National Institute for Public Health
and the Environment
*Ministry of Health, Welfare and Sport*

# Nanomaterial in consumer products

*Detection, characterisation and interpretation*

Report 320029001/2011

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RIVM Report 320029001/2011

# Colophon



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This investigation has been performed by order and for the account of the Ministry of Health, Welfare and Sport (VWS), on behalf of the Dutch Interdepartmental Working Group on the Risks of Nanomaterials (IWR)

# Abstract


**Nanomaterials in consumer products**
Detection, characterization and interpretation

In the research on health risks of nanomaterials, there is a demand for information on the presence of nanomaterials in consumer products. This information is required to estimate health risks, but is largely missing. A lot of information on nanomaterials in consumer products can be acquired with microscopic techniques. However, it is impossible to determine for all products if they contain nanomaterials, and if so to which extent. This appears from orientating research by the RIVM, commissioned by the Ministry of Health, Welfare and Sport (VWS) on behalf of the Interdepartmental Working Group on the Risks of Nanomaterials (IWR).

Various inventories and data bases exist in which products are included which bear the term 'nano', suggesting that these products contain nanomaterials or are manufactured with nanotechnology. However, it is unclear if these products actually contain nanomaterial. In addition, little is known to which extent products that do not bear the term 'nano' contain nanomaterial.

Twenty-five non-food consumer products were selected for the research, of which 22 could be obtained and analyzed. These products were investigated with microscopic techniques to investigate to which extent these techniques are appropriate to assess if the products contain nanomaterials. Furthermore, it is investigated if characteristics of the nanomaterials that are relevant for risk assessment can be determined. The products were selected on the basis of a nano claim, or on the basis of the expectation on the presence of nanomaterial.

Nanomaterials were not found in a number of products with a nano claim, or products contained another than the claimed nanomaterial. In addition, nanomaterials were found in some products without a claim. In order to obtain better insight in the presence of and exposure to nanomaterials via consumer products, it is of importance to improve the analytical techniques in such a way that a negative result guarantees the absence of nanomaterials in the specific product. Furthermore, it is desirable to be able to accurately measure the concentration of nanomaterial, and to develop other techniques which are well equipped to measure in liquid matrices or air after application of a spray. Considering the limited number of products investigated in the present orientating study, it is also of importance to investigate more consumer products on nanomaterials.


Keywords:
nanomaterials, consumer products, analysis, electron microscopy, nano claim

# Rapport in het kort

**Nanomateriaal in consumentenproducten**
Detectie, karakterisatie en interpretatie

In onderzoek naar risico's van nanomaterialen voor mensen is grote behoefte aan informatie over de aanwezigheid van nanomaterialen in consumentenproducten. Deze informatie is nodig om risico's in te kunnen schatten, maar ontbreekt vooralsnog grotendeels. Met microscopische technieken kan veel informatie over nanomateriaal in consumentenproducten worden verkregen. Het is echter nog niet mogelijk van alle producten te meten of ze nanomateriaal bevatten en zo ja, in welke mate. Dit blijkt uit een oriënterend onderzoek van het RIVM, dat in opdracht van het ministerie van Volksgezondheid, Welzijn en Sport (VWS) namens de Interdepartementale Werkgroep Risico's Nanomateriaal (IWR) is uitgevoerd.

Er bestaan diverse inventarisaties en databases waarin producten zijn opgenomen waarop de term 'nano' is vermeld, wat suggereert dat ze nanomateriaal bevatten of met nanotechnologie zijn vervaardigd. Het is echter niet duidelijk of deze producten daadwerkelijk nanomateriaal bevatten. Daarnaast is weinig bekend in hoeverre producten die de term 'nano' niet dragen toch nanomateriaal bevatten.

Voor het onderzoek zijn 25 non-food consumentenproducten geselecteerd, waarvan er 22 konden worden verkregen en doorgemeten. Hiervan is met behulp van microscopische technieken bekeken in hoeverre deze technieken geschikt zijn om na te gaan of de producten nanomaterialen bevatten. Daarnaast is bekeken of eigenschappen van het nanomateriaal (karakteristieken) die voor de risicobeoordeling relevant zijn, ermee kunnen worden bepaald. De producten zijn geselecteerd op basis van een nanoclaim of op basis van het vermoeden dat het nanodeeltjes bevat.

In een aantal producten met een nanoclaim werd geen nanomateriaal aangetroffen, dan wel een ander nanomateriaal dan geclaimd. Daarnaast is in sommige producten zonder claim wel nanomateriaal aangetroffen. Om beter inzicht in de aanwezigheid van en de blootstelling aan nanomaterialen via consumentenproducten te krijgen, is het van belang de meetmethoden zodanig te verbeteren dat een negatieve uitslag ook daadwerkelijk betekent dat een product geen nanodeeltjes bevat. Daarnaast is het wenselijk de concentratie van nanomateriaal goed te kunnen bepalen en andere technieken te ontwikkelen om goed te kunnen meten in vloeibare producten en in de lucht na gebruik van een spray. Gezien het beperkte aantal onderzochte producten in deze oriënterende studie is het van belang meer consumentenproducten door te lichten op nanomaterialen.

Trefwoorden:
nanomateriaal, consumentenproducten, analyse, elektronenmicroscopie, nanoclaim

# Contents

## Summary

Nanomaterials are being used in a large number of applications, amongst others in consumer products, but clear insight in the consumer exposure to nanomaterials is still lacking. Nanomaterials are considered to be materials with in at least one dimension a size at the nanoscale, and include nanoparticles as well as nanolayers. Inventories on nano consumer products exist, typically based on the claim on the presence of nanomaterials made by the manufacturers. As a consequence, products without a nanoclaim are generally not included in such inventories. In addition, little is known about the actual presence of nanomaterials in products with or without a nanoclaim. Furthermore, a lot of information on nanomaterials in consumer products can be acquired with microscopic techniques, but it is unknown to which extent these techniques are appropriate to actually assess the presence of nanomaterials and characteristics relevant for risk assessment. In order to address these issues, in the present orientating study 25 products with and without a nanoclaim were selected, of which 22 were investigated in high quality analytical facilities.

Analysis was performed by the combination of the electron microscopic techniques SEM and TEM, and EDX and XPS. EDX can be used to determine the chemical composition of the nanomaterial, whereas XPS can be used to determine the ratio of elements present in the measured area of the sample. The results of these measurements indicate that the combination of the above techniques enables to investigate the presence of nanomaterials and several nanocharacteristics. In general, size, shape and chemical composition of nanomaterials can be visualized and determined. However, in light of the applicability of the techniques and the results for risk assessment and enforcement, there are several limitations which should be taken in consideration. These are:

- It is impossible to be conclusive about the absence of nanomaterials in a product as it is only feasible to investigate a very limited area (± 1 $\mu m^2$) of the sample. As a consequence, false negative measurements are possible, i.e. nanomaterials are not detected but are present (in low concentrations) in the sample.
- The applied techniques are well suited for solid state samples. Important nanocharacteristics such as size distribution, shape, location and coating can in general be determined.
- The applied techniques have limitations for creams and viscous liquids. For these matrices the samples were treated with ethanol to separate most of the cream matrix from the nanomaterial. However, as a result of this treatment organic nanomaterials may fall apart, making it impossible to draw conclusions on the presence of organic nanomaterial. In addition, the treatment may affect nanocharacteristics such as aggregation/agglomeration status and coating of inorganic nanomaterial.
- The applied techniques are not suitable for aerosols. In the present study, several spray products were applied upon a solid surface and subsequently analyzed. Other approaches that measure particles in aerosols need to be considered for assessment of the exposure to nanomaterials via inhalation.
- The applied techniques are not analytically validated for the determination of nanocharacteristics in the matrices of consumer products. Validation is recommended.

- XPS was used to determine the total concentration of specific elements. The lower limit of detection for this analytical technique was in several cases too high for analysis of the element of the nanomaterial in a consumer product. Other approaches should be considered.
- XPS was used to determine the total concentration of specific elements. The thus determined concentration of an element does not necessarily represent the concentration of the nanomaterial in the product, as the same element may also be present in non-nano form.

In addition, several conclusions and observations can be made on the results of the analysis of consumer products:

- The present study shows that products without a claim can contain nanomaterials, whereas products with a claim not always contain nanomaterials.
- For some products with a claim describing the size and element of the nanomaterial, it was remarkable that these nanomaterials were not found in the present study. Yet, it should be considered that the absence of nanomaterials in consumer products in the present study means that it is unlikely that nanomaterials are in the product, but this is not unequivocally shown.
- Up till now, risk assessment of nanomaterials has focused on non-biodegradable, usually insoluble 'hard' particles as it is considered that they are potentially biopersistent and may behave different than their non-nano counterparts. It should be noted that in a number of products with a nanoclaim, organic 'soft' nanomaterials were found, indicating that a nanoclaim can be directed at either hard or soft nanomaterial.
- Several products that were investigated claim to use silver ions, i.e. not nanomaterial, as antibacterial agent. These are a t-shirt and deodorant. Indeed, in these products silver nanomaterial was not found.

# 1 Introduction, aim and approach

## 1.1 Introduction

Nanomaterials are being used in a large number of applications in amongst others consumer products. Nanomaterials can have specific properties which can improve the functionality of the product. Several inventories have been made to identify the consumer products in which nanomaterials are used (see section 2.1). The products ending up in the inventories are mostly based on the claim on the presence of nanomaterials as made by the manufacturers. Actual measurements to assess the presence, concentration and characteristics of nanomaterials have hardly been performed. This is mainly due to the lack of required expertise and equipment, and difficulties and uncertainties associated with the detection of nanomaterials in consumer products.

A definition for nanomaterials is presently under discussion. The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) of the European Commission published an opinion on the elements of the term 'nanomaterial' (SCENIHR, 2010). This opinion has been open for public consultation (until September 2010), and SCENIHR is working on a response to the reactions received. The term 'nanomaterial' is presently used in line with the SCENIHR document, and considers material with in at least one dimension a size in the nanorange. It includes nanoparticles as well as other nanolayers. For more details on the basis of the definition of nanomaterial, and what is in- and excluded in this term, is referred to this document (SCENIHR, 2010).

As the present inventories on products with nanomaterials are based on the claim on the presence of nanomaterials made by the manufacturers, very little information is available on products without a claim. In some cases products can be suspected to contain nanomaterials. For example, sunscreens with a high Sun Protection Factor (SPF), especially when the formulation is transparent caused by a different refraction of light due to the presence of nanomaterial. In addition, little is known about the actual presence of nanomaterials in products with or without a nanoclaim. In order to address the issues related to the detection and characterization of nanomaterials in consumer products, in the present study 22 products with and without a nanoclaim are investigated in high quality analytical facilities.

Information on the presence of nanomaterials in consumer products can be used to estimate the exposure to nanomaterials from specific products. A recent RIVM report identified that this information is essential for exposure assessment and is currently lacking (Wijnhoven et al., 2009b). The results on the presence and levels of nanomaterials in consumer products presented in this report can be used as a starting point to estimate and/or model the exposure to nanomaterials from consumer products. Also information on the characteristics of nanomaterials in the selected consumer products will be provided. However, the analytical results should be relevant for risk assessment and enforcement. The applicability of the presently used techniques to provide information that is relevant for risk assessment and enforcement will be discussed.

## 1.2 Background and aim

The aim of the present study is to investigate nanomaterials in consumer products and to put the applicability of the analytical techniques and the acquired results in a risk assessment perspective. To that end, 25 consumer products with and without a nanoclaim were selected, purchased and analyzed, and the results were put in a broader perspective.

Electron microscopic analysis is used as this is the only current approach to directly image and visualize nanomaterials in samples and is regularly used for nanomaterials in a scientific setting. Other techniques are being developed to detect nanomaterials in consumer products. An overview of the techniques that can be used to detect nanomaterials and the infrastructure of these techniques should become available from the European Framework Project QNano, which will probably start early 2011. RIKILT, part of Wageningen University and Reseach Centre, is a Dutch partner in this project.

The Dutch Interdepartmental Working Group Risks of Nanotechnology (IWR), commissioned by the Ministry of Health, Welfare and Sports (VWS), has assigned RIVM for coordinating the present project. The analyses were outsourced to the MESA+ Institute for Nanotechnology at the University of Twente, as it has high quality analytical facilities and knowledge for this purpose.

## 1.3 Approach

The research performed in the present project consisted of the following phases:

- Relevant features on information of nanomaterials in consumer products were described in the light of exposure and risk assessment of nanomaterials in consumer products. Relevant information for exposure and risk assessment included:
  - A screening method to assess the presence of nanomaterials in a consumer product.
  - A more thorough method that can assess several nanocharacteristics in case nanomaterials are found. Relevant nanocharacteristics at least include chemical composition, size distribution, primary particle size distribution, shape, aggregation/agglomeration status, coating, location, and the concentration of the nanomaterial.
  - The screening and more thorough method should be applicable in matrices that are relevant for (non-food) consumer products, which at least include solid products, creams, liquids, and air (for spray applications).
  - The information that is obtained should be robust and reliable.

- Inventories with consumer products with nanomaterials were examined. These inventories included:
  - A recent report of the Dutch Food Consumer Product Safety Authority (VWA) in which the Dutch consumer market has been searched for consumer products with nanomaterials (VWA, 2010). In this inventory both products with and without a nanoclaim were included. For products without a nanoclaim, there should be a plausible reason for possibly containing nanomaterial, for example based on other inventories or based on ingredients in products.
  - The Woodrow Wilson database (http://www.nanotechproject.org/inventories/ ) of which the latest update was performed on 25-08-2009.

  - The ANEC/BEUC inventory on consumer products claiming to contain nanomaterials (ANEC/BEUC, 2009). ANEC is the European Consumer Voice in Standardisation, BEUC is the European Consumers' Organisation.
  - Several inventories by RIVM (Dekkers et al, 2007 a, b; Wijnhoven et al, 2009 a, b).
  - A publication from Which? on the use of nanomaterials in cosmetics. Which? is a consumer organisation in Europe. In this article a survey among companies was reported (Which?, 2008).

- Subsequently, based on the examination of the inventories, 25 consumer products were selected by RIVM on the basis of:
  - The products were expected to contain nanomaterial. This could either be based on claims of the producer on the label or website, or based on the expectation of the presence of nanomaterial. In addition, some products without a claim were selected.
  - A broad range of different types of consumer products were to be investigated.
  - The matrix of the products. Liquid products were excluded as it was known beforehand that the applied techniques were not fit for this matrix. Sprays were included, but it was known that measurements in the air could not be performed. However, sprays were applied on a surface in which the presence and characteristics of nanomaterials were investigated. Mostly products with a solid or creamy matrix were selected.
  - The products could be purchased in shops or via internet.

  For the products that were investigated in the present study, the nanoclaim and the expected nanomaterials are addressed in chapter 2 and listed in Table 2.1.

- After acquiring the products, which appeared impossible for three products, all consumer products were screened on the presence on nanomaterial. The analysis focused on the presence of nanomaterials of the elements silver, silicon, titanium and/or zinc, as these are the insoluble 'hard' nanomaterials that are most likely to be present in consumer products.

- Based on the results in the screening phase, nine products were selected for more thorough characterization. Only products were selected that contained nanomaterials in the screening phase, with a focus on inorganic nanomaterials as this is considered to be most relevant for the assessment of potential health risks. In this phase more detailed information on nanocharacteristics was obtained, including size distribution as well as information on coatings that are often applied on nanomaterial.

- The results are put in perspective on what information the applied techniques can and cannot deliver, and what information is relevant for risk assessment and enforcement.

# 2 Consumer products investigated

## 2.1 Products that could not be purchased

Three products which were selected could not be purchased (for this reason product number 3, 6 and 12 in the table are missing). These were the:

- nano-silver chopping board;
- silver nano baby milk bottle;
- shoe cream.

The nano-silver chopping board and the silver nano baby milk bottle were both promoted on Korean websites. Information on these websites was in English and appeared professional, but actually purchasing the products appeared impossible.

The nano-silver food container, which was also advertised on one of the Korean websites, could also not be purchased. However, a retail company was found that still had the food containers in storage, although they were withdrawn from the market. Hence, this product was obtained via the unofficial way and is unlikely to be sold to consumers.

One of the shoe creams appeared to be difficult to purchase via internet or shops. As already shoe cream of another brand was included, this product was not included.

## 2.2 Products that were investigated by microscopic analysis

The consumer products investigated in the present study are listed in Table 2.1, as well as a general description of the product, the product category, the expected chemical composition of the nanomaterial, and information on the nanoclaim.

## 2.3 List of products

*Table 2.1. List of consumer products investigated.*

| Nr. | Description product | Category [1] | Matrix | Expected nanomaterial | Description of the nano claim |
|---|---|---|---|---|---|
| 1 [2] | Diaper cream | Personal care and cosmetics | Cream | ZnO | No claim |
| 2 | Food container | Household product and home improvement | Solid | Ag | Claim: A newly developed antimicrobial food container which is made by FinePolymer's unique nanotechnology.<br>… shows excellent antimicrobial properties against various bacteria and fungus due to the effect of finely dispersed nano-silver particles and hence it makes a food fresh longer compared with conventional food containers. |
| 4 | Lip balm | Personal care and cosmetics | Cream | $ZnO/TiO_2$ | No claim |
| 5 [2] | Shoe cream | Textiles and shoes | Solid | $SiO_2$ | No claim |
| 7 | Cuddly toy | Textiles and shoes | Solid | Ag | Claim: A company, that through the use of a patented technology, is offering anti-mite, anti-mold and anti-microbial plush toys. The technology involves infusing silver, a natural anti-mite, anti-mold and anti-microbe agent, nanoparticles — 25 nanometers thick, about one 200 thousandth of a human hair — inside memory foam.<br>Later (June 2008): … stopped using nano-silver because there were just too many questions about the material, how people will respond to its use, and how the government might regulate it. |

| Nr. | Description product | Category [1] | Matrix | Expected nanomaterial | Description of the nano claim |
|---|---|---|---|---|---|
| 8 [2] | Indoor wall paint | Household product and home improvement | Liquid | Ag | Claim: In German: ‘Hygienic Nanosilber Schutzfarbe’, ‘mit patentierten Nanosilber-Wirkstoff-komplex’, ‘resistent gegen Keim und Bakterienbefall’.<br>Claim: In Dutch: Het voornaamste bestanddeel van de nanovulstofcombinatie vormen de niet-giftige nanozilverpartikels, met een gemiddelde diameter van 13 miljoenste millimeter per deeltje.<br>Claim: translated to English: the major component of the nano-filling combination are the non-toxic nano-silver particles, with an average diameter of 13 nm. |
| 9 | Lip balm | Personal care and cosmetics | Solid | $TiO_2$ | No claim |
| 10 [2] | Anti-wrinkle cream | Personal care and cosmetics | Cream | $TiO_2$ | No claim |
| 11 [2] | Facial mask | Personal care and cosmetics | Cream | $TiO_2$ | No claim |
| 13 [2] | Socks | Textiles and shoes | Solid | Ag | Claim: Contains 7% SilverNODOR, a yarn with a polyamide fiber core and a surface consisting of 99.9% pure silver. Your body heat activates SilverNODOR, releasing charged silver ions that are totally safe to humans and non-reactive on your skin. But these silver ions mean certain death for bacteria and fungi living on your socks. |
| 14 | T-shirt | Textiles and shoes | Solid | Ag | Claim: The functional ‘effect’ fibres woven into the material and containing silver ions prevent the reproduction of bacteria and effectively stop the development of an unpleasant smell. Functions without chemicals, is very skin-compatible and offers optimal climatic comfort. |
| 15 | Window sealant | Motor vehicles | Spray | ? | Claim: The auto glass sealant is a coating material based on nano-technology, and easily outlasts other wax and silicone based products.<br>The windscreen sealant gives you clearer vision in the rain and improves night vision as well, which helps reduce accident figures. Above 40 km the rain is simply blown off the screen and your wipers are almost superfluous. |

| Nr. | Description product | Category [1] | Matrix | Expected nanomaterial | Description of the nano claim |
|---|---|---|---|---|---|
| 16 | Sunscreen | Personal care and cosmetics | Cream | $TiO_2$ | No claim |
| 17 [2] | Wound dressing | Medical | Solid | Ag | Claim: An unique range of antimicrobial barrier dressings for use over partial, full thickness and acute wounds. Unique Patented Silver technology: Nanocrystalline<br>Silver Antimicrobial protection<br>Effective barrier to over 150 wound pathogens. Faster kill rates, longer wear times |
| 18 | Toothbrush | Personal care and cosmetics | Cream | Ag | No claim |
| 19 | Anti-wrinkle cream | Personal care and cosmetics | Cream | $TiO_2$ | No claim |
| 20 | Leather maintenance | Textiles and shoes | Aerosol | - | Claim: 'Nano pro' |
| 21 | Anti-rain spray | Textiles and shoes | Aerosol | - | No claim |
| 22 | Anti-dirt spray | Textiles and shoes | Aerosol | - | Claim: 'With nanoparticles' |
| 23 [2] | Maintenance spray | Textiles and shoes | Aerosol | - | Claim: 'With nanoparticles' |
| 24 | Sunscreen | Personal care and cosmetics | Aerosol | $TiO_2$/ZnO | No claim |
| 25 [2] | Deodorant | Personal care and cosmetics | Aerosol | Ag | Claim: Deodorant Silver Protect anti-bacterial formula with silver ions fights bacteria and body odour. Delivers 24h confidence and anti-perspirant protection keeping you fresh and dry all day long. |

[1] The products were ordered in various categories. The categories were based on the Woodrow Wilson database (http://www.nanotechproject.org/inventories/), and used by RIVM since 2007 (Dekkers et al., 2007 a, b; Wijnhoven et al., 2009 a, b).
[2] The products that were marked by shading were selected after the first phase to be investigated in more detail

# 3 Analytical techniques employed

Electron microscopic techniques are the only current techniques that can visualize nanomaterials and are regularly applied in scientific studies on nanomaterials to assess the characteristics of the nanomaterials in the study. Therefore, in the present study the applicability and limitations of electron microscopic techniques for risk assessment purposes are assessed for (non-food) consumer products.

In the present study the following techniques are used:
- HR-SEM: High Resolution Scanning Electron Microscopy;
- TEM: Transmission Electron Microscopy;
- EDX: Energy dispersive X-ray;
- XPS: X-ray photoelectron spectroscopy.

