

**IMPACT TEXTILES FOR AEROSOLS WITH NANOPARTICLES**

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**ABSTRACT:** Manufactured nanomaterials (mnm) are released into the air and deposited on human airway epithelia in several daily life and occupational scenarios. Little is known about the aging processes of mnm, in particular with regard to a possible influence of the surrounding chemical matrix in marketed products. consideration of these aspects is necessary for a toxicological risk assessment of such goods as mnm are often altered by chemical substances and thus may possess a different toxicity than pristine mnm. Such changes may either arise from the products as used or from reactions in the atmosphere. two representative classes of mnm are to be considered for inhalation, the most relevant exposure scenario: 1) soluble particles with a substance-specific toxicity using the example of ag nanoparticles, 2) poorly soluble particles of low toxicity (pslt) using the example of CeO<sub>2</sub> nanoparticles. Different liquid formulations based on water-ethanol mixtures and additional additives with different size ranges of Ag and CeO<sub>2</sub> NP were investigated. samples were atomized and sprayed in a customized test system onto textile materials consisting of 100% cotton. The textiles were oleophobicized with the commercial repellent agent tubiguard before. Electron microscopy analyses by light field, high resolution and electron diffraction of selected areas highlighted the spherical and polyhedral form of the nanoparticles and the homogeneity of the nanoparticles in liquid dispersion. The particles staying stable in the atmosphere after spraying onto the textile plate were sampled and analyzed out of the chamber ventilation system. The number concentration and the number size distribution were measured using a condensation particle counter (cpc) and a scanning mobility particle sizer (smps). Uniformity, morphology and distribution of the nanoparticles on textile matrices were studied by scanning electron microscopy (sem), transmission electron microscopy (tem), energy-dispersive x-ray spectroscopy (eds) and laser ablation inductively coupled plasma mass spectrometry (la-icp-ms).

**KEYWORDS:** textiles, nanoparticles, additives, aerosol, spray

## 1. INTRODUCTION

Nanotechnology, the science of the extremely tiny, is an important emerging industry with a projected annual market of around one trillion US dollars by 2015 [1] and is being hailed as the “next industrial revolution” [2].MNM are now found in many products, ranging from cosmetics to clothing to food products. Inevitably, humans will be exposed to these nanomaterials (NM) as they are handled in the workplace, taken up with foods, worn as nano-enabled textiles or cosmetics using nano-caled additives, used in nano-appliances and disposed as waste mixed with particulate matter coming from MNM. Early scientific studies demonstrated the potential for materials that are benign in bulk form to become harmful at the nanoscale[3]. To address this, the European Commission requested the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) comment the existing risk assessment NM in 2005 resulting in a preliminary

opinion on "The appropriateness of the risk assessment methodology in accordance with the Technical Guidance Documents for new and existing substances for assessing the risks of nanomaterials" in March 2007 [4]. In general, SCENIHR concluded that it is “unclear” whether existing EU risk assessment methods could capture the potential environmental impacts of nanomaterials, though it was “generally likely” to identify risks to human health [3].

## 2. AIM OF THIS STUDY

To elucidate possible effects and hazards of NP-containing formulations and their aerosols especially in regard of textile applications at first the characterization of the NP in solution as well as aerosol was conducted. Therefore formulations differing in complexity and containing Ag and CeO<sub>2</sub> MNM were analyzed and used to treat textile materials by padding or spraying approach.

### 3. MATERIALS AND METHODS

Nanoparticles (NP) with diameters below 50 nm were chosen: NM 300K (JRC) and NM212 (JRC) for Ag and CeO<sub>2</sub> respectively. These NP are part of the materials repository of the JRC assigned only for applied research and are also included in the international testing program OECD WPMN (OECD Paris 2009-ENV-JM-MONO-2009-20 ENG Manual) [5-7]. Selected NP formulations were based on the ongoing NANOaers project to emulate NP containing impregnation sprays and assess the toxicological impact and possible interaction with additives [8]. The formulations are either: water-based or water / ethanol-based NP dispersions. Additional compounds and surface-active additives were used in the water / ethanol-based dispersion to result in three distinct NP formulations.

