular, inorganic–organic triflouronitrile membranes (also known as mixed-matrix membranes) have attracted growing research interest in recent years and a few examples are available on the European market. Incorporation of nanomaterials has the potential to improve membrane permeability and fouling resistance as well as to add contaminant degradation and self-cleaning properties. Nanomaterials used for such applications include metal oxide nanoparticles (**aluminium oxide, titanium dioxide** and **zeolites**), antimicrobial nanoparticles (**silver** and **carbon nanotubes**) and photocatalytic **titanium dioxide**(anatase) nanoparticles (Qu, Alvarez et al. 2013). Mixed-matrix membranes with micro-scale particles have been commercially available for many years; however, nano-scale particles are just emerging (Pendergast and Hoek 2011), e.g. for seawater desalination by reverse osmosis.

Photocatalytic UV irradiation systems with **titanium dioxide** nanoparticles as a catalyst are applied for the removal of trace contaminants and pathogens (Savage and Diallo 2005; Qu, Alvarez et al. 2013). Two configurations are commonly used: slurry reactors and immobilized. Photocatalytic water-treatment applications have almost become a mature market, as systems based on artificial UV light have been on the market for several years and systems for treating municipal, industrial, swimming facility, drinking and ballast water are also available (Saari, Iler et al. 2010).

Nano-silver has been incorporated into ceramic microfilters as a barrier for pathogens which can be employed in remote areas, and some commercial devices utilizing **nano-silver** are currently available.

TABLE 15
TYPE OF POSSIBLE NANOMATERIAL USED FOR WATER TREATMENT (NON-EXHAUSTIVE TABLE).

Effect	Titanium dioxide	Zero-valent iron	Iron oxide	Silver	Aluminium oxide	Zeolites	Carbon nanotubes
Covered by the definition*?	X	X	X	X	X	X	X
Adsorption	X	X	X				
Membrane	X				X	X	X
Photocatalytic UV irradiation	X						
Disinfection				X			

* Is the material assumed to be considered a nanomaterial according to the definition applied in the present survey?

8.3 Use and user groups

All systems are used for water purification and for waste-water treatment. Most of the commercially available products in this category are used by professionals, while only a few products are consumer products, e.g. water-treatment systems with silver for hiking. An insignificant amount of titanium dioxide is used in the products, since it is applied as a thin layer, and no or very low amounts of the titanium dioxide can be leached from the surface.

8.4 Future trends

Much research has been and is being carried out on the incorporation of nanomaterials and nanotechnology in water treatment. The work is carried out at national as well as international levels. At European level, more than 15 relevant research activities concerning the application of nanotechnology for water treatment are being funded by the European Commission in the scope of the 7th Framework Programme (FP7).

Solar photocatalytic water treatment plants are at a demonstration phase and pilot projects for drinking water purification in developing countries are being tested (Saari, Iler et al. 2010). Iron oxide and zero-valent iron have been investigated in numerous field studies in Denmark for the removal of chlorinated compounds, e.g. in Environmental Project No. 1198, 2007, for the Danish EPA.

Some concern about the use of nanomaterials in water treatment has been raised. Therefore, retention and/or reuse of nanomaterials are key aspects in the market penetration of water treatment using nanotechnology (Qu, Alvarez et al. 2013). Moreover, higher manufacturing costs of most nano-enabled devices can potentially delay a market penetration (Pendergast and Hoek 2011).

Membrane fouling is one of the most important problems in membrane technology as the permeate flux and recovery rate decrease, which lead to increased operating costs and a reduced membrane life. Incorporation of nanomaterials in the membrane has been shown as a possible solution to the fouling challenges and is expected to be more prevalent in the near future (Pendergast and Hoek 2011). The focus on reduced fouling was particularly addressed in a recent FP7 call 'Active nanomembranes, -filters and -adsorbents for efficient water treatment with stable or regenerable low-fouling surfaces'.

Adsorbents exploiting the large surface-to-mass ratio of nanomaterials are heavily explored, and, while some commercial products are already available, an increased use of nano-adsorbents in water treatment is expected.

Water treatment highlights

It is widely recognized that nanotechnology and its applications hold the promise to resolve issues relating to water shortage and water quality.

Significant potential product types
- Nano-adsorbents
- Membranes
- Photocatalytic UV irradiation
- Disinfection.

Significant potential materials
- Titanium dioxide, iron oxide, zero-valent iron, silver.

Use and users
- Mainly used by professionals.

Considerable efforts are underway to explore uses of nanomaterials in applications such as adsorption, catalysis and membrane separation. Most applications of nanomaterials in water treatment are at research stage, while a few technologies have been commercialised.

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Supplementary Survey of Products on the Danish Market Containing Nanomaterials

The Supplementary Survey maps the prevalence of products possibly containing nanomaterials on the Danish market among the product groups: Food; feed; food contact materials; cosmetics; pesticides; medical devices and water treatment systems. The survey is based on existing literature and interviews with key actors in the relevant industries.

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