SEM and TEM can provide information on the size and shape of nanomaterial. In case the product has a solid matrix, it is not necessary to perform any additional steps: the sample is measured by these techniques 'as received'. Information on the size (distribution), shape, aggregation/agglomeration status, and sometimes coating of the nanomaterials can be obtained.
If the sample is a cream, additional sample preparation is needed in order to firmly fix the sample, which is a prerequisite for achieving high resolution. For spray products the material was sprayed onto a solid surface. The effect of the sample preparation on aggregation/agglomeration of nanomaterials is not known, and needs further investigation.

EDX can be applied in conjunction with SEM or TEM. Following SEM imaging, an area of interest is selected, which for this type of samples can be as small to cover a few or only one nanoparticle. EDX determines the elements which are present within this area. This information is crucial for risk assessment as it can be used to verify whether the nanoparticles consist of the expected or other element(s), and whether the nanoparticles consist of organic or inorganic material. Non-conduction samples, such as thick organic matrices, pose a problem with electron microscopy and EDX. These problems can be circumvented by coating the sample with a metal material.

XPS can be applied to identify the elements present in a piece of surface of a sample, which is typically 5 μm wide and a few nm thick. A depth profile on the presence of elements in the sample can be obtained, if subsequent layers are analyzed and removed. XPS can be applied to obtain more general information on the elements present in the sample, but has a relatively high detection limit (about 0.01 mass%, or about 0.1 to 0.8 g/kg depending on the element). XPS is more sensitive to heavy elements and less sensitive to lighter elements.

A more thorough description of the analytical techniques applied, including a photo of the apparatus, is provided in Appendix 1.

# 4 Results

The results of the combined techniques SEM, TEM, EDX and XPS analysis are summarized in Table 4.1. In this table the major findings are described whereas the results are also ordered according to various physicochemical characteristics. If no information is found for a specific characteristic this cell of the table is left empty. A more detailed description and photos of the product as well as photos made by the Electron Microscopy can be found in Appendix 1, in which Mesa+ described the results per product.

*Table 4.1. Results of the analysis ordered in various physicochemical characteristics.*

| **Nr.** | **Product** [1] | **Expected nanomate rial** | **Clear claim on the presence of nano-material**[2] | **Description of the major findings** | **Nano-material found** | **Size information primary particles** | **Shape** [3] | **Aggregates and agglomerates** | **Coating** | **Total concentra-tion of an element** | **Pretreatment and remarks** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 [4] | Diaper cream | ZnO | No | Zinc nanoparticles were found having sizes from 50 to 500 nm and appeared to be surrounded by an organic layer with probably a thickness of 50 nm. Titanium nanoparticles (size 50 to 100 nm) were probably also present. SEM did not show the presence of silver nanoparticles, whereas silver was also not found (detection limit total silver 0.85 g/kg). | ZnO | 50-500 nm. | Irregular. | | Coating of organic material of 50 nm thickness. | 12.1% (120 g/kg), not necessarily all Zn in form of nanoparti-cles. | Ointment was diluted in ethanol before imaging. |
| | | | | | Ti | 50-100 nm. | Roundish to irregular. | | | < 0.4 g/kg. | |

| **Nr.** | **Product** [1] | **Expected nanomaterial** | **Clear claim on the presence of nano-material** [2] | **Description of the major findings** | **Nano-material found** | **Size information primary particles** | **Shape** [3] | **Aggregates and agglomerates** | **Coating** | **Total concentra-tion of an element** | **Pretreatment and remarks** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | Food container | Ag | Yes, finely dispersed nano-silver particles. | No nanomaterials were found. | | | | | | No silver measured (detection limit 0.85 g/kg). | |
| 4 | Lip Balm | ZnO/ $TiO_2$ | No. | Organic nanostructures were observed of about 50 nm, but not of the elements Si, Ti, Ag or Zn. | Organic. | About 50 nm. | | | | | Balm was diluted in ethanol before imaging. |
| 5 [4] | Shoe Cream | $SiO_2$ | No. | Organic nanoparticles with a mean size of 30 nm, and a standard deviation of 8 nm. | Organic. | Size distribution: mean 30 nm, stdev 8 nm. | Roundish. | | | | Cream was diluted in ethanol before imaging. |
| 7 | Cuddly Toy | Ag | Yes, but since 2008 they stopped using nano-silver. | Possibly some organic nanoparticles. No silver, silica, zinc or titanium was found (detection limit approx. 0.8 g/kg). Analysis was performed on a number of fibers, not on the foam within the bear. | Some organic particles. | | | | | No silver measured (detection limit 0.8 g/kg). | |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentra-tion of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 [4] | Indoor wall paint | Ag | Yes, silver nanoparticles with an average diameter of 13 nm. | Ti nanoparticles were found with a distribution described by a mean value of 168 nm and a standard deviation of 35 nm. Silver was not found (detection limit 0.84 g/kg). | Ti | Size distribution: mean 168 nm, stdev 35 nm. | Roundish. | | | No silver measured (detection limit 0.84 g/kg). | The wall paint was applied (after thorough mixing) directly onto a surface before imaging. |
| 9 | Lip balm | $TiO_2$ | No | Clusters of Ti nanoparticles were observed. The Ti nanoparticles have a primary size in the range of 20 to 100 nm. Clusters vary in size from 200 to 500 nm. Cluster formation can be an artefact of the preparation of the sample with ethanol.<br>Also Si particles seem to be present having irregular shapes and size (from 20 nm to close to 1 µm). | Ti | 20-100 nm. | Roundish. | Clusters of 200-500 nm. Can be an artefact of preparation of the sample with ethanol. | | Total Ti 16 g/kg. | The product was diluted in ethanol before imaging. |
| | | | | | Si | 20 nm to close to 1 µm. | Irregular. | Agglomerates. | | Total Si 1 g/kg. | |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentra-tion of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 [4] | Anti-wrinkle cream | $TiO_2$ | No | Ti nanoparticles and Si agglomerates of nanometer size were observed. Ti nanoparticles appear small, spherical, with some straight edges, having a size distribution for primary particles with a mean of 17 nm and standard deviation of 6 nm. Si nano-particles are slightly larger (50 nm) and appear more irregularly shaped. Total Ti (2g/kg), total Si 9 g/kg. | Ti | Size distribution: mean 17 nm, stdev 6 nm. | Spherical, with some straight edges. | | | Total Ti 2 g/kg. | The product was diluted in ethanol before imaging.<br>All particles seem to contain both Ti and Si. |
| | | | | | Si | About 50 nm. | Irregularly shaped. | | | Total Si 9 g/kg. | |
| 11 [4] | Facial mask | $TiO_2$ | No | Ti nanoparticles are observed with a size distribution of 121 ± 59 nm, and appear spherical with some flat facets. Si, Ti and Al are constituents of the sample at concentrations of 23, 2 and 14 g/kg, respectively. | Ti | Size distribution: mean 121 nm, stdev 59 nm. | Spherical with some flat facets. | Large clusters, may be an artefact from the preparation in ethanol. | | 2 g/kg. | The product was diluted in ethanol before imaging. |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentra-tion of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 [4] | Socks | Ag | A yarn with a polyamide fiber core and a surface consisting of 99.9% pure silver | A silver nanolayer is present on 1 to 5 out of 100 fibers from the bottom part of the sock. The nanolayer was estimated to be 100-200 nm. | Ag | Silver is not present as individual nanoparticles, but forms a continuous layer. It appears as if the silver has been sputtered on these fibrils. | Nanolayer. | | Silver is at the outer part of the fibril. Diameter of fibril is 40 µm, the silver layer is 150 nm. Not a smooth layer. | Assuming 1 silver-containing fibril upon 40 organic ones, approximately 0.2 volume % is silver, or about 10 g/kg. | Silver is only present on 1 to 5 out of 100 fibers in the bottom part of the sock |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentra-tion of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 | T-shirt | Ag | The fibres containing silver ions prevent the reproduction of bacteria and stop the development of an unpleasant smell. | No nanomaterials nor total silver (detection limit 0.8 g/kg) were found. | No nanomaterials found. | | | | | No silver measured (detection limit 0.8 g/kg) | |
| 15 | Window sealant | ? | Coating material based on nano-technology. | Some small nanometer sized particles were found, as well as strangely shaped micrometer tin particles. | Some small organic nanometer sized particles. | | | | | | The window sealant liquid was applied directly onto a surface for imaging. |
| | | | | | Micrometer sized Sn particles. | | Strangely shaped. | | | | |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentration of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | Sunscreen | $TiO_2$ | No | Clusters of Ti nanoparticles were found. Clusters range from 200 nm to many microns. Ti nanoparticles were canoe-shaped ranging in size from 4×20 nm to 10×100 nm. Also small square nanoparticles of 5 nm were found but the element could not be elucidated. | Ti | Ranging in size from 4×20 nm to 10×100 nm. | Canoe-shaped. | Large clusters from 200 nm to many microns. Clusters can be an artefact from the preparation in ethanol. | | | The product was diluted in ethanol before imaging.<br>Ti particles contain also some Si. |
| | | | | | Unknown. | 5 nm. | Squares. | | | | Impossible to determine element. |
| 17 [4] | Wound dressing | Ag | Silver technology: Nanocrystall-ine | The wound dressing consists of fibrous material coated with a 300-500 nm silver layer on both sides. Within this layer 95 mass% is silver. The surface reveals a nanometer scale roughness having features of 10-15 nm. | Ag | The wound dressing consists of fibrous material, which has been coated with a 300-500 nm silver layer on both sides. Within this layer 95% of the mass is silver. On the nanometer scale the silver does not consist of isolated individual particles, but forms a continuous layer. Silver is probably sputtered onto the dressing material. The surface reveals a nanometer scale roughness, having features of 10-15 nm. | | | | | |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentra-tion of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18 | Toothbrush | Ag | No | In samples from hairs and tongue rub (back side toothbrush) no nanomaterials were found. Silver was not detected (detection limit 0.8 g/kg). | No nano-material found in samples of hairs or tongue rub. | | | | | No silver measured (detection limit 0.8 g/kg). | |
| 19 | Anti-wrinkle cream | $TiO_2$ | No | Ti nanoparticles were observed having sizes of 50-200 nm. Si was present in irregularly shaped agglomerates of varying sizes. | Ti | 50-200 nm | | Elongated | | 3.0 g/kg. | The product was diluted in ethanol before imaging. |
| | | | | | Si | | | Irregular shaped agglomerates of varying sizes. Can be an artefact from ethanol treatment. | | | |
| 20 | Leather mainten-ance product | ? | ‘Nano pro’ | Organic nanometer structures of 30-50 nm were observed. No nanomaterials were observed. | Organic | 30-50 nm sized structures. | | Network | | | The spray has been applied to a surface before imaging. |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentra-tion of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | Anti-rain spray | ? | No | | No nano-material found | | | | | | The spray has been applied to a surface before imaging. |
| 22 | Anti-dirt spray | ? | 'With nano-particles' | Zn aggregates of 0.3 to 10 µm were observed. Primary size could not be determined since they are not clearly visible within the clusters. | Aggregates of 0.3 to 10 µm found, consisting of mainly Zn. Primary size could not be determined as they were not clearly visible. | | | | | | The spray has been applied to a surface before imaging. |
| 23 [4] | Mainten-ance spray | ? | 'With nano-particles' | Si and Zn nanoparticles were found. Total concentration less than 0.5 and 0.2 g/kg, respectively (below detection limit). | Zn | Image of insufficient quality, probably due to the preparation in which the aerosol is too viscous and forms a layer that is too thick from high resolution. | | | | < 0.5 g/kg. | The spray has been applied to a surface before imaging. |
| | | | | | Si | | | | | < 0.2 g/kg. | |

| Nr. | Product [1] | Expected nanomaterial | Clear claim on the presence of nano-material [2] | Description of the major findings | Nano-material found | Size information primary particles | Shape [3] | Aggregates and agglomerates | Coating | Total concentra-tion of an element | Pretreatment and remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24 | Sunscreen | $TiO_2$/ ZnO | No | Si nanoparticles were found with a broad size distribution with a mean of 57 nm and a standard deviation of 40 nm. Ti was not detected (detection limit 0.4 g/kg). | Si | Size distribution: Mean 57 nm, stdev 40 nm. | | | | 3.8 g/kg. | The spray has been applied to a surface before imaging. |
| | | | | | | | | | | No Ti measured (detection limit 0.4 g/kg). | |
| 25 [4] | Deodorant | Ag | Anti-bacterial formula with silver ions fights bacteria and body odour. | No nanomaterials were detected. Total silver was less than 0.8 g/kg (below detection limit) | No nano-material found. | | | | | No silver measured (detection limit 0.8 g/kg). | The spray has been applied to a surface before imaging. |

[1] See Table 2.1 for more details on the product.
[2] See Table 2.1 for more details on the nanoclaim.
[3] See Appendix 1 for SEM and/or TEM image.
[4] The products that were marked by shading were selected after the first phase to be investigated in more detail.

# 5 Discussion and recommendations

## 5.1 Applicability of the analytical techniques for risk assessment and enforcement

The results of the measurements indicate that *the combination of analytical techniques described in chapter 3 is applicable for measurement of nanomaterials and several nanocharacteristics in consumer products.* With SEM and TEM the presence, size and shape of nanomaterials can be visualized and determined. The combination with EDX is crucial as information about the chemical composition of nanomaterials is required in order to be able to distinguish between the nanomaterial of interest, other nanomaterials, and small organic matter such as fat droplets that are considered to be harmless. XPS is a useful technique to determine the elements present in a larger area of the product.

However, it is important to be aware of the limitations of the present analysis of nanomaterials in consumer products. *The limitations and some remarks associated to the present microscopic techniques in the view of exposure and risk assessment are described in sectors 5.1.1 to 5.1.5.* Other techniques and the infrastructure for analysis of nanomaterials are briefly addressed in sector 5.1.6.

### *5.1.1 Reliability and robustness of the results of the presently used techniques*

*It is impossible to be conclusive about the absence of nanomaterials in a product.* For several products no silver, zinc, silicon or titanium nanomaterial was detected in the product, although this was expected based on the nanoclaim on the products (e.g. the food container, the indoor wall paint, respectively number 2 and 8 in Table 4.1). However, if nanomaterials are not found, it is impossible to be conclusive about the absence of nanomaterials in the product. With SEM and/or TEM only a small area – approximately 1 $\mu m^2$ – of the product can reasonably be investigated, which is relatively randomly selected. In addition, products consist of a third dimension, the depth of a sample. Hence, the results of the analysis depend on the exact piece of material that is investigated, and may for some reason not (representatively) contain the nanomaterial. Therefore the results may differ depending on the area of the sample analyzed. This could also explain why in some samples one type (element) of nanomaterial was found by SEM analysis, while another type of nanomaterial was found by TEM (see Appendix 1).

For creams and viscous liquids, samples are diluted in ethanol in order to get useful images. However, *it is unknown what the effect of this treatment is on organic nanomaterial*. Such nanomaterial may or may not fall apart. In two products that were treated with ethanol, lip balm and shoe cream (products 4 and 5), organic nanomaterial was found despite the treatment. However, this may be due to the nature of the organic nanomaterial and it is unlikely that all types of organic nanomaterial survive the ethanol treatment. Therefore, when ethanol treatment is applied and nanomaterial is not detected, there is another aspect that makes it impossible to be conclusive about the absence of nanomaterials.

*It is therefore concluded that false negative measurements are possible, which is a major drawback for risk assessment and enforcement. Conclusive information about the presence of nanomaterials in (consumer) products would be of great value. A method that can unequivocally assess if nanomaterials are present can be used as a screening tool. In the absence of nanomaterials further nanospecific exposure or risk assessment is not necessary, whereas additional information requirement (see section 5.2) may apply in the presence of nanomaterial.* In order to prevent false negative measurements two issues need to be addressed:

First, the present sample preparation step is not resulting in concentrating the nanoparticles, which is needed to unequivocally conclude that nanoparticles are not present in the product. One possible way for sample preparation might be to get rid of the organic phase material, such that the concentration of nanoparticles becomes larger. Burning the material in a controlled manner to ashes is one suggestion. Dissolving the organic phase and perform a separation step is another approach that might be an option. It should be considered that techniques aiming to get rid of organic phase material of the consumer products will probably also affect organic nanomaterial.
Alternatively, a sample containing a large and representative piece of the product could be investigated with the present microscopic techniques – which is very labour intensive – or with another technique. Such a screening tool, including sample preparation and analytical techniques, would be valuable for enforcement as well. Therefore, further development of such a tool is recommended.

Second, it should be decided if the unequivocal demonstration of the presence of organic nanomaterial should be included in the screening tool. For risk assessment this seems to be a smaller issue than for enforcement, as most health risks are considered to be related to inorganic 'hard' nanomaterial. However, for enforcement it may be relevant to be able to investigate if a nanoclaim, either or organic or inorganic nanomaterial, is justified. In this case, other approaches to unequivocally assess the presence of organic 'soft' nanomaterial should be developed as well.

### *5.1.2 Applicability of the techniques for various matrices*

*Both SEM and TEM are techniques that are well suited to provide high resolution images of solid-state samples, but these techniques have their limitation for creams and viscous liquids, and are less useful for liquids and aerosols.* SEM provides an image of the surface (topography) and TEM is doing this all through the sample. Some of the products were solid, but others were creams, viscous liquids or aerosols. The main issue with creams, viscous and liquid samples is that atoms can move, which lowers the resolution to a point that nanoparticles can no longer be observed. For that reason it was decided *to dilute creams and viscous liquid into ethanol*, after which the sample was ultra-sonicated in order to get a well-dispersed sample. This resulting dispersion was then brought onto a grid for imaging. It is assumed that due to the ethanol treatment the organic material, which makes up most of the cream will be separated from the nanoparticles, such that these can be seen. This approach did indeed seem to work, in the sense that nanoparticles of many products could be observed clearly. *However, it is not clear what influence this treatment has on the determined characteristics of the nanoparticles.* We think that it is unlikely that ethanol changes the characteristics of the silicon, silver, titanium and zinc nanoparticles themselves, such as shape and size, but it is possible that the

treatment influences the aggregation state of these nanoparticles, as well as the possible organic coating covering the nanoparticles. In many samples large clusters of nanoparticles were reported and it is not clear whether this is representing the aggregation state of the nanoparticles within the sample or whether this is an artefact from the sample preparation steps taken. In addition, *organic nanoparticles may fall apart due to the ethanol treatment, thereby making it impossible to draw solid conclusions on the presence and characteristics of organic nanomaterial when ethanol treatment is applied.*
It is therefore recommended to assess the effect of the ethanol treatment on the aggregation and/or agglomeration state, and on a potential coating surrounding 'hard' inorganic nanomaterial. Verification that the ethanol treatment has no effect on the size and shape of 'hard' nanomaterial is required as well. In addition, the applicability of other techniques to provide useful information on the presence and characteristics of nanomaterials in cream and liquid matrices should be considered.

*The presently applied techniques are not suitable for analysis of nanomaterials in aerosols as the techniques can only be applied on a (solid) surface.* For exposure and risk assessment, information on nanomaterials and their characteristics in aerosols would be highly relevant as inhalation is considered to be a major route of exposure for nanomaterial. However, in the present study, aerosols were sprayed onto a surface, and the volatile component evaporates. Hence, not the sample as in the spray can itself is assessed, neither in the air, but rather after application of the spray on a surface. Such information may be relevant for dermal exposure after application of the spray and gives indication on the element and size of the nanomaterials that can be present in the aerosol. However, it is unknown to which extent nanomaterials (de)aggregate, (de)agglomerate, form complexes with other constituents, or are present in droplets of potentially increasingly smaller droplets due to the volatilization. *Other analytical techniques are required for measurement of nanomaterials in aerosols and the behaviour in time, which is considered relevant to assess the exposure via inhalation.*
Physicochemical characterization of nanomaterials in aerosols is to be investigated in the NanoNextNl programme.

### *5.1.3 Analytical validation*

In this study SEM, TEM, EDX and XPS have been used on samples for which the nanomaterials presence and characteristics were not known. However, *the techniques have not been validated for the present matrices*. To the knowledge of the authors, validation has not been performed for these techniques elsewhere either. *If these techniques are to be used in the future to get accurate, reliable, quantitative data on the size distribution, nature and type of nanomaterial, analytical validation is necessary.* Therefore, analytical validation of the presently used techniques is recommended, especially for consumer products consisting of a hard matrix as the used techniques are most useful for this application.
Accurate quantitative data will be required to distinguish products containing nanomaterial. The draft opinion of SCENIHR proposes to define nanomaterials based on size and size distribution (SCENIHR, 2010). They propose that if a certain fraction of the size distribution – SCENIHR describes an example with > 0.15% – has a size of 100 nm or less the material is considered to be a nanomaterial.
Validation of the techniques may be done by using samples, that are characterized, well-controlled, and reproducible, that can serve as references. As

a start, such samples can be obtained by mixing a certain amount of nanoparticles of known type and size into an organic matrix and characterizing this with the above mentioned techniques in order to see if it gives the right size distribution, type, etc.

### *5.1.4 Concentration of nanomaterial*

*The concentration of nanomaterials in a product cannot be measured by SEM or TEM.* Instead, the total concentration of an element is measured by XPS. However, this concentration not necessarily reflects the mass concentration of the nanomaterial, as also non-nano material of that specific element may be present in the product. Approaches to quantify the concentration (e.g. mass, number or surface area) of nanomaterials should be developed.

### *5.1.5 Total element concentration*

*The techniques used to determine the total concentration of an element have a high detection limit. Other techniques may be more appropriate.* XPS is used to determine whether a certain element is present, but because of the high lower limit of detection (0.01% or approximately 0.3 to 0.8 g/kg, depending on the element) it is possible that the elements of interest are not detected. For many applications where the material is made of one type of material this limit is not an issue. However, in the case of nanoparticles within a matrix, which is usually the case for consumer products, the amount of the nanoparticles in comparison with that of the matrix is very low, and gets close to this lower limit of detection. This means that there is a chance that certain elements were not detected because of this limit of detection of the XPS. This may have been the case for silver in the food container, the wall paint, the cuddly toy, and the deodorant. The food container and the wall paint are expected to contain silver as the label and/or website of these products claim that the products contain silver nanoparticles, whereas the deodorant claims to contain silver ions. The producer of the cuddly toy used to claim that the plush toy contained silver nanoparticles, but has stopped with doing that because 'there were just too many questions about the material, how people will respond to its use, and how the government might regulate it'. Hence, the absence of silver nanoparticles in this product may just be because the producer does not apply silver nanoparticles any more. Other techniques such as sample digestion followed by ICP-MS or ICP-AES may result in lower detection limits for the total elements.