For the padding approach a preliminary treatment system, model BVHP/100 and drying/condensation system, model TFO/S500mm both from Roaches International LTD. were used. The process comprises three steps: a) padding, b) drying at 110°C and CO condensation for 2 minutes at 150°C.

Textile oleophobicity and NP treatment were performed in the same bath using: 200 ml NP - dispersion of the following formula for each treatment: the NP were dispersed via sonication in ultra-pure water (UPW) to a final concentration of - 0.8 g/L UPW. The dispersion was adjusted to a pH of 5 using HCl and repellent agents either Tubiguard VCN (Bezema Group, Germany,) Rucodry and RukoLink (Rudolf Group, Germany) at concentration of 70g/L or 50 g/L. To obtain a suitable NP aerosol for the spraying approach a specialized test setup was developed by Technical University of Dresden (fig.1) which also applied for inline cell exposure studies (2D&3D) models. It is comprising: 1) ventilation system, 2) spray can (SG 700, hvg, Germany) and activator 3) tubing for refilling and re-pressurizing the spray can while keeping the spray chamber closed and 4) an impaction plate holding the textiles samples in a defined distance of 30 cm. Additionally an access for a probing tube is installed which allows the sample extraction at different position in chamber for online analyses exposure experiments.

For on line analyses a condensation particle counter (CPC,TSI) or a scanning mobility particle sizer (SMPS) was connected.

Spraying of textiles and the subsequent online analysis was done as follows: the textile was placed onto the impaction plate and the spray chamber was purged until the particle number

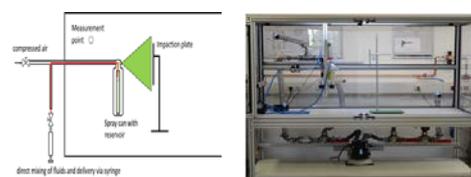


Figure 1: Schematic (left) and installation (right) of the developed spray chamber

concentration was below 10 #/cm<sup>3</sup> before the ventilation was switched off. The spray can was loaded with a freshly prepared NP formulation using compressed air at a pressure of 6 bar. A spray pulse of 5 s was applied. Online measurement of the particle number concentration was done for 15 minutes after single spray pulse or as long as a whole spraying sequence lasted whilst particle sizes from 18.1 nm to 947 nm were observed. For determination of the particle size distribution three SMPS measurements - each 3 minute long - were conducted for each spray pulse: one directly during spraying, and one at 3.5 and 7 minutes after spraying, respectively. After ventilation of the chamber the sprayed textiles were removed, dried and analyzed.

### 3. RESULTS AND DISCUSSIONS

#### NP application by padding

Atomic absorption spectroscopy (AAS) was performed to quantify the overall NP amount on the surface of the samples treated by padding technology. Results indicate that depending on the repellent agent used different quantities could be found. After Tubiguard VCN treatment 29,3 ppm Ag NP and 15,3 ppm CeO<sub>2</sub> NP were found, respectively, whereas Rucodry/ Ruko/ Link treatment led to - 20,1 ppm Ag NP and 21,44 CeO<sub>2</sub> NP.

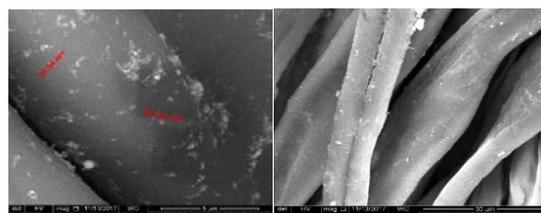


Fig.2: SEM images of a 100% cotton textile after treatment with Tubiguard(VCXN) and CeO<sub>2</sub> NP (padding technique)

Figure (2) shows the scanning electron microscopy (SEM) and the energy-dispersive X-ray spectroscopy (EDS) for the 100% cotton textile treated with CeO<sub>2</sub> NP (0.5g/L) and Tubiguard (VCN) (5g /L). In SEM micrographs, the presence of CeO<sub>2</sub> NP on the surface and amongst the fibers in the fabric structure resulting in an uniform dispersion and sizes ranging from 29 to 34 nm. The similar micrographs performed for Ag NP have not revealed their existence on the surface of the textile material as they likely are embedded in the fabric structure.