XPS has been applied to the sample 'as received' without any further preparation or dilution steps. This is important in order to determine the accurate concentration of a particular element in the product. However, it only detects the elements in a very thin layer close to the surface (about 5 nm). Nanoparticles can be surrounded by an organic matrix which forms a layer around the particles. It is probably not as a shell around each particle, but may act as a continuous, dynamic phase around them. Because there can be an interaction between this organic phase and the nanoparticles, the nanoparticles will always have a thin layer of organic material around them, even if they appear at the surface of the product. If this layer is 20 to 50 nm, XPS will not detect the elements of the nanoparticles, resulting in an error in the mass concentration determination. On the other hand, XPS may give an indication on the presence of a coating surrounding the nanomaterial.

In the present study, depth profiles on the presence of elements are provided for some of the products (see Appendix 1). An XPS spectrum is recorded after removing increasingly deeper layers of the material, micrometers deep into the sample. This is sufficient to detect the nanoparticle material despite the presence of an organic coating. For some samples this has not been done, and might explain discrepancies of not detecting certain elements with XPS, although they have been detected using EDX (either with SEM-EDX or TEM-EDX).

#### *5.1.6 Other techniques and infrastructure*

As indicated in 5.1.2, other analytical techniques will be required for liquid matrices. These other techniques have not been applied in the present project. Techniques such as HDC-ICPMS, which is in the Netherlands operated at RIKILT (Dekkers et al., 2010), and Field Flow Fractionation (FFF) seem to be suitable to determine hydrodynamic particle size and element in solutions. At the moment, these techniques are not fully validated, but experience has been gained with liquid food matrices, especially for the HDC-ICPMS. RIKILT is working on other analytical methods as well, amongst others in the European Framework Project Nanolyse (anticipated term 2010-2013).
Dynamic Light Scatting can be used to determine the size distribution of nanoparticles in suspensions. However, there is no option to determine the element of the particles so that in most cases no clear distinction can be made between the nanoparticles of interest and small organic material, fat droplets and other material. Therefore, this technique is considered to be not useful for the analysis of nanomaterials in consumer products.

Also for analysis of nanomaterials and its characteristics in aerosols other analytical techniques will be required. As indicated before, this issue will be addressed the NanoNextNl programme (anticipated term 2011-2015).

In the present study the analyses were outsourced to the MESA+ Institute for Nanotechnology at the University of Twente. This work was outsourced to MESA+ as MESA+ is one of the parties in Nanolab and this setting creates a link between nanotechnology related research and risk assessment. From a risk assessment point of view, it would however be relevant to know the infrastructure for analytical research on nanomaterials in Europe. The European Framework Project QNANO (anticipated term 2011-2014) will provide information on the European infrastructure on the analysis of nanomaterial. WUR/RIKILT is one of the partners within the project.

### 5.2 Information requirements for nanomaterials in consumer products

Although it is clear that only information whether nanomaterials are present or not in a consumer product is insufficient for exposure and risk assessment, the information requirements from the perspective of risk assessment are not clear yet.
Guidance documents on relevant characteristics of nanomaterials for risk assessment are being developed by both OECD (Working Party on Manufactured Nanomaterials of the OECD (SubGroup 4)) and ISO (International Standardisation Organisation, working group ISO TC229/SC/WG3).

According to a draft guidance document of the Working Party on Manufactured Nanomaterials of the OECD (SubGroup 4) on sample preparation and dosimetry for safety testing, characterizations of nanomaterials might include (but are not limited to): chemical composition, particle size, size distribution, aggregation, agglomeration state, shape, surface area, surface chemistry, dissociation constant, crystal structure, surface charge, zeta potential, Hamaker constant, interfacial tension, and porosity.

In the ISO draft document the following parameters were considered to be of main importance for characterization in toxicological tests with nanomaterial: particle size/distribution, aggregation/agglomeration state, shape, specific surface area, composition, surface chemistry, surface charge, solubility, and dispersibility.

In the present study physicochemical characterization of nanomaterials in consumer products is assessed with microscopic analysis using various approaches. Information that is aimed to retrieve comprises:

- the presence of nanomaterial;
- the chemical composition of the nanomaterial;
- the concentration of nanomaterial;
- the size distribution of the nanoparticles;
- the presence of a coating;
- information on aggregation/agglomeration;
- location of the nanoparticles in the product.

As indicated in Table 4.1 and the discussion above, this information could be obtained in several but not all cases with the presently used techniques, see Table 4.1. This is partly due to limited research for products that were only investigated in a first phase. Nine products were investigated in a more detailed second phase. Also in these products not all the information elements could be addressed due to technical issues. Especially information on the concentration of nanomaterial, presence of a coating and the aggregation or agglomeration state could not always be provided, which is mostly related to the non-solid matrix or the organic nature of the nanomaterial.

## 5.3 Conclusions and observations on the results of the analysis of the consumer products

Present inventories that list consumer products with nanomaterial, such as the Woodrow-Wilson database, have primarily selected the products on the basis of a nanoclaim on the label or website of the product. *At present there is no legal basis for the use of the term 'nano' on consumer products, which means that manufacturers can use the term as they like.* In the present investigation both products with and without a nanoclaim were investigated. *The present results show that products without a claim can contain nanomaterials whereas products with a claim not always contain nanomaterials.* As a consequence, based on the nanoclaims only, consumers will not be informed correctly about the presence of nanomaterials in consumer products.

For some products with a clear claim it was remarkable that nanomaterials were not found in the present study. This was especially the case for the wall paint and the food container, where both the presence of nanomaterial and the element of the nanomaterial (silver) was claimed. Yet, it should be considered that the absence of nanomaterials in consumer products in the present study means that it is unlikely that nanomaterials are in the product, but this is not unequivocally shown (see section 5.1).

Up till now, risk assessment of nanomaterials has focused on insoluble 'hard' particles as it is considered that they are non-biodegradable and potentially biopersistent and may behave different than their non-nano counterparts. Particles that easily dissolve are assumed to change readily into their non-nano counterparts, whereas 'soft' nanomaterials are often biodegradable and non-biopersistent and are (considerably) less likely to pose a health risk than insoluble hard nanomaterials. Hard and soft nanomaterials are addressed in more detail by SCENIHR (2010). *However, it should be noted that in a number of products with a nanoclaim, organic 'soft' nanomaterials were found, indicating that a nanoclaim can be directed at either hard or soft nanomaterial.* This was for example the case for shoe cream (number 5), car window sealant (number 15), and a leather maintenance product (number 20).

*Several products which claim to use silver ions*, i.e. not nanomaterial, as an antibacterial agent. These are a t-shirt and deodorant (product numbers 14 and 25, respectively). Indeed, in these products no silver nanomaterial was found.

# 6 Conclusions

A short overview of the conclusions and recommendations of the study on the presence of nanomaterials in consumer products is presented here. These issues are described and discussed in more detail in chapter 5. The applied analytical techniques are described in chapter 3. Features that are considered relevant for risk assessment beforehand and the selection procedure of the consumer products are described in chapter 1. A description of the consumer products investigated is presented in chapter 2, whereas an overview of the analytical results is presented in 4. More details on the analytical results are presented in Appendix 1.

## 6.1 General conclusions and recommendations on the usefulness of the analytical techniques for risk assessment and enforcement

The combination of the analytical techniques SEM, TEM, EDX and XPS provides relevant information on nanomaterials in consumer products. Information that *can* be obtained includes presence, size (distribution), shape, chemical composition, coating, location of the nanomaterial in a consumer product and the total mass of a specific element. However, the analytical techniques as applied have presently some major drawbacks for risk assessment and enforcement which are listed below. <u>Recommendations are underlined.</u>

- It is impossible to be conclusive about the absence of nanomaterials in a product. Therefore false negative measurements can occur. This also means that the techniques cannot be applied as such as a screening tool. <u>Further research to develop a tool to unequivocally determine if nanomaterials are present (sample preparation and analysis) is recommended.</u>
- The applied techniques are not validated for the analysis of nanocharacteristics in the matrices of consumer products. <u>For a robust and accurate method, analytical validation is recommended.</u>
- The applied techniques are most useful for solid state samples. In products that were investigated more thoroughly the nanocharacteristics size distribution, shape, chemical composition and location could be determined.
- The applied techniques have limitations for creams and viscous liquids. Not all nanocharacteristics could be determined. Creams and viscous liquid products were treated with ethanol in order to get rid of the organic phase material. However, this treatment may affect characteristics of inorganic 'hard' nanomaterial, and may even cause organic 'soft' nanomaterials to fall apart. It should therefore be decided if the unequivocal demonstration of the presence of organic nanomaterial should be included in the screening tool. For risk assessment this seems to be a smaller issue than for enforcement, as most health risks are considered to be related to inorganic 'hard' nanomaterial. However, for enforcement it may be relevant to be able to investigate if a nanoclaim, either or organic or inorganic nanomaterial, is justified. <u>If a method to unequivocally assess the presence of organic 'soft' nanomaterial is considered necessary for e.g. enforcement, other approaches should be developed. In addition, it is recommended to</u>

assess the effect of the ethanol treatment on the aggregation and/or agglomeration state, and on a potential coating surrounding 'hard' nanomaterial. Verification that the ethanol treatment has no effect on the size and shape of 'hard' nanomaterial is required as well. Alternatively or in addition, the applicability of other techniques to provide useful information on the presence and characteristics of nanomaterials in cream and liquid matrices should be considered.

- The applied techniques are not suitable for aerosols. In the present study, several spray products were applied upon a solid surface and analyzed. This provides some information on the presence and characteristics of nanomaterials in these products, but this information is considered less relevant for risk assessment as exposure via inhalation can be a major exposure route for these products. Consideration of other approaches that measure in aerosols is recommended. Physicochemical characterization of nanomaterials in aerosols is already to be investigated in the NanoNextNl programme.
- The concentration of nanomaterials cannot be determined. XPS was used to determine the total concentration of specific elements, but this includes both nano and non-nano material. In addition, the lower limit of detection for this analytical technique was in several cases too high for analysis of the element of the nanomaterial in a consumer product. It is recommended to consider other approaches to accurately determine the concentration of nanomaterials (e.g. mass, number or surface area).

## 6.2 Conclusions and observations on the results of the analysis of the consumer products

The present results show that products without a claim can contain nanomaterials whereas products with a claim not always contain nanomaterials.

For some products with a clear claim it was remarkable that nanomaterials were not found in the present study. Yet, it should be considered that the absence of nanomaterials in consumer products in the present study means that it is unlikely that nanomaterials are in the product, but this is not unequivocally shown.

Up till now, risk assessment of nanomaterials has focused on insoluble 'hard' particles as it is considered that they may keep their nano-character for a longer time and behave different than their non-nano counterparts. However, it should be noted that in a number of products with a nanoclaim, organic 'soft' nanomaterials were found, indicating that a nanoclaim can be directed at either hard or soft nanomaterial.

Several products claim to use silver ions, i.e. not nanomaterial, as antibacterial agent. These are a t-shirt and a deodorant. Indeed, in these products no silver nanomaterial was found.

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# Appendix 1: Detection and characterization of nanoparticles in consumer products

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# PROJECT DESCRIPTION

Within the framework of this project MESA+ Nanolab has characterized 21 different consumer products on the presence of silver (Ag), zinc (Zn), titanium (Ti) and/or silicium (Si) nanoparticles. Techniques used in this study are scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Both techniques have the possibility to perform energy-dispersive X-ray spectroscopy (EDX). Furthermore X-ray photoelectron spectroscopy (XPS) was used.

The project is defined in two separate phases:

**Phase 1**:
In this phase 21 different consumer products (within a solid, cream, liquid or aerosol matrix) have been analyzed to determine the presence of Ag, Zn, Ti and/or Si nanoparticles. SEM has been used to make high-resolution images, in order to visualize the nanoparticles and has been complemented with EDX, that allow the determination of the chemical nature of the nanoparticles. Finally XPS has been used to determine the mass concentration of the nanoparticle element within the product.

The list of 21 products is presented in the next section.

The results of this phase are presented in this report, where for each product the following information will be presented:
- a picture of the product, as received;
- representative EM pictures of 1 x 1 µm and 100 x 100 nm;
- mass concentration of the elements Ag, Zn, Ti and Si within the product;
- particle size, morphology (first indication).

**Phase 2:**
In this second phase 10 out of the 21 products will be further characterized. The parameters that will be determined are:
- distribution of the particle size;
- location of the nanoparticles (if applicable);
- presence and chemical nature of a coating of the nanoparticles.

The products that have been selected for phase 2 are indicated in the next section. The results of this phase 2 characterization are presented in this report.

# LIST OF PRODUCTS PHASE 1

| Nr. | Name product | Matrix | Chem. |
|---|---|---|---|
| 1 | Diaper Cream | Creme | ZnO |
| 2 | Food container | Solid | Ag |
| 4 | Lip Balm | Creme | ZnO |
| 5 | Shoe Cream | Solid | $SiO_2$ |
| 7 | Cuddly toy | Solid | Ag |
| 8 | Indoor wall paint | Liquid | Ag |
| 9 | Lip balm | Solid | $TiO_2$ |
| 10 | Anti-wrinkle cream | Cream | $TiO_2$ |
| 11 | Facial mask | Cream | $TiO_2$ |
| 13 | Socks | Solid | Ag |
| 14 | T-shirt | Solid | Ag |
| 15 | Window sealant | Solid | - |
| 16 | Sunscreen | Cream | $TiO_2$ |
| 17 | Wound dressing | Solid | Ag |
| 18 | Toothbrush | Cream | Ag |
| 19 | Anti-wrinkle cream | Cream | $TiO_2$ |
| 20 | Leather maintenance | Aerosol | - |
| 21 | Anti-rain spray | Aerosol | - |
| 22 | Anti-dirt spray | Aerosol | - |
| 23 | Maintenance spray | Aerosol | - |
| 24 | Sunscreen | Spray | $TiO_2$ |
| 25 | Deodorant | Aerosol | Ag |

NOTE: The numbering in the Table is not continuous for the reason that certain products were not included because they cannot be ordered (anymore).

# LIST OF PRODUCTS PHASE 2

| Nr. | Name product | Specific questions to be addressed |
|---|---|---|
| 5 | Shoe Cream | - Determination of size distribution of nanoparticles (SEM)<br>- Detect presence and characterize nature of coating (if present) |
| 8 | Indoor wall paint | - Verify presence of nanoparticles in more detail (TEM) |
| 10 | Anti-wrinkle cream | - Determine size distribution of Ti and Si nps<br>- Determine shape and coating |
| 11 | Facial mask | - Determine size distribution of Ti nanoparticles (and Si, Al if present in nanoparticles) |
| 13 | Socks | - Determine distribution of size of nanoparticles or clusters<br>- Perform XPS on isolated fibers<br>- Perform optical microscopy to find out how many fibers are Ag-coated |
| 17 | Wound dressing | - Determine whether these are individual nanoparticles or a continuous layer, and if particles, the distribution of sizes<br>- Presence of coating<br>- Perform microscopy analysis, to see if it is a layer or not |
| 23 | Maintenance spray | - Determine size distribution of nanoparticles<br>- Presence and nature of coating |
| 25 | Deodorant | - Focus on finding Ag particles |

# DESCRIPTION OF CHARACTERIZATION TECHNIQUES USED

**Scanning electron microscopy (SEM)**
SEM is a very widely used technique to study surface topography. A high energy (typically 10 keV) electron beam is scanned across the surface. The incident electrons cause low energy secondary electrons to be generated, and some escape from the surface. The secondary electrons emitted from the sample are detected by attracting them onto a phosphor screen. This screen will glow and the intensity of the light is measured with a photomultiplier. The incident electrons will also cause X-rays to be generated which is the basis of the EDX technique. Some of the incident electrons may strike an atomic nucleus and bounce back into the vacuum. These electrons are known as backscattered primaries and can be detected with a backscattered electron detector.

*Scanning electron microscope: LEO 1550 (Now Carl Zeiss) equipped with NORAN EDS and WDS*

Backscattered electrons can also give information on the surface topography and on the average atomic number of the area under the electron beam. The surface sensitivity of the SEM can be increased by reducing the energy of the primary beam. This can be done by raising the voltage on the sample to just below the incident primary beam energy.

The high resolution SEM, the HRSEM allows samples to be analyzed with much greater resolution and accuracy using lower voltages of the electron beam. This situation is reached by using a field emission source for the electron beam which in turn allows for a much more coherent and smaller electron beam to be produced. This needs however a much better vacuum system, higher quality lenses and is accompanied by more complicated electron detection systems. This type of SEM does come at a cost but means nanostructures can be readily observed in the SEM.

In general, solid samples can be images with SEM in high resolution. Liquid and creamy samples are a little more challenging, because materials can move around which does not allow high resolution imaging. For that reason it is important to prepare the sample such that the material, or at least the nanoparticles that are of interest are fixed with respect to the surface.

**Transmission electron microscopy (TEM)**

*Transmission electron microscope: Philips CM300ST using the standard 300 KV and Noran system 6 EDX equipment*

The transmission Electron Microscope or TEM is a highly advanced microscope which uses an electron beam to explore the internal structure of different solid state materials on the nanostructure scale. The electron beam passes through the material or the sample and provides internal structural information by means of diffraction, x-ray chemistry and imaging which can be used for the characterisation of materials. The sample usually has to be able to withstand reasonably high vacuum conditions, be not too sensitive to electron beam damage and must be less than 100 nm maximum in thickness. The TEM is an excellent apparatus for the study of nanoparticles and thin films. Limitations are often related to sample preparation in order to reveal the nanostructure and also to the sample phase for example oils and liquids.

For TEM the same limitation as for SEM holds: solid phase samples can be imaged readily at high resolution. Liquid and creams needs to be prepared such that the sample or at least the part that you want to image (i.e. nanoparticles) are firmly fixed.

**Energy-dispersive X-ray spectroscopy (EDX)**
Energy Dispersive X-ray analysis (EDX) is often used in conjunction with SEM and is not a surface science technique. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20keV. This causes X-rays to be emitted from the point where the material is irradiated by the primary electron beam. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth, and thus EDX is not a surface science technique. By moving the electron beam across the material an image of each element in the sample can be acquired in a manner similar to Scanning Auger Microscopy. Due to the low X-ray intensity, however, the acquisition of images is usually very time consuming (in the order of hours). Elements of low atomic number are difficult to detect by EDX.

The detector used in EDX is the Lithium drifted Silicon detector. This detector must be operated at liquid nitrogen temperatures. When an X-ray photon strikes the detector, it will generate a photoelectron within the body of the Si. As this photoelectron travels through the Si, it generates electron-hole pairs. The electrons and holes are attracted to opposite ends of the detector with the aid of a strong electric field. The size of the current pulse thus generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Thus, an X-ray spectrum can be acquired giving information on the elemental composition of the material under examination.

EDX is also used very often in conjunction with TEM. In this case the lateral resolution is significantly better than in an SEM because TEM specimens are inherently thin to be electron transparent. The energy of the primary electron beam is typically in the range 100 - 300 keV.

Non-conducting samples do pose a problem with EDX, because the bombardment of the sample with electrons starts to charge the sample itself, which prohibits the X-rays from coming out in an efficient way. This means it is not possible to extract an EDX spectrum. One way to avoid excessive charging is to coat the sample with a metal material that acts as a conducting layer to get rid of the electrons.

**X-ray photoelectron spectroscopy (XPS)**

XPS is the acronym for X-ray Photoelectron Spectroscopy. The principle is that an X-ray beam pointed at a material penetrates the material and frees electrons from their atoms. The freed electron can escape from the material and fly into an analyzer-detector system. The detected electrons are counted as function of their energy (spectroscopic).

Why can it be used for small particles? The X-ray beams in some standard systems (no synchrotron sources) can be as small as 5 µm. This is much bigger then a nanoparticle diameter. However, the escape depth of the freed electrons is of the order of just a few nanometers. XPS can measure films that have a very small thickness. In combination with scanning electron microscopy that can measure the size and form of nanoparticles, but not their contents, XPS can detect the atomic constituents of these particles if the particles are abundant enough.

*XPS: QuanteraSXM from Physical Electronics*

The XPS used can also cool samples down to 150 K which can freeze some crèmes and thick liquids that otherwise would have a too high pressure and low viscosity. The Ar-ion sputter beam and electron flood gun can neutralize all charging samples and get rid off (an)organic shell material.

The XPS can detect elements with an abundance ≥ 0.1 atomic % in a layer as thick as 5 nm. It is more sensitive to heavy elements and less sensitive to lighter elements. The elements H and He cannot be detected at all.

# PREPARATION OF THE SAMPLES

Before a product can be imaged or characterized with electron microscopy and or X-ray spectroscopy, the product needs some pre-processing.

Samples were prepared by several ways depending on their 'as received' state.

**Aerosols**
Samples in the form of an aerosol were sprayed on to two substrate types:
- a piece of silicon (for SEM characterization);
- a TEM grid coated with a carbon layer (for TEM characterization).

**Solid matrix, creams, liquid**
Samples in solid form, for example, clothing garments and samples in tubes were prepared in the 'as received' state on to a piece of silicon. In case of a viscous liquid sample or creams, a small amount was taken using a spatula and diluted in ethanol and ultrasonically dispersed. A droplet was then placed on to a TEM grid and another droplet onto a piece of silicon.

These prepared samples were then placed on aluminium holders for viewing in the SEM, and the TEM grids were also viewed in the HR-SEM and the TEM.

The samples were observed in the SEM using different voltages according to the information that was required. Sometimes a higher voltage was used in order to carry out EDX (energy dispersive x-ray analysis) and also to envisage nanoparticles where atomic number difference was important and did not degrade the SEM vacuum.

**Specification of equipment**
The TEM analysis was carried out on a Philips CM300ST using the standard 300KV and Noran system 6 EDX equipment.