Study of kinetic migration of NP deposited by padding technology was performed by SEM analysis. The comparative analysis of SEM images of samples subjected to the alkaline perspiration test showed neither Ag NP on the surface, nor morphologic degradation of the fibres. Acid perspiration test of these samples resulted in a low level of Ag NP load, unevenly distributed on the fibres' surface and in slight morphologic degradations of the fibres. Fabric subjected to the washing test showed the same characteristics as samples subjected to alkaline perspiration test , but without an Ag NP load or morphologic degradations. The sample from 100% cotton treated with CeO<sub>2</sub> NP indicates a reduced level of NP load no identification of morphologic fiber degradation within the fabric's structure when subjected to all tests.

#### NP application by spraying

Although the spray chamber was sufficient for textile spraying and online aerosol characterization, preliminary results indicated that its big gas space made complete aerosol collection and transport for exposure experiments difficult. Since then a smaller, more mobile version has been developed.

Spray experiments and CPC as well as SMPS measurements using Ag and CeO<sub>2</sub> NP dispersions in different complexity revealed varied spray behaviors regarding particle concentration and particle size distribution. This is most likely related to the spraying process itself and the influence of the compounds and additives on the process of droplet formation. Repeated spraying processes with defined spray intervals and pulses were used to observe this behavior (figure 3).

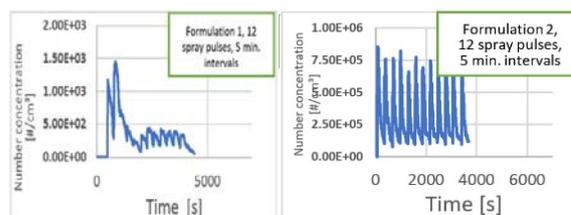


Fig. 3 CPC measurements during repeated spraying inside a spray chamber highlighting the difference in maximum particle concentration between a water-based dispersion (formulation 1, left) and an ethanol/water-based NP dispersion with additives (formulation 2, right)

Purely water-based NP dispersions yielded lower particle concentrations whereas ethanol/water-based dispersions often showed higher particle concentration and distinct peaks. The use of additives like butanone, hydrochloric acid, triethanolamine or per fluorinated silanes impacted the spraying behavior even further. Additionally, humidity level within the spray chamber was found to be of importance as only after some first spray puffs equilibrium was reached resulting in reproducible sprays.

In order to evaluate any influence of the chemical additives, used during the textile oleophobicization, on the morphology and dimension of the Ag and CeO<sub>2</sub> NPs, the formulas which were used to treat 100% cotton woven fabrics and contained CeO<sub>2</sub> or Ag NP (0.5 g/L each), and either Tubiguard VCN (5 g/L), RucoDry (5 g/L) or RukoLink (1 g/L) were analyzed by TEM. TEM analyses revealed the influence of chemical additives on NP agglomeration tendencies. This is more pronounced in the case of the applied CeO<sub>2</sub> NP after conditioning the textile with Tubiguard VCN. In comparison Ag NP are uniformly spread (figure 4).

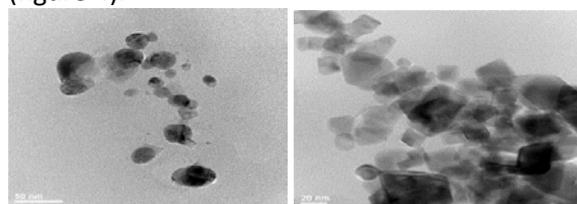


Fig.4 : Comparison of TEM images of the respective CeO<sub>2</sub> (left) and Ag (right) NP dispersions using a Tubiguard VCN repellent.

There were no changes in NP shape or specific crystallographic planes visible compared to HR-TEM measurements of the respective pristine NP. Nevertheless, a decrease in size was recorded for Ag NP when the textile was treated with RucoDry/RukoLink repellent.

NP uniformity, morphology and distribution after preparation of the textile material with Tubiguard

VCN (5 g/L) was analyzed. The determination was performed after spraying with CeO<sub>2</sub> NP (NM 212) using formulation 1 plying TEM and EDS using a Titan Themis 200 (Thermo Fisher Scientific, Germany) (figure 5). The oleophobic treated samples using the spray composition of CeO<sub>2</sub> NP in UPW (formulation 1) resulted in NP deposited on the fabric's surface and between the yarns.