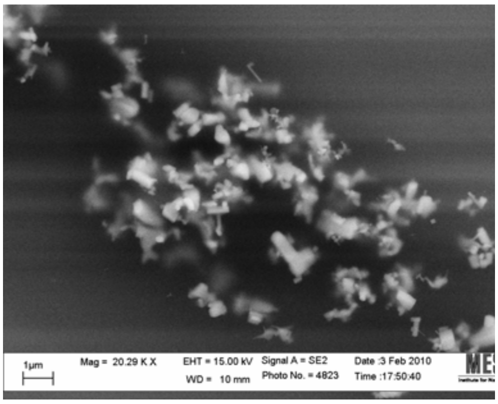
HRSEM observation was carried out using a LEO 1550 (now Carl Zeiss) equipped with NORAN Vantage EDX system.

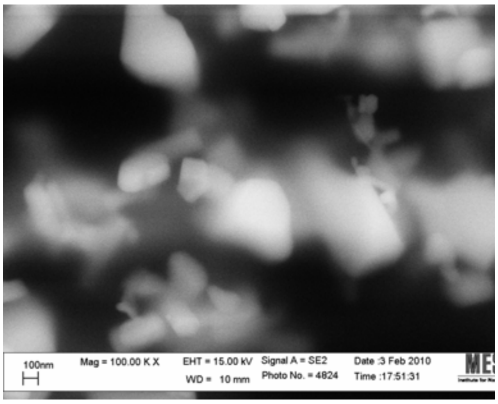
# RESULTS

| | | | |
|---|---|---|---|
| 1 | Diaper cream | Cream | ZnO |

**Information from the manufacturer**
Contains ZnO according to the product description.

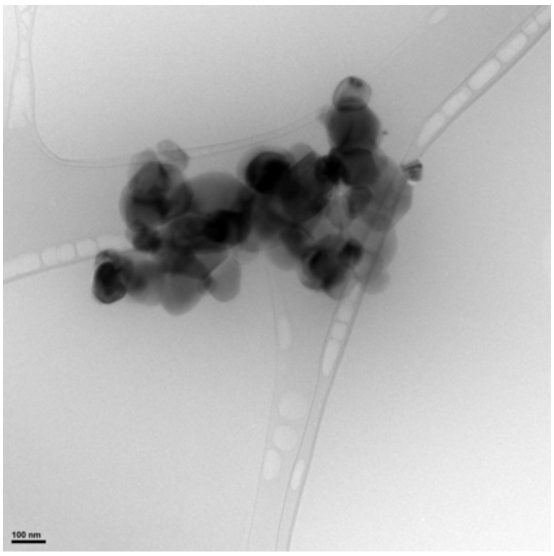
**Electron micrographs (SEM)**




SEM-EDX on this sample clearly indicates that the nanoparticles observed are Zn.

**Electron micrographs (TEM)**




Scale bar = 100 nm

With TEM-EDX the nanoparticles were characterized and showed to be Ti nanoparticles.

**Conclusions**

For the SEM images the ointment was diluted in ethanol and ultrasonically dispersed before imaging. Nanoparticles were found having sizes from 50 to 500 nm and appear to be surrounded by a continuous phase of organic material. SEM-EDX showed that they are Zn nanoparticles. Further analysis of the ointment in TEM again revealed nanoparticles, but they appear to be Ti nanoparticles. The sizes are from 50 to 100 nm. Zn was not detected in the TEM-EDX spectrum.

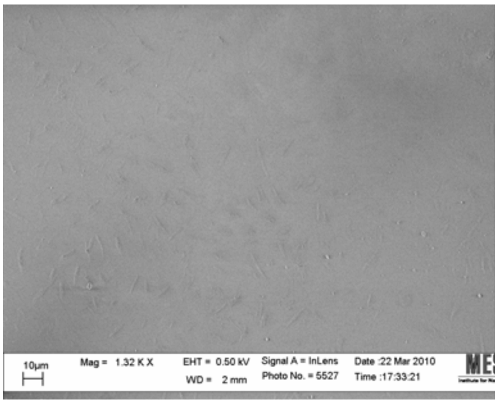
XPS has been performed on the ointment 'as received' that has been spread onto a surface, without further dilution. In a first attempt, which only analyzed the upper surface no Zn was detected. Only when the sample was cooled down to allow sputtering away of material, the signal indicating the presence of zinc was coming up. At a depth of 50 nm the signal indicating the presence of Zn started to grow and leveled off at about 315 nm. This indicated that the nanoparticles have an organic layer of about 50 nm thickness. At this depth a mass concentration of 12.1% (i.e. 120 g/kg) was found. From the XPS spectra it was clear that the Zn was present in the form of ZnO. Ti was not detected by XPS indicating a concentration lower than 0.4 g/kg.

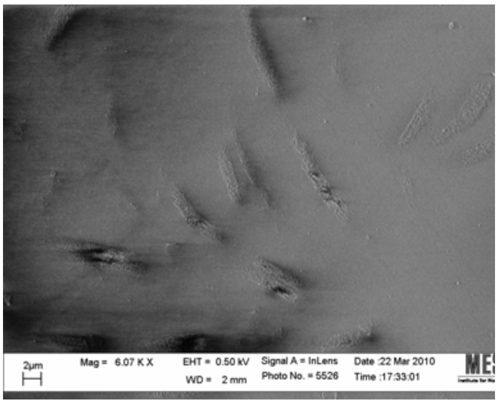
It is not possible to conclude that all Zn is present in the form of 50 to 500 nm diameter nanoparticles.

| | | | |
|---|---|---|---|
| 2 | Food container | Solid | Ag |

**Information from the manufacturer**
Containers that inhibit the growth of bacteria for 99.9%

**Electron micrographs (SEM)**




**Conclusions**
The container is made of polypropylene that appears as opaque white plastic material. For analysis a small piece of the box was cut out and analyzed with XPS and SEM. The SEM was applied to the upper surface and did not reveal any nanoparticles. Larger crystals of 1 x 4 µm and some smaller structures were observed but these were not metal nanoparticles. With XPS a volume of 600 x 300 x 2 µm was analyzed and no Ag detected, that is the concentration of Ag is lower than 0.85 g/kg.

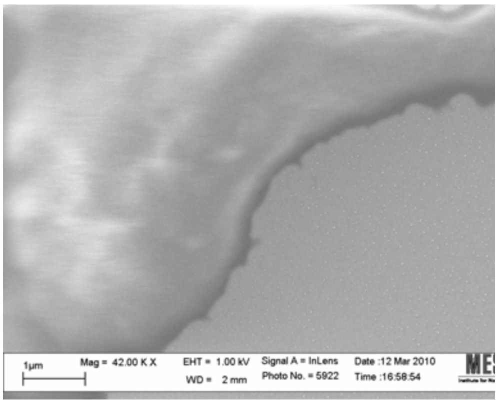
**Discussion**
The producer claims that the container has anti-fungal, anti-bacterial and anti-microbial properties due to presence of the finely dispersed nano-silver particles permanently imbedded in the containers. Both SEM and XPS did not show the presence of these Ag nanoparticles. Since the container seems to consist of one type of plastic we analyzed only one particular piece, assuming that in order to have these anti-bacterial and anti-microbial properties the Ag has to be everywhere in the box material. It is possible that Ag is in the material but in smaller quantities, that is smaller than 0.85 g/kg.

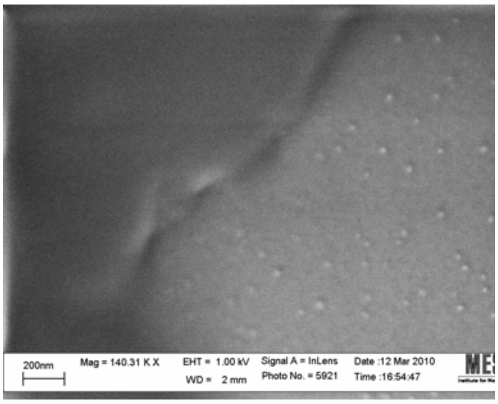
| | | | |
|---|---|---|---|
| 4 | Lip Balm | Cream | - |

**Information from the manufacturer**

-

**Electron micrographs (SEM)**




**Conclusions**

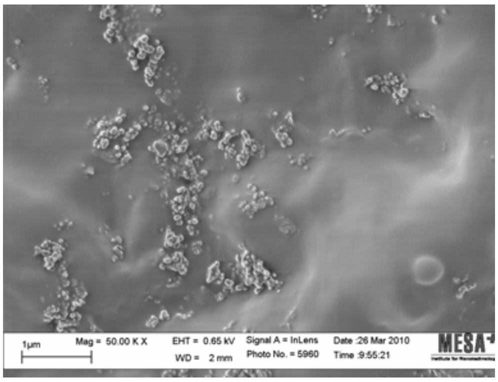
The lip balm was diluted into ethanol and ultrasonically dispersed as a preparation step before analysis in SEM. Within the SEM small nanosized particles were observed, but no Si or metallic ones. Sizes are about 50 nm, and they appear organic. This was confirmed by the XPS analysis were the lip balm was added ‘as received’ to the surface. This analysis indicated about 95% C and 5% O, which is typical for organic material. Metal or Si (or any other inorganic) element was not detected.

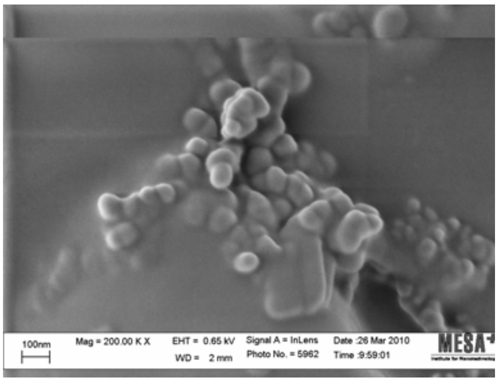
| | | | |
|---|---|---|---|
| 5 | Shoe cream | Cream | $SiO_2$ |

**Information from the manufacturer**

-

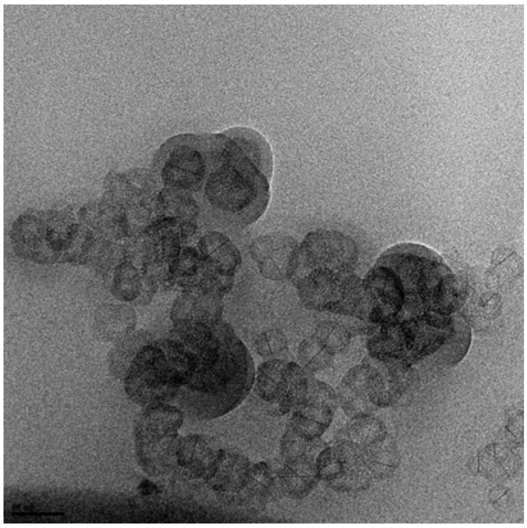
**Electron micrographs (SEM)**



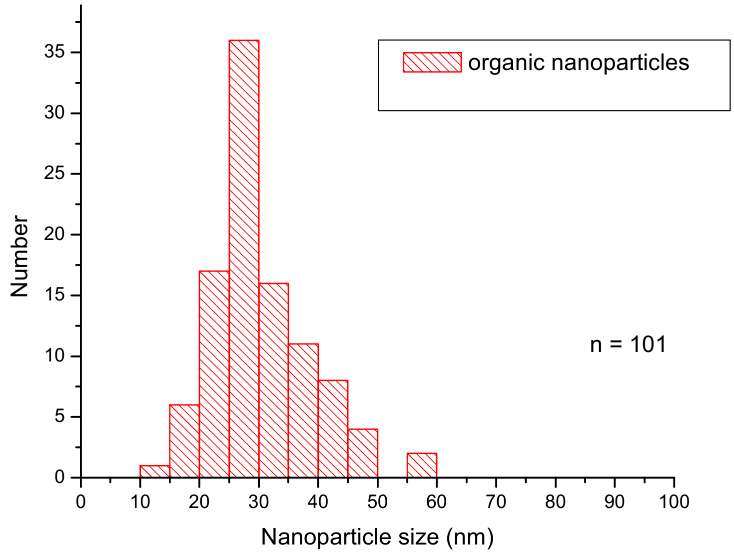




**Nanoparticle size distribution**

Using TEM analysis a number of images have been recorded and from these images 101 nanoparticles have been measured. The histogram of the sizes is created, resulting in a mean value for the size of 29.9 nm and a standard deviation of 8.2 nm.



TEM image (scale bar = 50 nm)




**Conclusions**

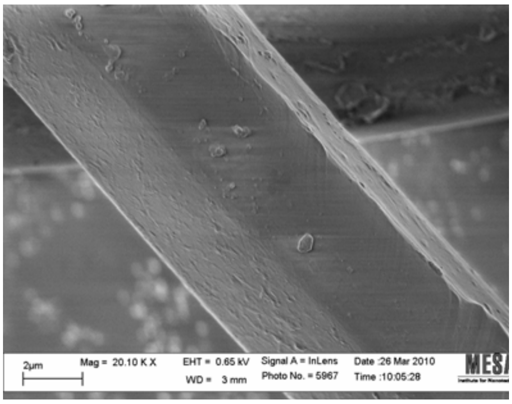
For the SEM analysis the shoe cream was diluted into ethanol and ultrasonically dispersed. The mixture that resulted from this was spread onto a surface and analyzed by SEM (see images). The images clearly show nanoparticles of sizes between 40 to 70 nm, but they appear to be organic material. XPS on the shoe cream smeared onto a surface (without dilution) revealed mostly C and some O (and a little Si).

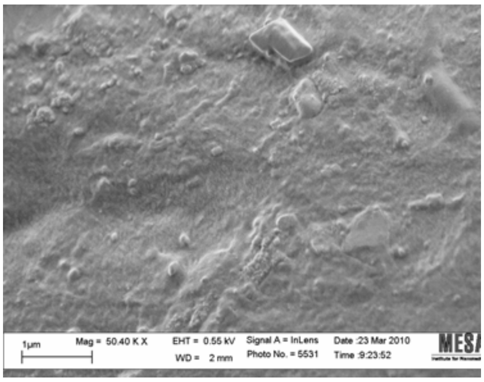
High resolution images made with TEM showed a distribution of nanoparticles sizes with a mean +/- sd value of 29.9 +/- 8.2 nm. The claim of having nanoparticles is therefore correct, but they are not Si, Ag, Zn, or Ti. They are organic nanoparticles.

| | | | |
|---|---|---|---|
| 7 | Cuddly toy | Solid | Ag |

**Information from the manufacturer**
Anti-mite, anti-mold and anti-microbial plush toys
The technology involves infusing silver, a natural anti-mite, anti-mold and anti-microbe agent, nanoparticles — 25 nanometers thick, about one 200 thousandth of a human hair — inside memory foam.
The manufacturer states that they stopped using nano-silver because there were just too many questions about the material, how people will respond to its use, and how the government might regulate it.

**Electron micrographs (SEM)**




**Note:** EM is performed on a single fiber drawn from the cuddly toy.

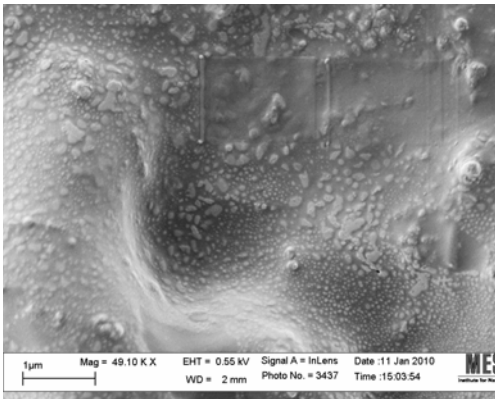
**Conclusions**
For the SEM analysis a number of fibers have been taken from the cuddly toy and were analyzed directly within the SEM. Different fibers have been analyzed and show the same morphological characteristics. Zooming in onto one of these fibers (diameter of 5 – 10 µm) does show some nanoparticles. XPS analysis did not reveal any Ag (that means less than 0.8 g/kg). The nanoparticles are most probably organic materials, since no other inorganic elements were detected.

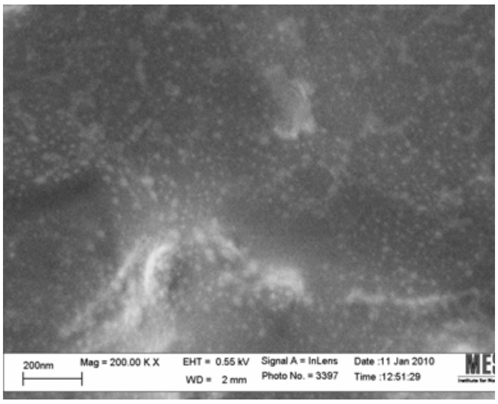
The fact we did not find any Ag nanoparticles might be because the manufacturer is not using them anymore, or the nanoparticles are most probably not in the fibrils on the outside, but more within the foam, which is most probably to be found within the cuddly toy.

| | | | |
|---|---|---|---|
| 8 | Indoor wall paint | Liquid | Ag |

**Information from the manufacturer**
According to the manufacturer the product contains 13-nm Ag nanoparticles

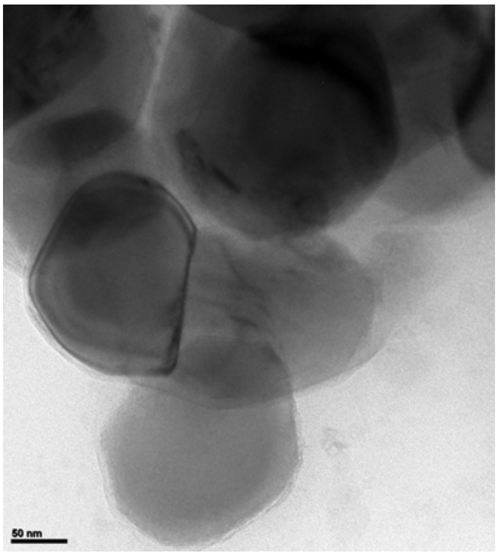
**Electron micrographs (SEM)**



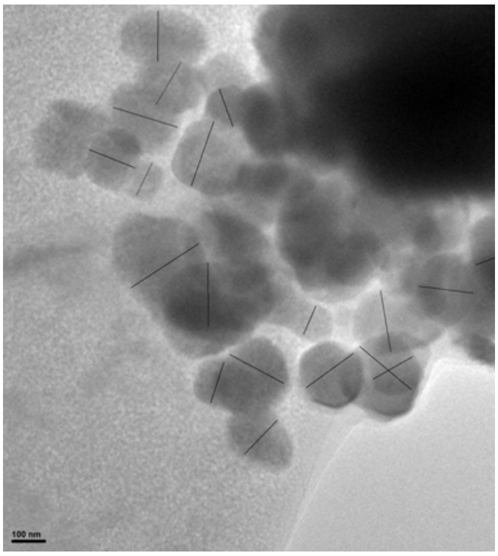




The SEM did reveal nanoparticles, but most probably not Ag ones.

**TEM analysis**
In a next step the paint was analyzed by TEM. Two examples of images are given here:



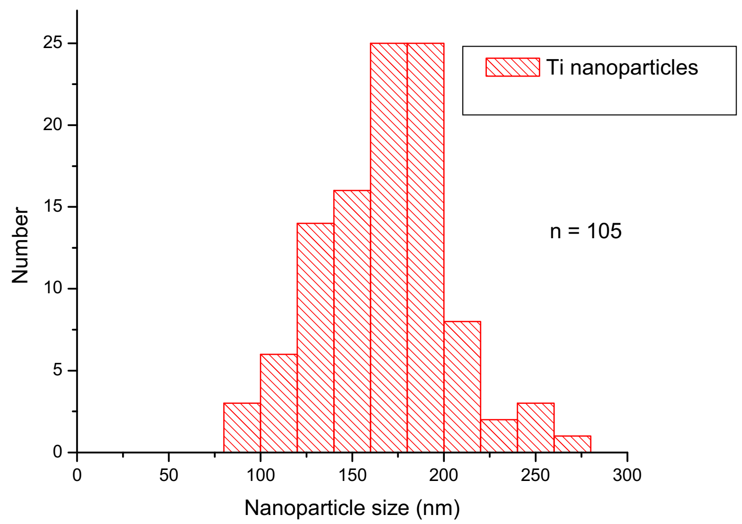

Scale bar = 50 nm



Scale bar = 100 nm

TEM images clearly showing Ti nanoparticles. In the right images black lines indicate some measurements of sizes of nanoparticles.

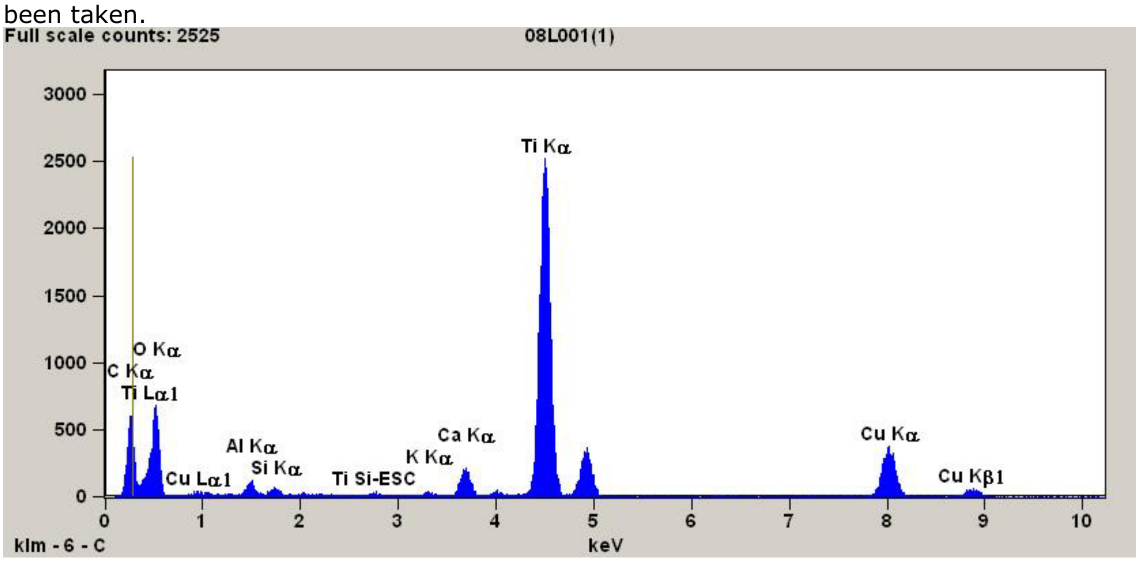
105 nanoparticles have been measured and the distribution is calculated from this:




Mean value of Ti nanoparticles is 167.8 nm with a standard deviation of 34.5 nm.

**TEM-EDX on single nanoparticles**

In order to verify the chemical nature of the nanoparticles, EDX spectra have been taken.




These indicate that the particles are Ti nanoparticles. Other elements (Ca, Si, Mg, Al) are there in smaller amounts. Cu is the TEM-grid used to put the sample upon.

**Conclusions**

The wall paint has been applied (after thorough mixing) directly onto a surface to create a thin layer. The SEM analysis did reveal nanoparticles, which were confirmed to be Ti nanoparticles using EDX. The nanoparticles were further examined using TEM. From the TEM-EDX they were again confirmed to be

Ti nanoparticles, which have a mean size of 167.8 nm with a standard deviation of 34.5 nm. The TEM images did not show any Ag nanoparticles.

XPS did not show any Ti or Ag, which indicates that the concentrations are below 0.37 g/kg (for Ti) and 0.84 g/kg (for Ag). Other elements such as Na, Ca, Si, Mg, K and Al were found.

**Discussion**
There is a slight discrepancy between the TEM analysis and XPS analysis with respect to the Ti nanoparticles. In the TEM a large number of Ti nanoparticles have been observed and measured, and the XPS (even in a depth profile) did not show significantly any Ti. At this moment there is no clear explanation for this.

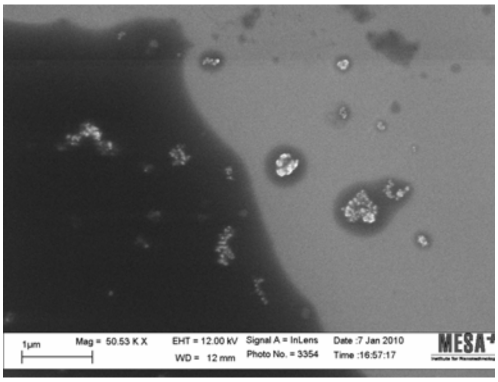
Ag nanoparticles were not detected, although the producer does claim that the product contains 13-nm nanoparticles. The only explanation in this case is that the concentration in the paint is to low to be detected. This means that the mass concentration of Ag is lower than 0.84 g/kg.

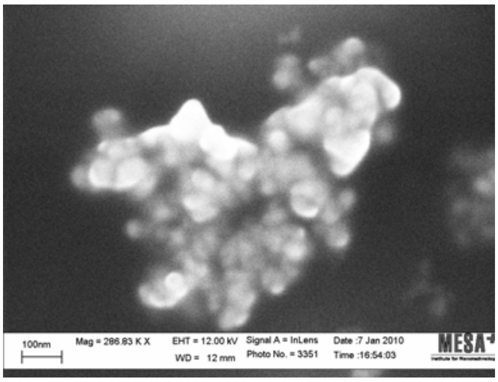
| | | | |
|---|---|---|---|
| 9 | Lip balm | Solid | $TiO_2$ |

**Information from the manufacturer**

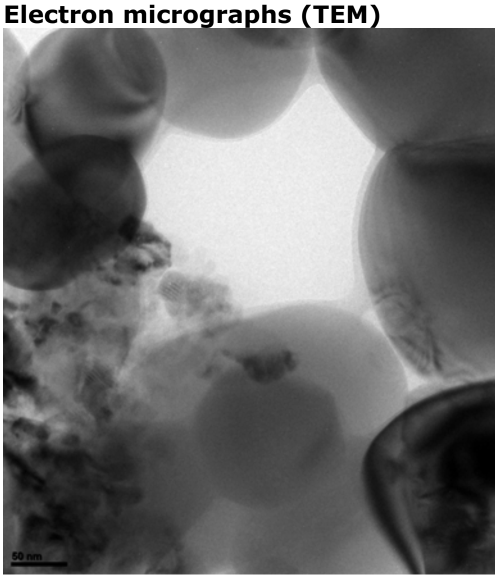
-

**Electron micrographs (SEM)**

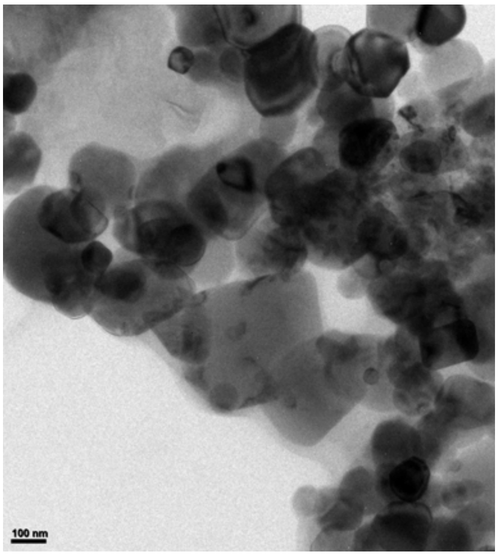



**Electron micrographs (TEM)**




Scale bar = 50 nm




Scale bar = 100 nm

**Conclusions**

Before analysis with SEM the sample was mixed with ethanol and ultrasonically dispersed. The analysis shows clustered Ti nanoparticles. The clusters vary in size from 200 nm to 500 nm. The Ti nanoparticles have a primary size in the range of 20 to 100 nm. Total concentration of Ti is 16 g/kg, as measured by XPS on the lip balm as received.

With TEM the presence of Ti nanoparticles was confirmed, and furthermore Si agglomerates of varying sizes and shapes were present. Ti nanoparticles typically have a rather spherical appearance with some straight edges, probably crystal facets, while Si nanoparticles seem to be agglomerates, having irregular shapes and vary enormous in size (from 20 nm to close to 1 µm).

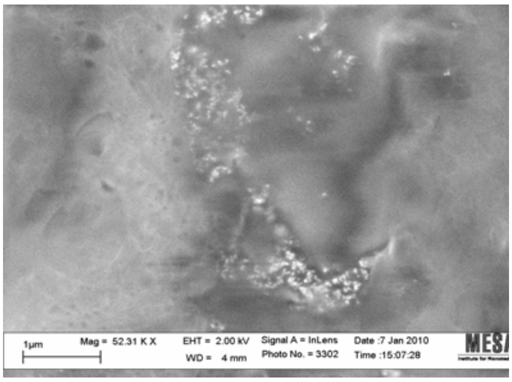
XPS also indicated a 1 g/kg of Si material, but this was not detected in the SEM to be present in nanoparticle form. Please note that the cluster formation can be an artefact of the preparation of the sample with ethanol.

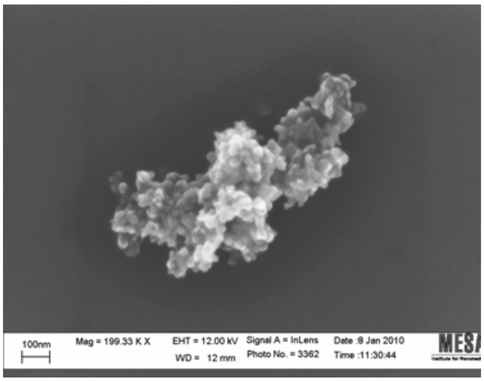
| | | | |
|---|---|---|---|
| 10 | Anti-wrinkle cream | Cream | $TiO_2$ |

**Information from the manufacturer**

-

**Electron micrographs (SEM)**

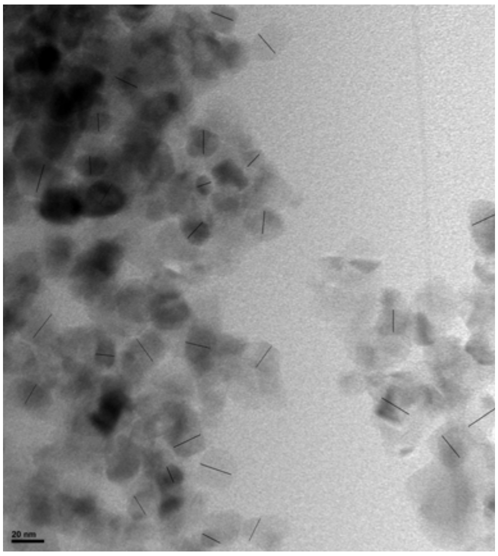


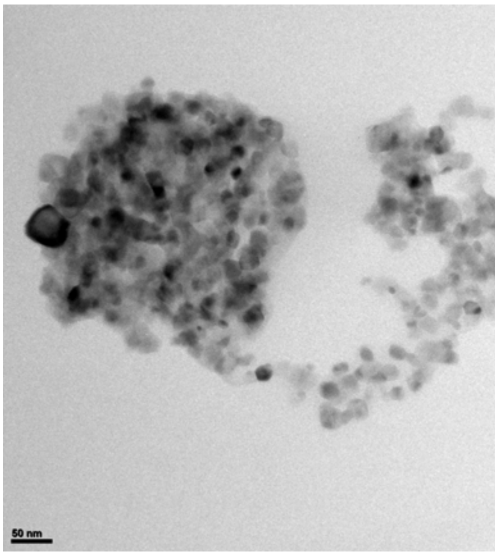

From the SEM analysis both Ti nanoparticles and Si agglomerates of nanometer size were observed. Ti nanoparticles appear small, spherical, with some straight edges, having a size of 5-20 nm, and the Si ones are slightly larger (about 50 nm) and appear more irregularly shaped. XPS on the cream as received reveals a 2 g/kg Ti and 9 g/kg Si in the sample.

**Nanoparticle size distribution (of Ti)**

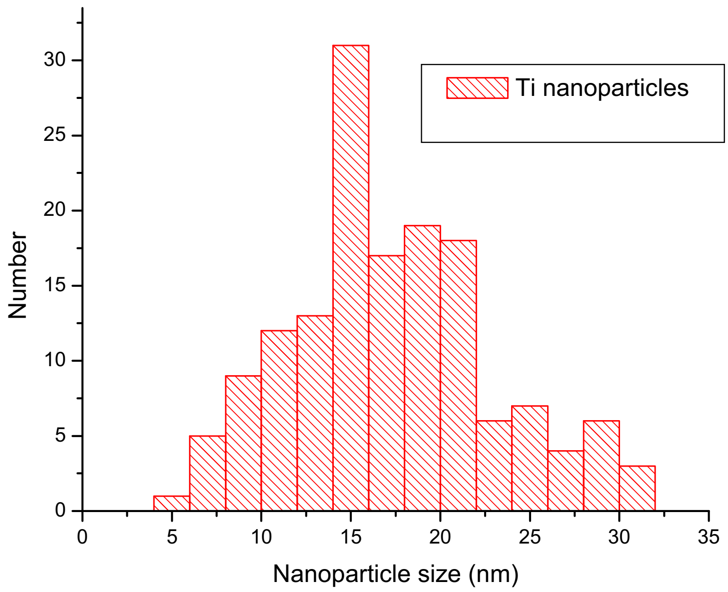
Using high resolution TEM a number of 151 Ti nanoparticles have been measured and a size distribution histogram has been calculated. Typical TEM images are shown.




Scale bar = 20 nm




Scale bar = 50 nm




The mean value for the Ti nanoparticle is 16.7 nm (primary size) with a standard deviation of 5.7 nm. With EDX the nature of the nanoparticles was verified and it turned out that all particles that have been analyzed with EDX contained both Ti and Si. As concluded from the SEM images, the Si forms more irregular nanometer-sized agglomerates and most likely sits very close to the Ti nanoparticles.

A detailed analysis of the Si nanoparticles has not been done, because they appear as very irregularly shaped, and seem to be agglomerates as opposed to crystal nanoparticles.

**Chemical characterization of the coating and shape of nanoparticles**
The Ti particles have a spherical shape with some straight edges, probably representing some crystal facets. Si nanoparticles are more irregularly shaped and are more like agglomerates. Both nanoparticles/-agglomerates do not show any coating in the SEM and TEM images.

**Conclusions**
Detailed characterization of the sample shows clearly that Ti nanoparticles and Si agglomerates of nanometer dimensions are present. The Ti nanoparticles appear as spherical with some crystal facets and have of a size 16.7 +/- 5.7 nm (mean +/- sd). Si I is present in irregularly shaped agglomerates of varying size. Concentrations of Ti and Si are respectively 2 g/kg and 9 g/kg.

Please note that the aggregation observed in the SEM and TEM images can be a result of the preparatory steps (dilution in ethanol).

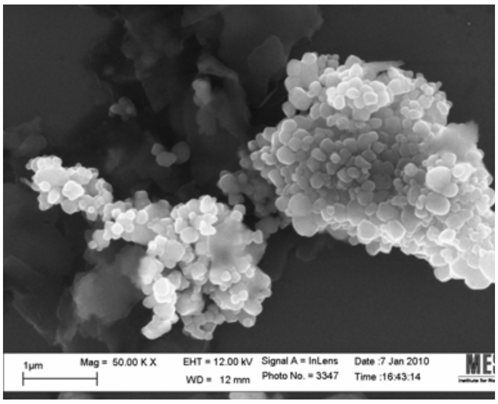
Zn has not been detected in this sample indicating it is not there or at a concentration lower than 0.3 g/kg.

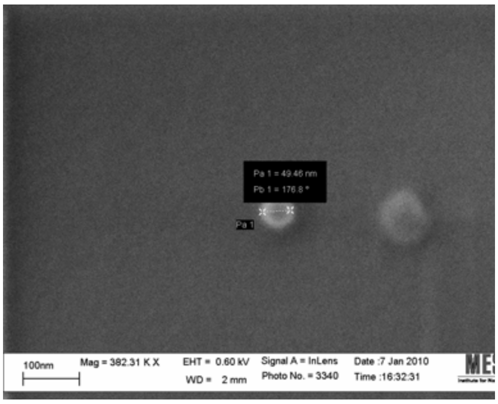
| 11 | Facial mask | Cream | $TiO_2$ |
|---|---|---|---|

**Information from the manufacturer**

-

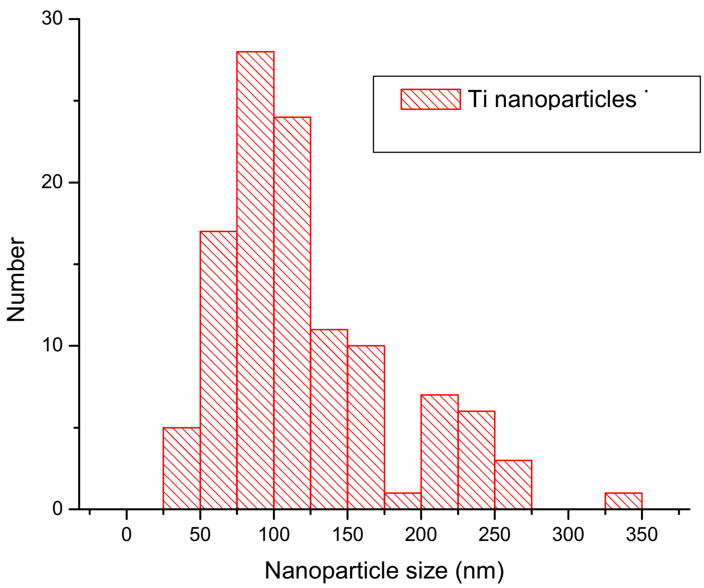
**Electron micrographs (SEM)**



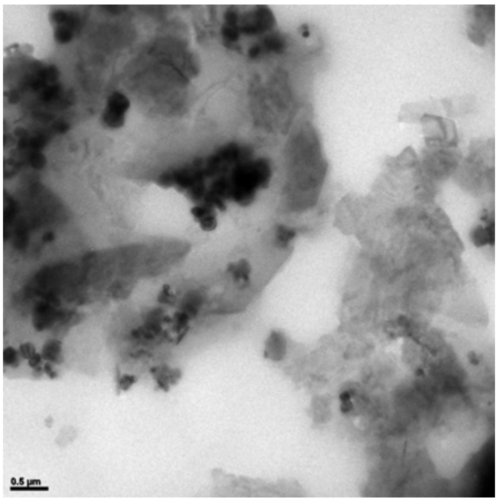

**Nanoparticle size distribution and shape (Ti)**

A total number of 113 nanoparticles has been measured and a size distribution histogram is created.

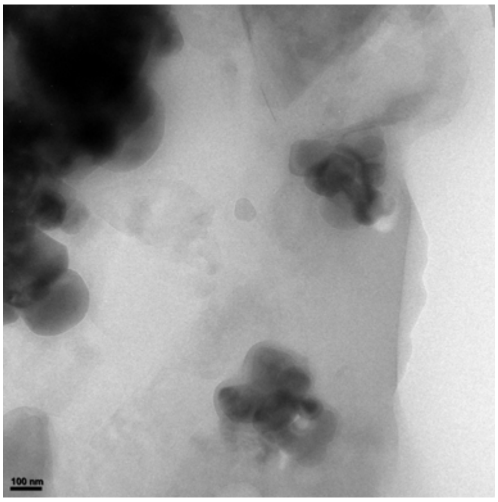



The mean value is 121 nm with a standard deviation of 59 nm.

Some typical TEM images are presented below.



Scale bar = 500 nm



Scale bar = 100 nm

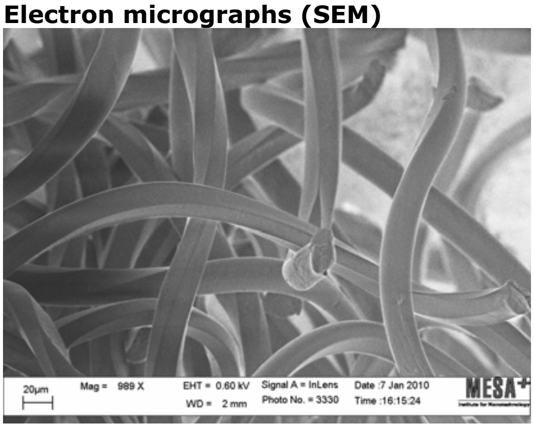
**Conclusions**
The sample is diluted in ethanol and ultrasonically dispersed and shows huge clusters of nanoparticles when imaged with SEM. XPS reveals that Ti, Si and Al are the metal constituents in the sample. From the SEM images it can be seen that the Ti is present in nanoparticles of 20-200 nm in size, and appear spherical with some flat facets. The Si (and possibly) Al form larger agglomerates, and do not seem to have a primary nanoparticle size. They are not spherical, but more irregularly shaped. These might be zeolite crystals. Concentration of Si, Ti and Al respectively is 23 g/kg, 2 g/kg and 14 g/kg. More detailed analysis of the particle size of the Ti nanoparticles reveals a 121 +/- 59 nm (mean +/- sd).

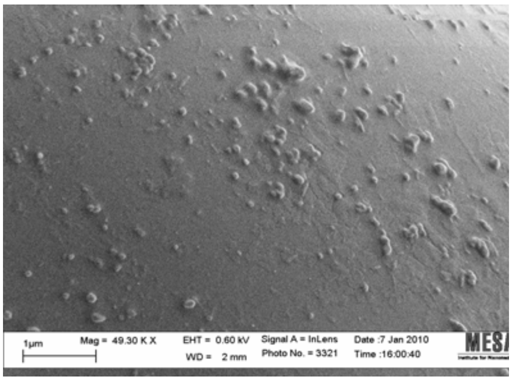
Please note that the aggregation of nanoparticles as observed in the images might be an artefact resulting from the preparation with ethanol.

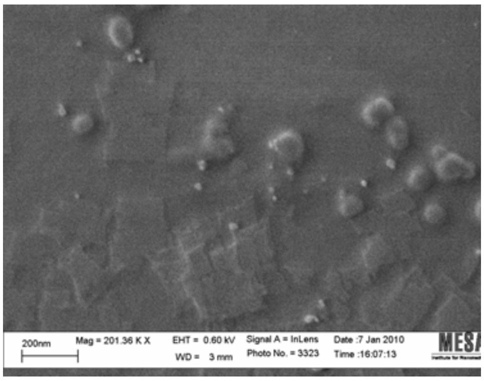
| | | | |
|---|---|---|---|
| 13 | Socks | Solid | Ag |

**Information from the manufacturer**
The yarn contains an active bacteriostatic substance which will not transfer to the skin. This significantly reduces bacterial growth, assuring long-term protection against common complaints such as foot-odor.