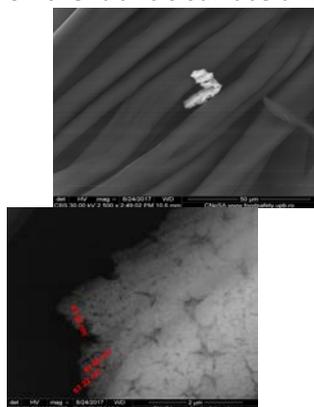


Fig.5 SEM and TEM images showing CeO<sub>2</sub> NP agglomerates on textile treated with Tubiguard VCN after spraying of formulation 1

The EDS spectrum confirms the presence of CeO<sub>2</sub> in these deposited particles. In contrast, after hydrophobic textile treatment and spraying with CeO<sub>2</sub> NP (formulation 1) similar morphologic properties were observed as after oleophobic treatment and spraying with the more complex ethanol/water-based (formulation 3). Rare agglomerations of NP were observed on the fibers surface and confirmed to be CeO<sub>2</sub> by EDS spectroscopy. The dimensions of NP were determined to be between 76.6 and 120.7 nm.

The study of kinetic migration of NP deposited by the spraying technology was performed by tests regarding resistance to acidic / alkaline perspiration and washing, using an Air counter (COM-3200PRO) system. Results showed that all fabrics treated with either Ag NP or CeO<sub>2</sub> NP exhibit the tendency of a decreased number of ions in case of the acidic / alkaline perspiration test being more pronounced at acidic conditions. The washing test also revealed a significant decrease of ion content for all fabrics (e.g. 86% decrease after spraying with CeO<sub>2</sub> NP using an UPW dispersion with 1% Tween-20). The sample sprayed with CeO<sub>2</sub> using formulation 3 was the most resistant to washing and showed the least ion release.

Further textile analysis in regard to the different textile treatments and NP distribution was done at the German Institute for Risk Assessment (BfR, Germany) using inductively-coupled plasma mass spectrometry in combination with laser ablation (LA-ICP-MS) on a XSeries II (Thermo Fisher Scientific, Germany) / Cetac LSX 213 (Teledyne, USA). The fixed samples were consecutively ablated resulting in imaging for the detected isotopes <sup>13</sup>C, <sup>107</sup>Ag and <sup>140</sup>Ce. <sup>13</sup>C isotope was used as a marker to localize the fabric, whereas <sup>107</sup>Ag and <sup>140</sup>Ce were chosen for the respective NP. As no LA-ICP-MS reference material for NP on textile structures is available evaluation was performed using the signal intensity (cps), as shown in Fig. 6.

Using a histogram approach four differently treated textile samples could clearly be distinguished as is evident by comparing the distribution and distribution maxima. Thus, <sup>140</sup>Ce signals observed for unsprayed control textiles can clearly be distinguished from the CeO<sub>2</sub> NP signals and identified to originate from the underlying glass carrier. Similarly <sup>107</sup>Ag signal spots visible in the contour plots - even for samples only sprayed with CeO<sub>2</sub> NP - could be correlated to the ablation of the glass and resin as they also occurred in control samples.

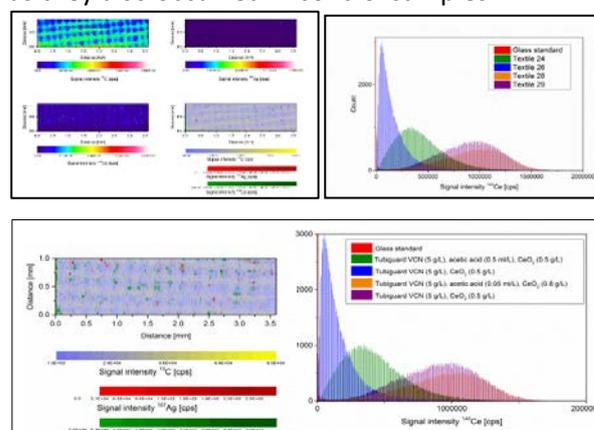


Fig.6: LA-ICP-MS contour plot (left) and resulting histogram (right) of the detected isotopes of textiles treated sprayed with CeO<sub>2</sub> NP.

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