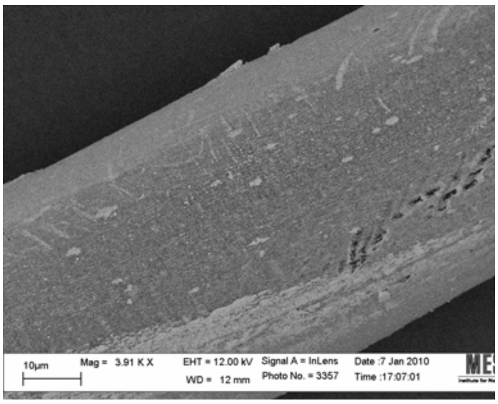
**Electron micrographs (SEM)**

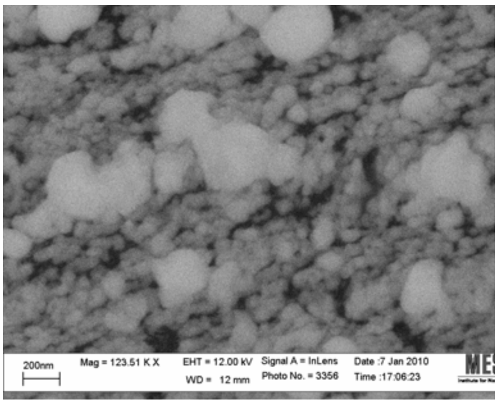



**Note:** EM images are made on single fibrils that do not contain Ag.

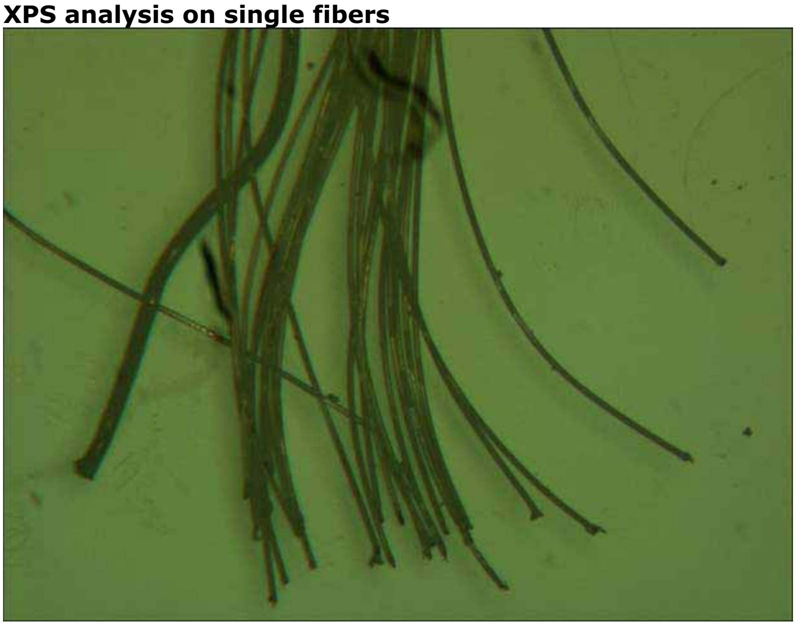



**Note:** EM images are made on single fibrils that do contain Ag.

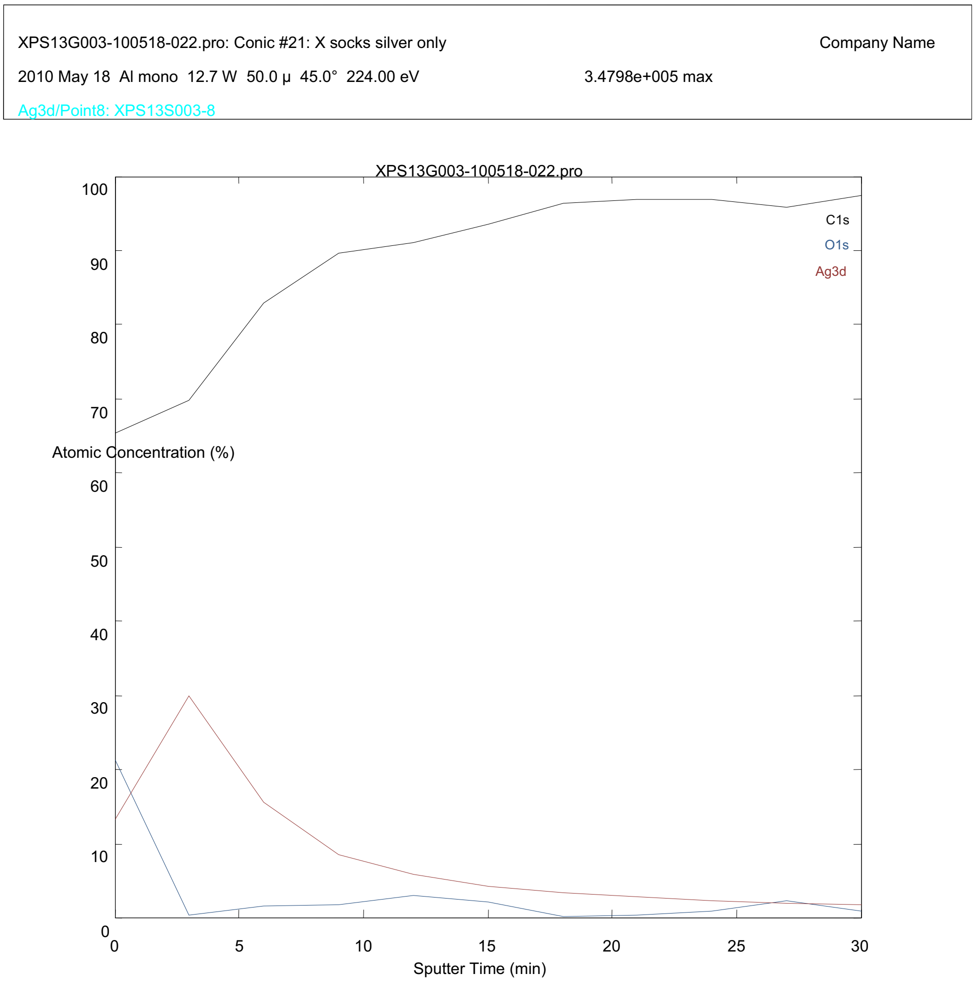
**Nanoparticle/-cluster size distribution**
The Ag is only present on 1 to 5 out of 100 fibers in the bottom part of the sock. These fibers contain Ag and organic material and appear thicker than the other surrounding them. The Ag is not present as individual nanoparticles, but forms a continuous layer. It appears as if the silver has been sputtered on these fibrils.

**XPS analysis on single fibers**



Optical microscopic image revealing 2 Ag-containing fibers (thick ones, on the left of the image) within a large number of fibrils that are consisting of organic material.

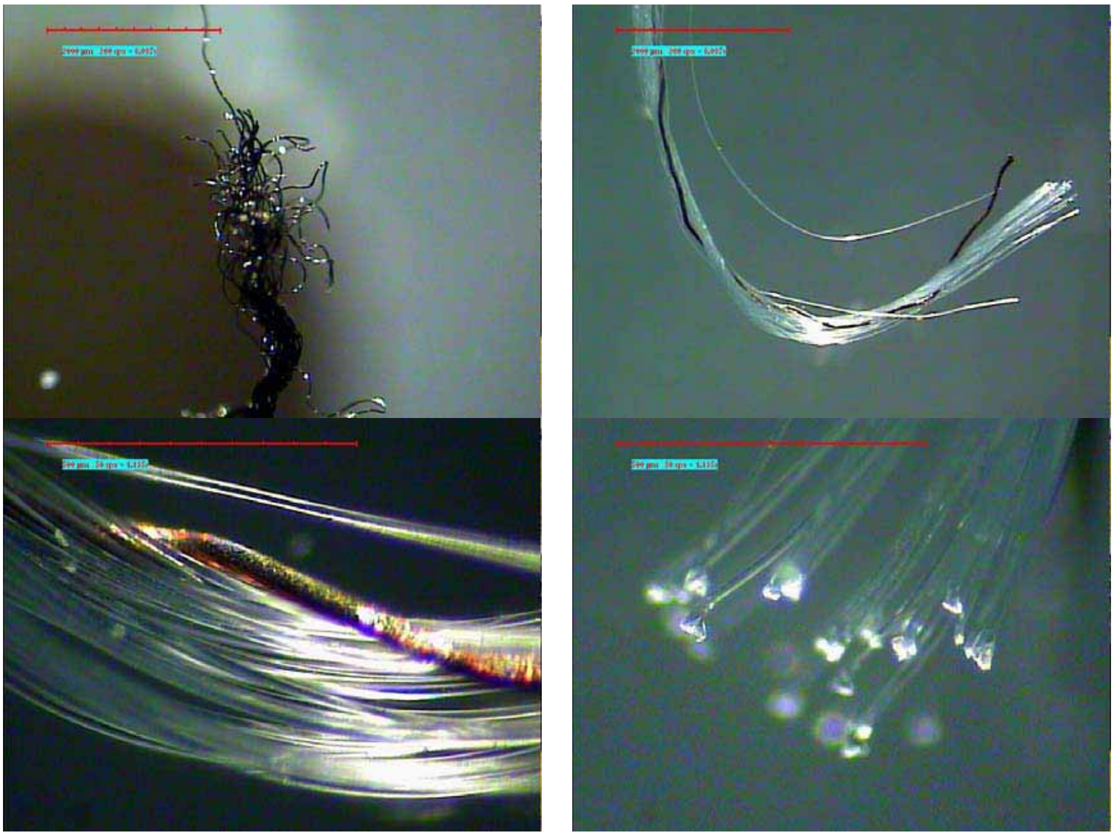
Initially the XPS did not reveal the presence of any Ag in the material, but upon closer look it appears that Ag-containing fibers (thick one on the left in the image) are woven with a large number of other fibrils that do not contain any Ag (thin fibers in the image). This obscured the Ag for the XPS. This one fibril containing Ag has been isolated and a depth profile has been made.




As the sputter time is increased, the concentration of Ag decreases indicating that the amount of Ag is higher at the outer part of the fibril and that the inner part is more organic material.

### Optical microscopy imaging of fibers

In order to determine the total amount of Ag in the product we performed some optical microscopy experiments on the fibers as they are found in the bottom part of the sock.



Some more optical microscopy images that show that 1 to 5 out of a 100 fibrils are Ag-containing.

**Concentration of Ag in the bottom part of the sock.**

The Ag-containing fiber has a diameter of 40 µm, which is covered with 150 nm of Ag. The other organic fibers are about 20 µm in diameter. Assuming that 1 Ag-containing fibril upon 40 organic ones, it is possible to calculate the volume fraction of Ag in the material, which is 0.18%. In terms of mass, this means that Ag makes up about 1%.

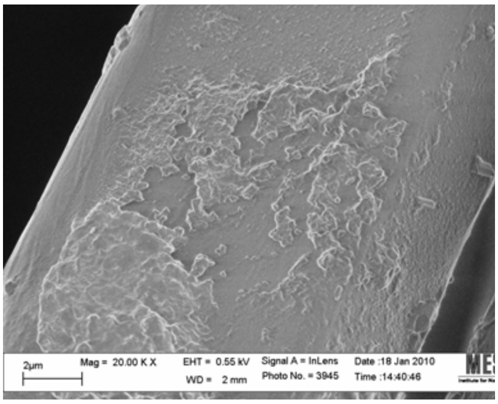
**Conclusions**

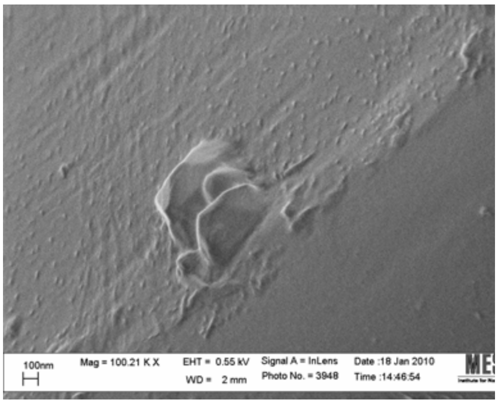
Different parts of the sock have been analyzed and only the bottom part was found to contain Ag. Within this part of the sock only 1 to 5 fibers out of 100 is a Ag-containing one. The remainder of the fibers is just organic material. Using SEM and XPS (in depth profiling mode) on these Ag-containing fibers clearly reveal a continuous layer of Ag which is present on the surface of these fibrils. Thickness of this layer is estimated to be 100-200 nm. The Ag appears in clusters on the fibril having sizes of 50 to 500 nm.
Concentration of Ag in the grey part of the sock is about 1%, that is 10 g/kg.

| | | | |
|---|---|---|---|
| 14 | T-shirt | Solid | Ag |

**Information from the manufacturer**
The functional fiber reduces the smell of sweat in the underwear. Thanks to the antibacterial effect of silver.

**Electron micrographs (SEM)**



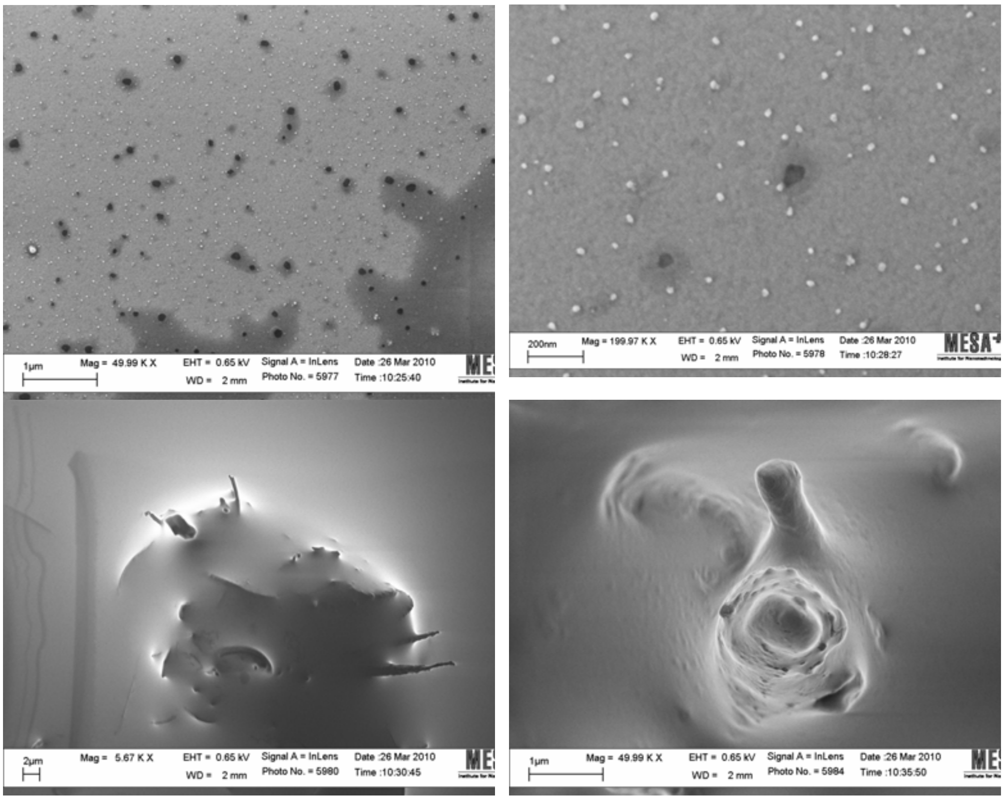

**Conclusions**
Different parts of the t-shirt have been cut out of the shirt and analyzed: the entire shirt consists of fibers with diameters of typical 10 µm. The fibers have a hexagonal cross-section, which is most probably resulting from the way the fibers are fabricated. Zooming in on the surface of these fibers, there were no nanoparticles detected. XPS and EDX analysis did not reveal the presence of Ag, which indicates that it is not there or present in a concentration lower than 0.8 g/kg.

| | | | |
|---|---|---|---|
| 15 | Window sealant | Liquid | - |

**Information from the manufacturer**

-

**Electron micrographs (SEM)**



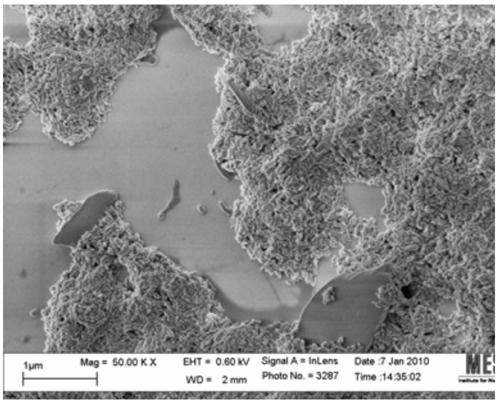

**Conclusions**

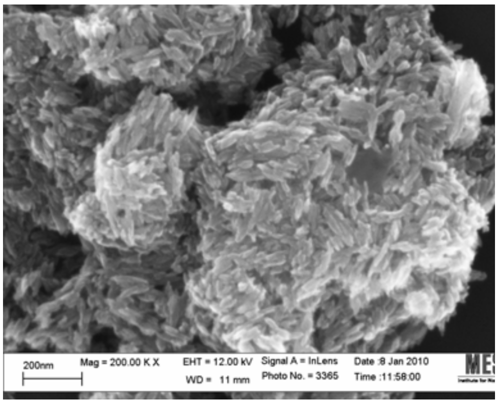
The electron micrographs are made from the window sealant liquid directly applied onto a surface. In some areas small nanometer-sized particles are visible, while on other positions strangely-shaped micrometer-sized Sn particles are found. Sn appears to be form wires of about 300 nm thickness (third EM image). The smaller structures are not metal nanoparticles, but organic in nature. SEM-EDX analysis on these micron-sized particles show Sn, C and F elements. With XPS a larger area is analyzed and C, O and F is detected. Sn is not measured, most probably because it is lower than 0.9 g/kg.

| | | | |
|---|---|---|---|
| 16 | Sunscreen | Cream | $TiO_2$ |

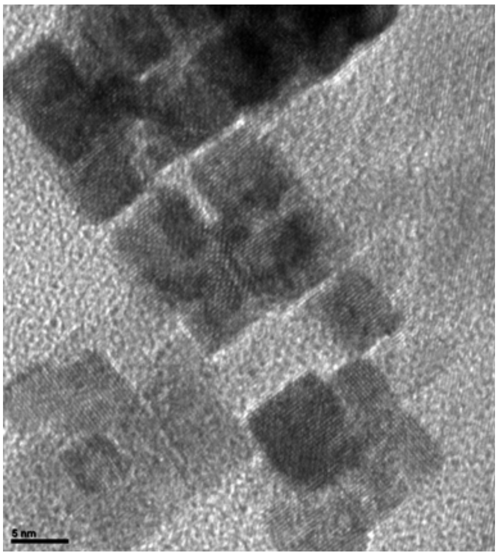
**Information from the manufacturer**
Sun Protection Factor (SPF) 50

**Electron micrographs (SEM)**

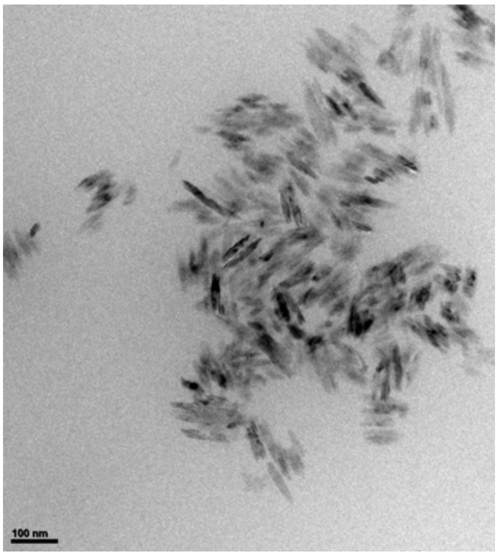



**Electron micrographs (TEM)**

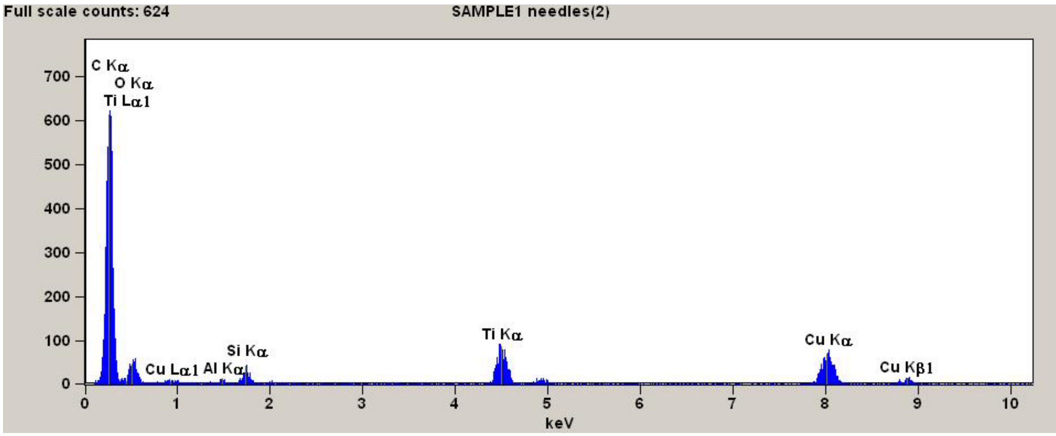



Scale bar = 5 nm

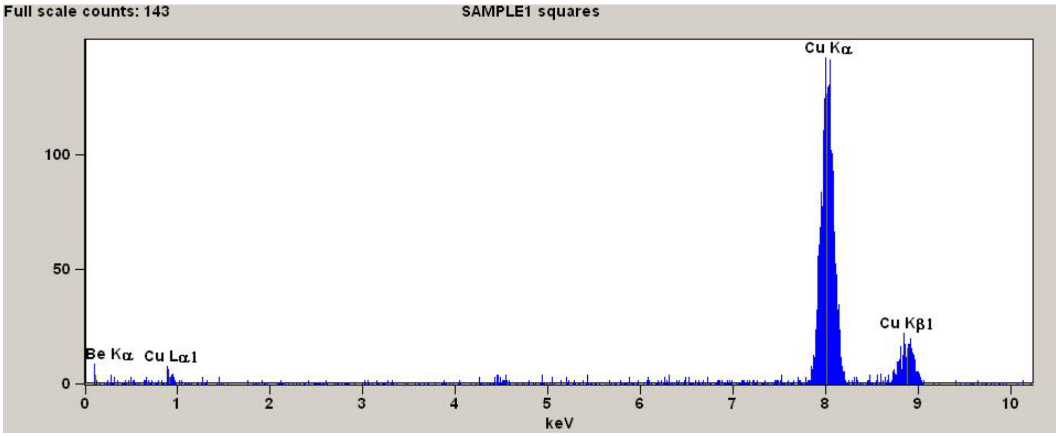



Scale bar = 100 nm

## TEM-EDX on the canoe-shaped nanoparticles




## TEM-EDX on the squares



**Conclusions**
The sun milk was diluted in ethanol and ultrasonically dispersed before analysis with the SEM. The electron micrographs show large clusters of Ti nanoparticles. Clusters range from 200 nm to many microns. The Ti nanoparticles are not spherical but elongated (canoe-shaped) ranging in size from 4 x 20 nm to 10 x 100 nm. This was further confirmed with TEM imaging (right image). Besides the canoe-shaped nanoparticles, also smaller square ones were found (left image). TEM-EDX on the canoe-shaped ones revealed a clear signature of Ti with some Si. TEM-EDX on the square ones did not clearly indicate any element, most probably because of too little material. The Cu in both spectra is the TEM-grid itself.

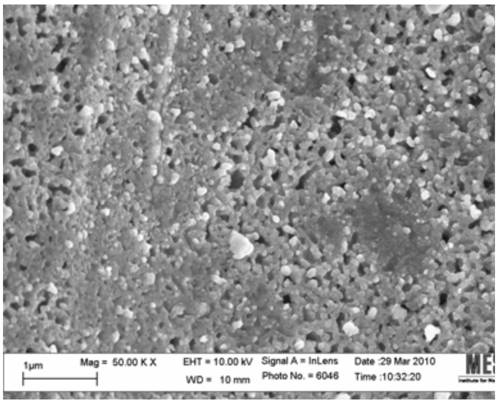
Other elements that are detected are Si and Al, and possibly they form some zeolites, but it is not clear whether these are nanoparticles.

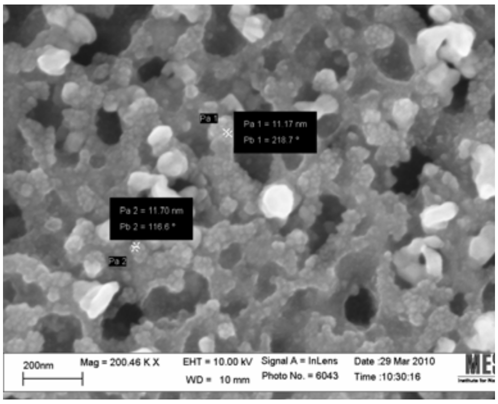
Clusters observed can be an artefact of the preparation with ethanol.

| 17 | Wound dressing | Solid | - |
|---|---|---|---|

**Information from the manufacturer**
Antimicrobial

**Electron micrographs (SEM)**

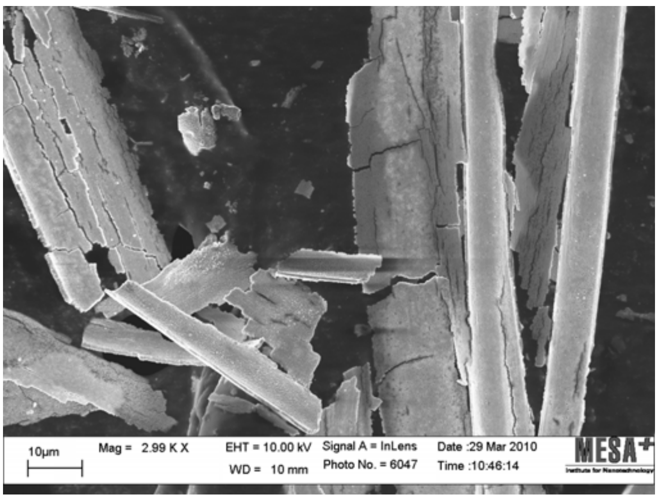


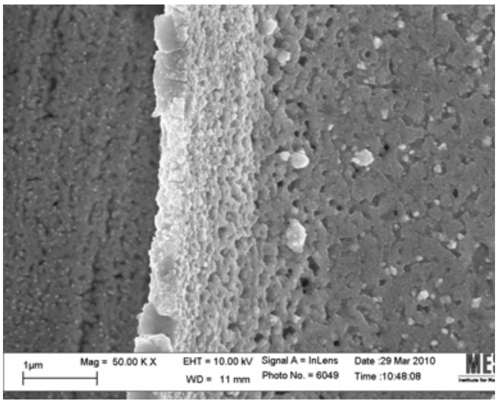

The electron micrograph clearly reveals nanosized featured silver, and appear to be nanoparticles. Having a closer look however it is not absolutely clear whether they are isolated nanoparticles or forming a large aggregate with nanosized features.

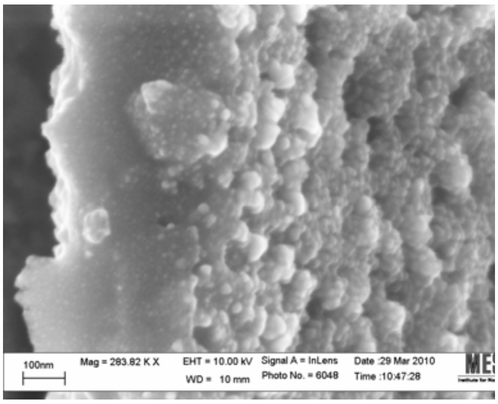
The XPS reveals that mass of Ag in the sample makes up 95% of the total mass in the first 200 nm of the sample.

**Analysis of Ag layer (continuous or individual nanoparticles)**
From the XPS data which revealed a 95% mass of Ag in the first layer, combined with the SEM images, it seemed that the layer is not a layer of individual particles, but more a continuous layer. Additional SEM images have been made.




SEM image showing large pieces of Ag that are detached from the fiber, clearly showing that the layer is a continuous one.




These SEM images clearly show that the coating is having an Ag layer, most probably resulting from sputtering Ag onto the dressing material. The thickness can be seen in the last two images and is around 400 nm.

**Optical microscopy imaging**

Using the optical microscope on a bundle of fibers of which the wound dressing consists, it is clear that a continuous layer of Ag is covering the bundle. On the left part of the image clear fibers can be seen, while on the right part they are covered with the Ag-layer.

**Conclusions**

The wound dressing consists of fibrous material, which has been coated with a 300-500 nm Ag layer on both sides. Within this layer 95% of the mass is Ag. On the nanometer scale the Ag does not consist of isolated individual nanoparticles, but forms a continuous layer, that even when it detaches from the fibril material forms sheets of 300 to 500 nm thick and 10 to 100 µm large. The surface does reveal a nanometer-scale roughness, having features of 10-15 nm.

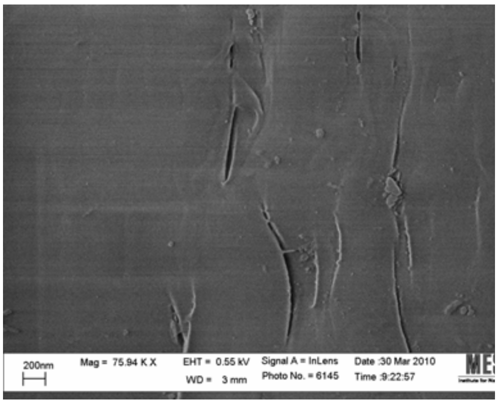
| | | | |
|---|---|---|---|
| 18 | Toothbrush | Solid | Ag |

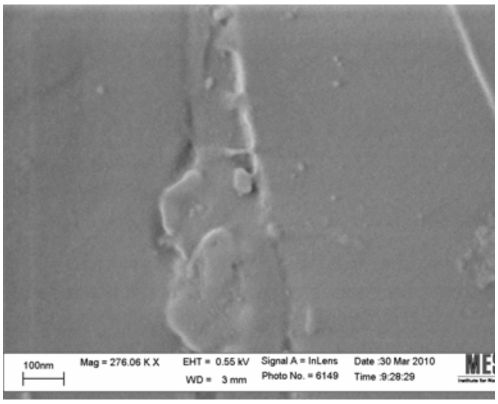
**Information from the manufacturer**

-

**Electron micrographs (SEM)**

Both EM pictures are made of a hair of the toothbrush.



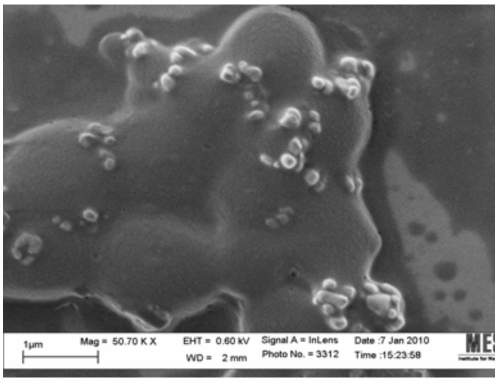

**Conclusions**

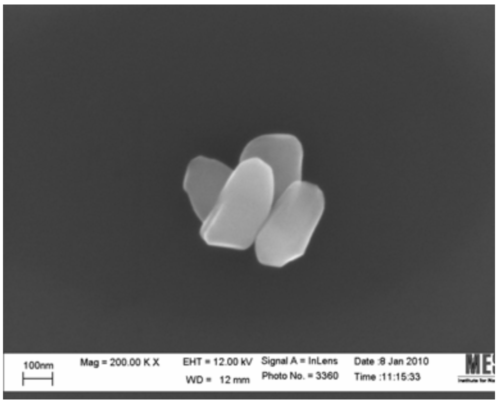
For the first sample individual hairs of the toothbrush were torn out of the brush and analyzed with SEM and XPS. The electron micrographs do not show any metal nanoparticles. The XPS analysis indicated the elements C, O, N and some Si. Ag was not found. In a second experiment we tested the back side of the toothbrush, which is to be used to rub your tongue, in order to remove bacteria. Also this analysis did not indicate the presence of Ag, indicating it is not there or at a concentration lower than 0.8 g/kg.

| | | | |
|---|---|---|---|
| 19 | Anti-wrinkle cream | Cream | $TiO_2$ |

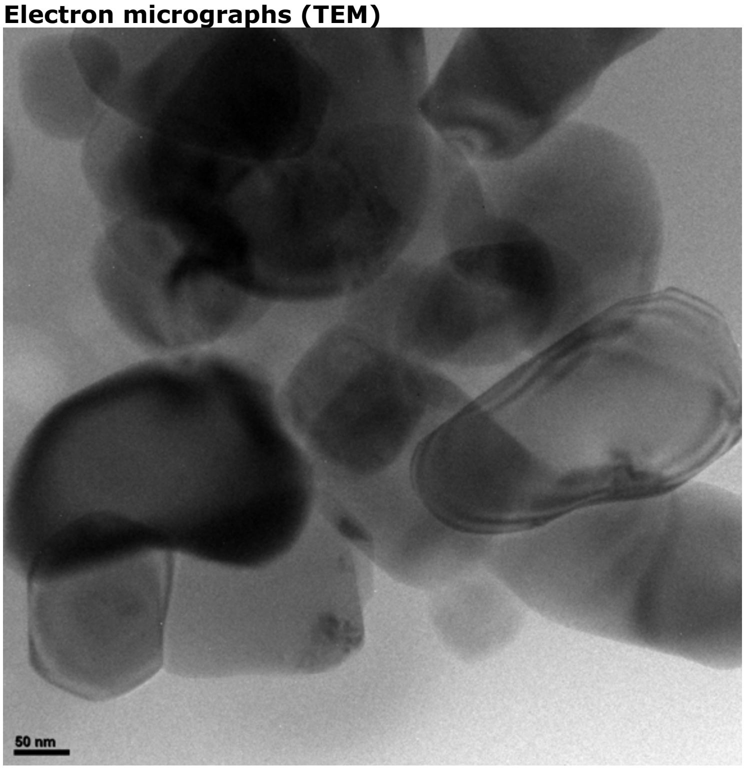
**Information from the manufacturer**
SPF15

**Electron micrographs (SEM)**




**Electron micrographs (TEM)**

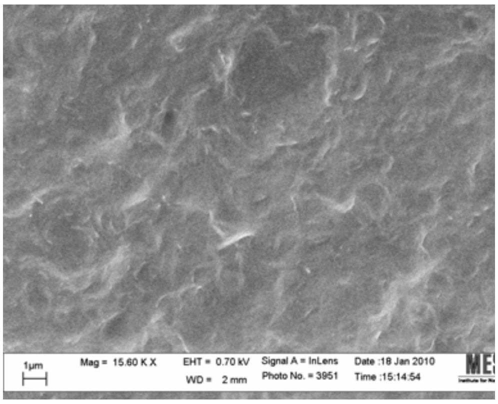


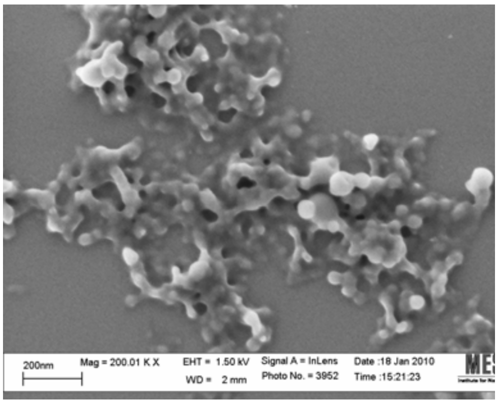
**Conclusions**
The anti-wrinkle cream was mixed with ethanol, ultrasonically dispersed and spread out onto a surface for SEM analysis. SEM-EDX indicated presence of both Ti and Si (and Na, C and O). XPS on the sample as received indicated a concentration of 3.0 g/kg Ti in the sample, but. Ti nanoparticles were observed having sizes of 50-200 nm (primary size). Si was present in irregularly shaped agglomerates of varying sizes.

| | | | |
|---|---|---|---|
| 20 | Leather maintenance | Aerosol | - |

**Information from the manufacturer**
Nano mentioned on the product.

**Electron micrographs (SEM)**



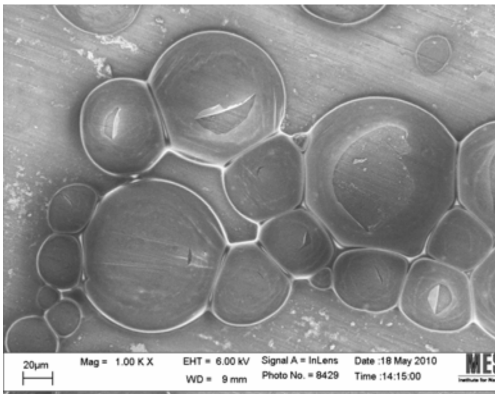

**Conclusions**
The spray has been applied to a Si surface after which it was analyzed using SEM. At high resolution nanometer-sized structures were observed with feature size of 30-50 nm, but they are not metallic or Si nanostructures. It is also not clear whether they are individual nanoparticles or whether it is an aggregate. SEM-EDX and XPS did not detect any metal, indicating that the nanostructures/ -particles detected are organic materials.

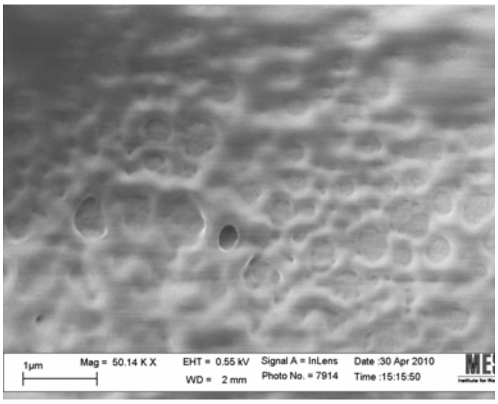
| | | | |
|---|---|---|---|
| 21 | Anti-rain spray | Aerosol | - |

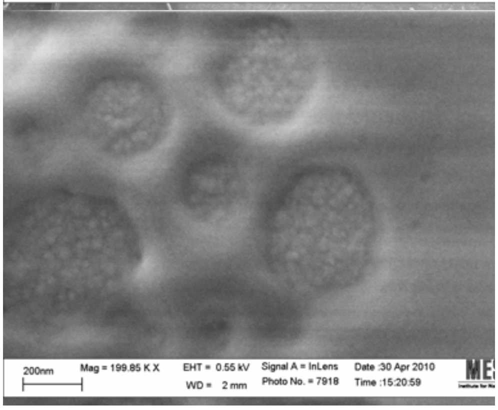
**Information from the manufacturer**

-

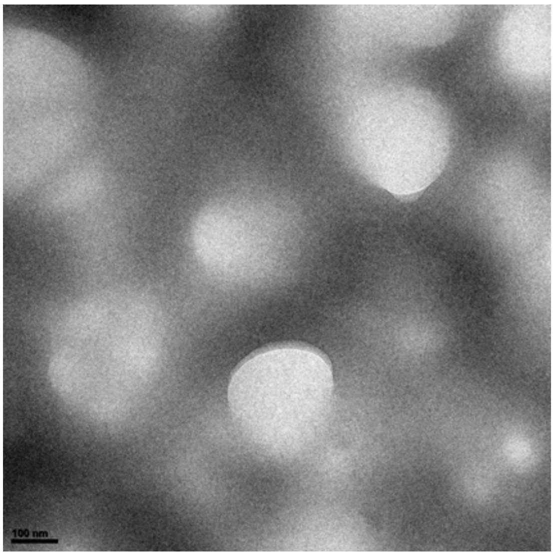
**Electron micrographs (SEM)**



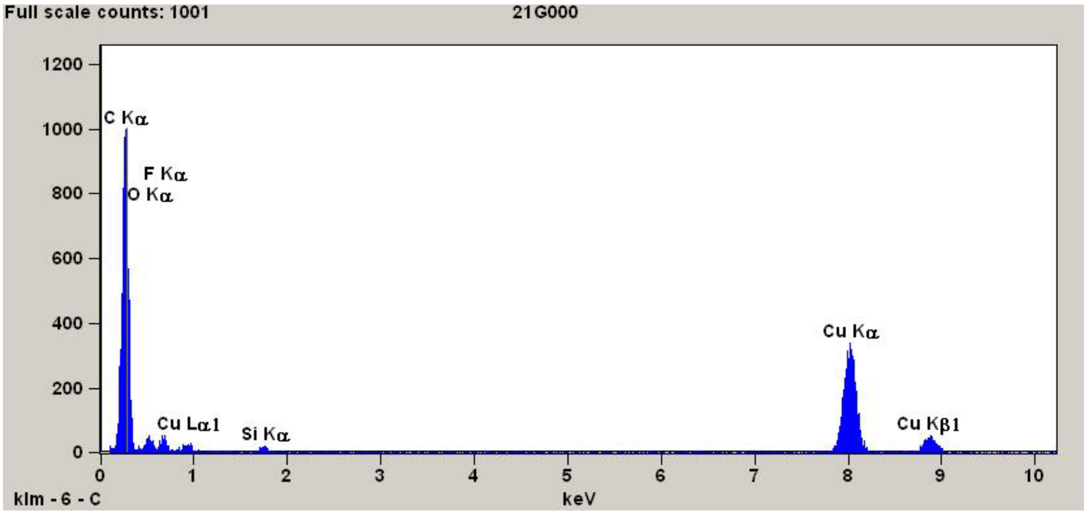



**Electron micrographs (TEM)**




Scale bar = 100 nm

**TEM-EDX**




**Conclusions**

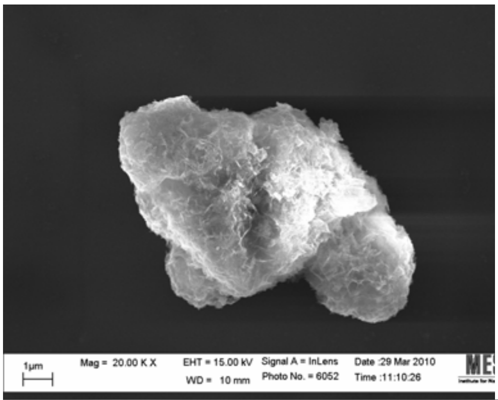
The aerosol was directly sprayed onto a Si surface for SEM analysis. No metal nanoparticles were observed in the electron micrographs. The TEM image did not give a high-resolution image but showed 100 nm features. Chemical analysis of these (TEM-EDX) did reveal it is organic material. XPS indicated a PTFE type composition (polytetrafluoroethylene, Teflon) and no metal elements were detected.

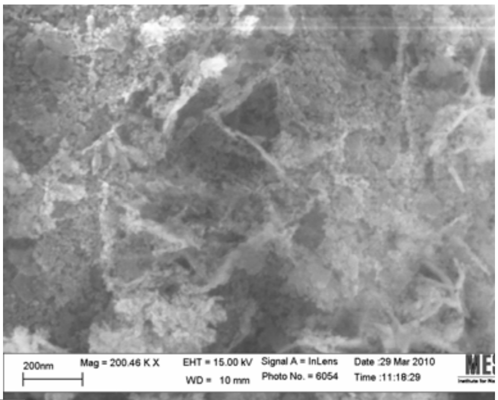
| | | | |
|---|---|---|---|
| 22 | Anti-dirt spray | Aerosol | - |

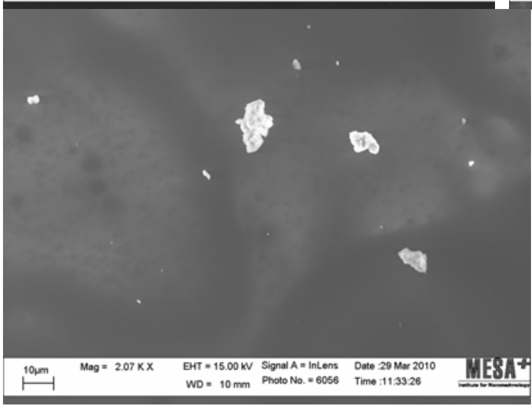
**Information from the manufacturer**

-

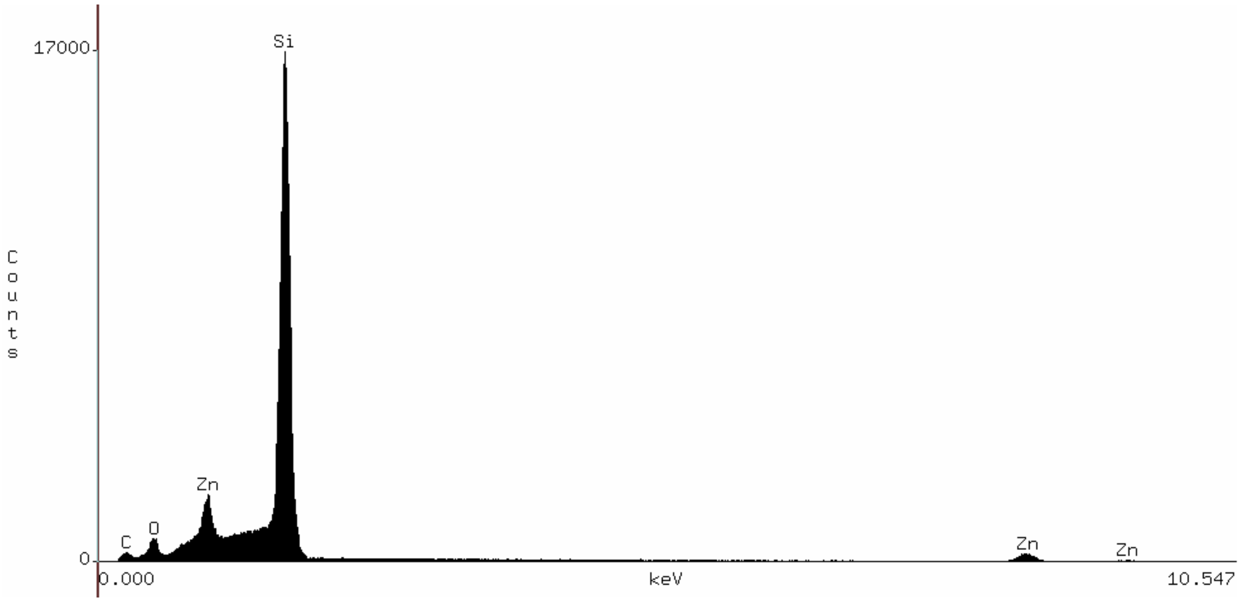
**Electron micrographs (SEM)**



**SEM-EDX on 1 microparticle**

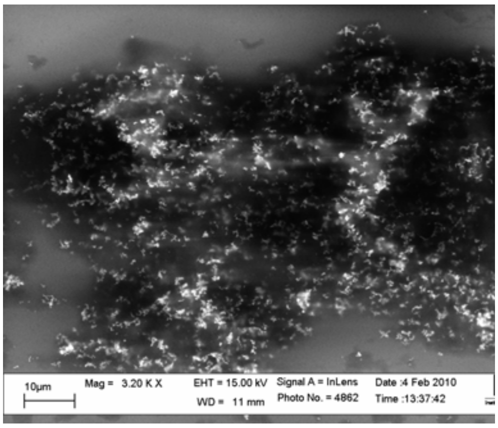


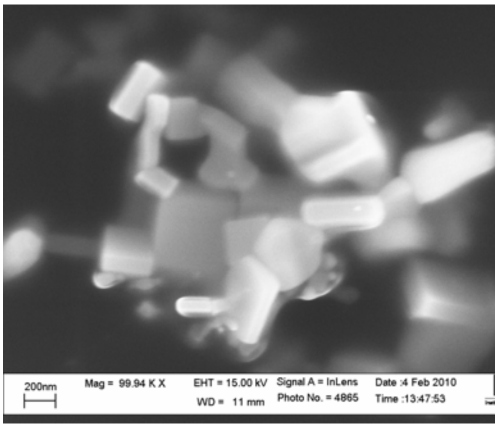

**Conclusions**
The product was directly sprayed onto a Si surface and analyzed by SEM. Aggregates of 0.3 to 10 µm have been observed. Detailed chemical analysis using SEM-EDX indicated that these aggregates are mainly Zn. Primary size of the nanoparticles could not be determined since they are not clearly visible within the clusters. XPS did not reveal the Zn, most probably because of the low concentration (lower than 0.5 g/kg).

| | | | |
|---|---|---|---|
| 23 | Maintenance spray | Aerosol | - |

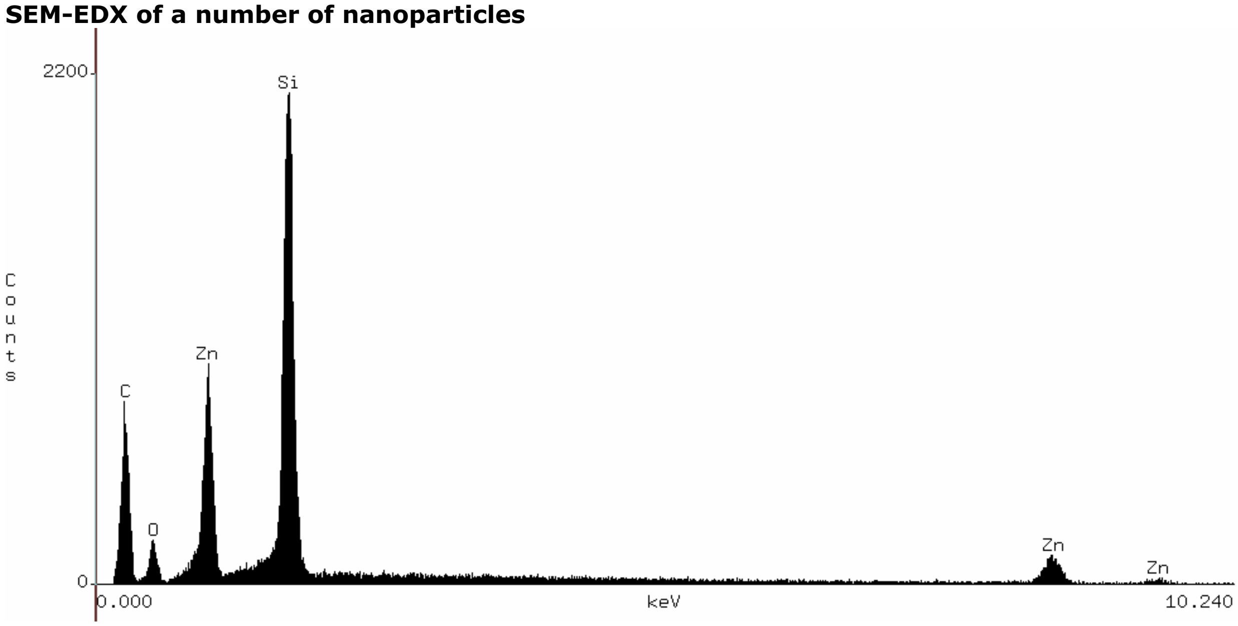
**Information from the manufacturer**
Nano mentioned on the product.

**Electron micrographs (SEM)**



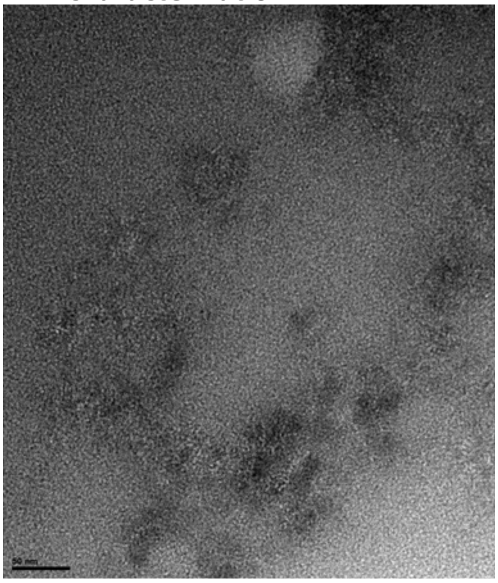




**SEM-EDX of a number of nanoparticles**

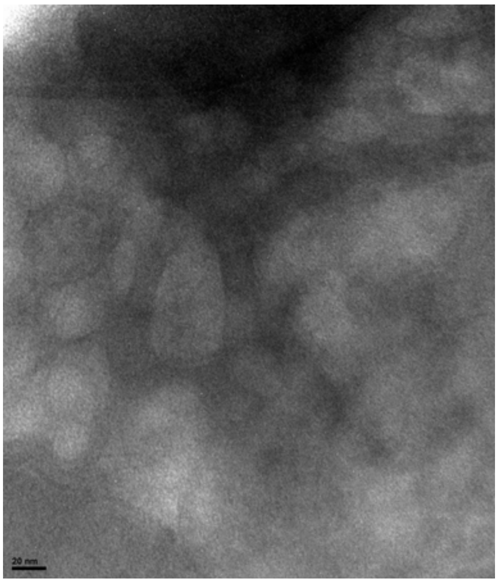



The spectrum clearly reveals Zn and Si. It is not completely clear whether Si is in the sample or whether it is the support.

**TEM characterization**



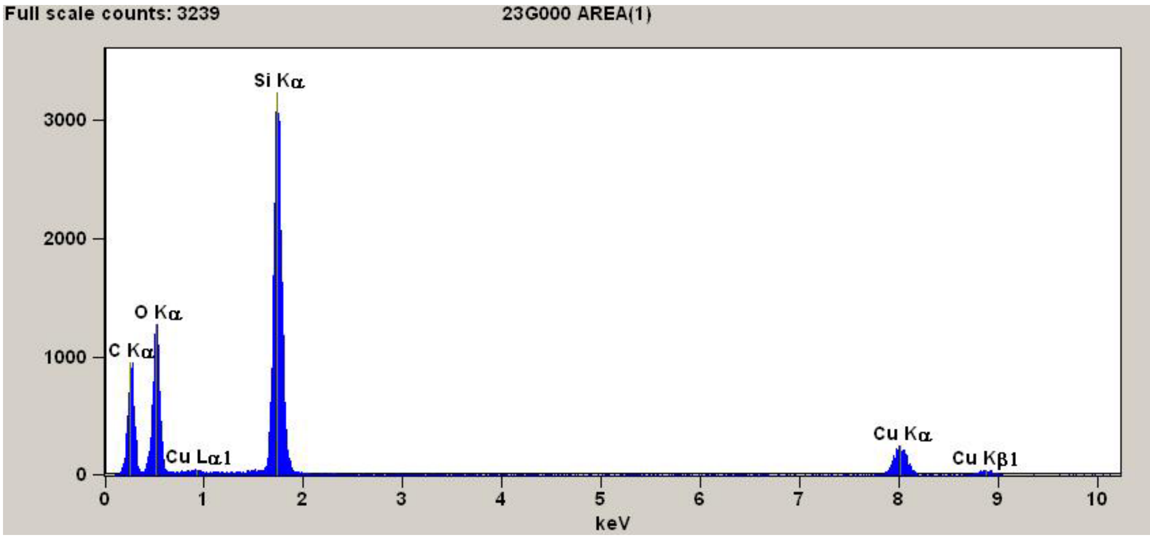
Scale bar = 50 nm



Scale bar = 20 nm

TEM images do not come out clear enough to allow measurement of the nanoparticles.

**TEM-EDX analysis**



**Conclusions**

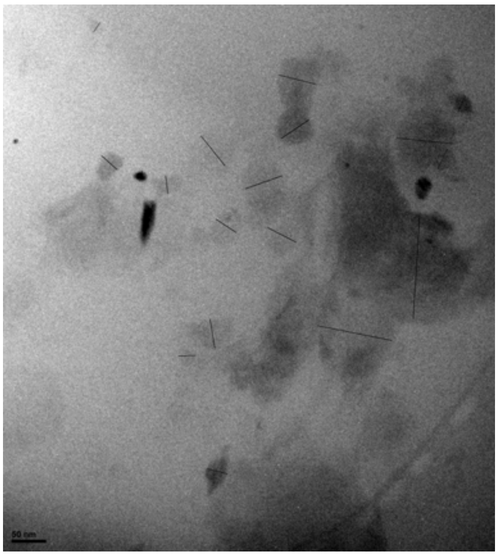
For SEM preparation the spray is applied directly onto a Si surface. EDX-SEM indicated the presence of Zn and Si nanoparticles, although Si can be from the support. TEM-EDX clearly revealed a Si peak which indicates that the sample is indeed containing Si. However, this spectrum does not show any Zn. None of the two (Zn or Si) was detected with XPS, which indicates it is either absent or present in concentrations lower 0.5 g/kg (for Zn) and 0.2 g/kg (for Si).

The SEM images clearly revealed crystals with flat faces with sizes of 50 to 200 nm. The TEM however did not provide any image that had sufficient quality to see or measure the nanoparticles. Most probably this is due to the preparation, in which the aerosol is too viscous and forms a layer that is too thick for high resolution TEM imaging.

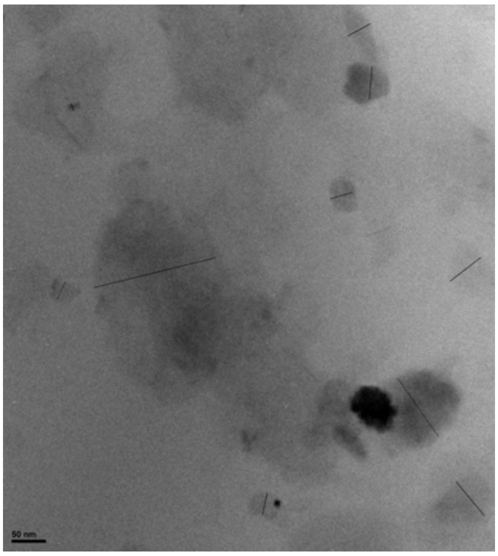
| 24 | Sunscreen | Cream | $TiO_2$ |
|---|---|---|---|

**Information from the manufacturer**
Sun Protection Factor (SPF) 30

**Electron micrographs (TEM)**



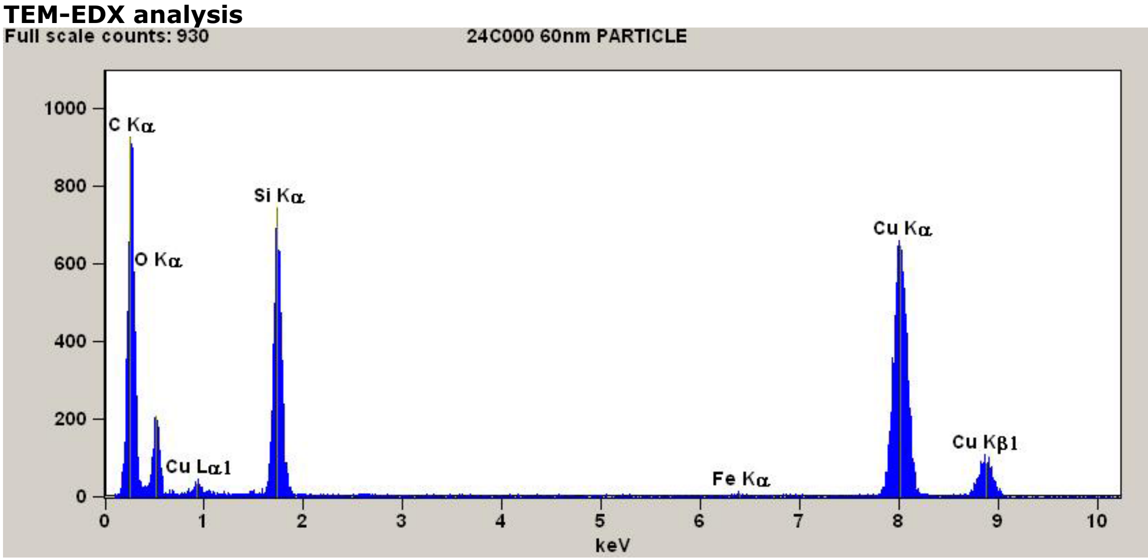
Scale bar = 50 nm



Scale bar = 50 nm

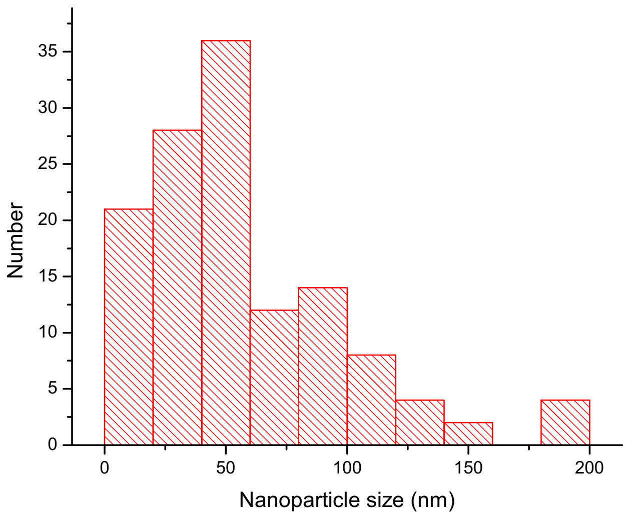
**NOTE:** The black lines in the image indicate the size measurements.

**TEM-EDX analysis**



**Nanoparticle size distribution**

Using several TEM micrographs a distribution of sizes has been calculated.

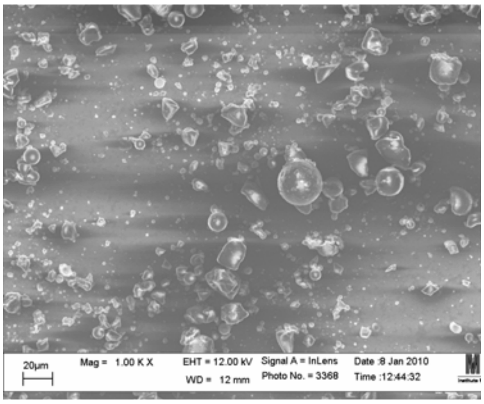


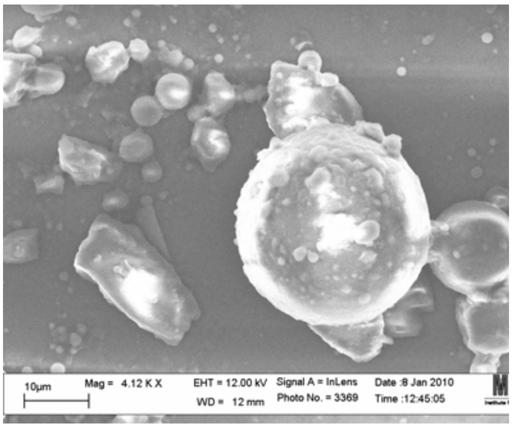

**Conclusions**
The sun blocking spray has been directly sprayed onto a TEM grid, for analysis. Nanoparticles are observed with a broad range of sizes with a mean value of 57.1 nm and a standard deviation of 39.8 nm. TEM-EDX clearly reveals that the particles are Si and from XPS it was calculated to be present in the sample at a concentration of 3.8 g/kg. XPS did not show Ti in significant amounts, which means it is not in there or at a concentration lower than 0.4 g/kg.

| | | | |
|---|---|---|---|
| 25 | Deodorant | Aerosol | Ag |

**Information from the manufacturer**
Anti-bacterial protection, silver molecules.
Eliminates body odors with antibacterial silver molecules.

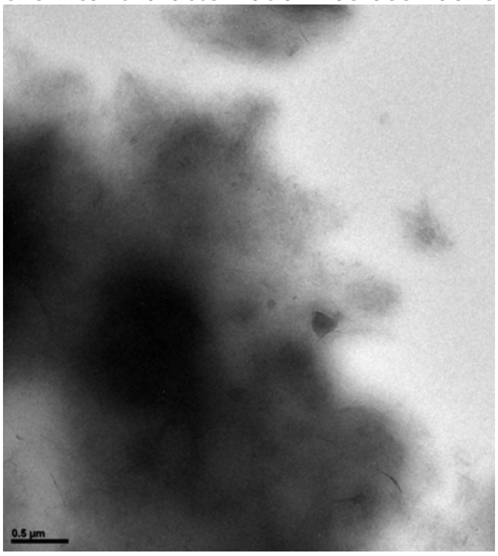
**Electron micrographs (SEM)**



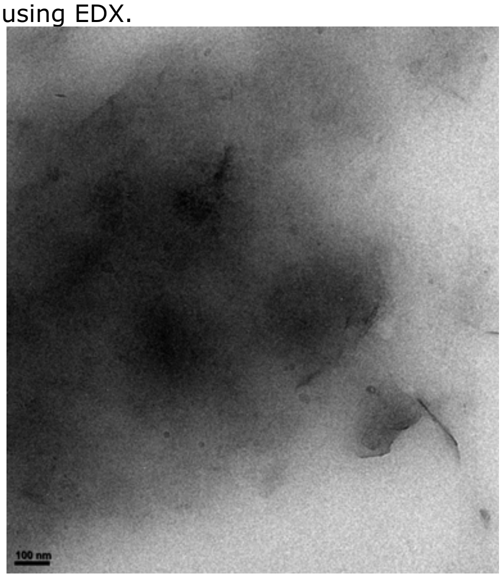




**XPS analysis**
XPS analysis shows that 37% of the mass is Mg, and another 22% as Si, which can be explained by the support onto which the sample is sprayed. Furthermore a small amount of Cl has been detected 1.7% of the total mass. Ag, however was not detected, indicating it is not in the sample or at a concentration lower than 0.8 g/kg.

**TEM analysis**
TEM has been used to make high-resolution images of the sample, and the chemical characterization has been done using EDX.

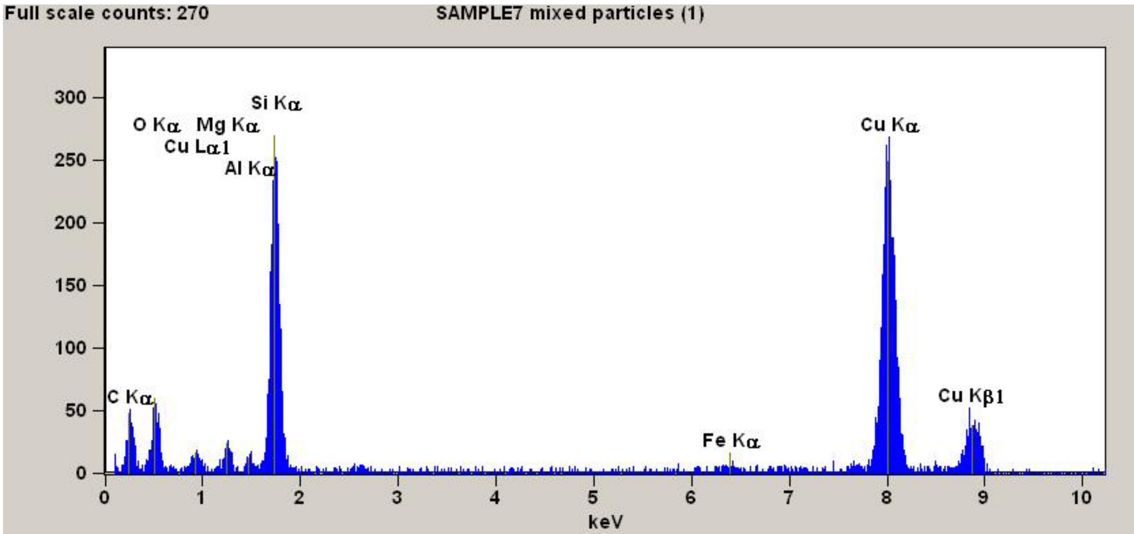


Scale bar = 500 nm



Scale bar = 100 nm

Again no nanoparticles were found.



TEM-EDX reveals Mg and Al (as seen before with XPS), but no Ag.

**Conclusions**

The aerosol was directly sprayed onto a Si surface for analysis with SEM. The micrographs reveal very interesting micron-sized structures but no nanoparticles. XPS analysis shows that 37% of the mass is Mg, and another 22% as Si. The presence of Si can be explained by the support onto which the sample is sprayed. Furthermore a small amount of Cl (1.7% of the total mass) and Al (0.8% of the total mass) was detected. Ag, however was not detected, indicating it is not in the sample or at a concentration lower than 0.8 g/kg. TEM confirmed that there are indeed no nanoparticles and the EDX spectrum did not show Ag.

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