Safe use of nanomaterials in the textile finishing industry

newsletter # 02
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Life cycle analyses and Risk Analyses of nanomaterials used in textile finishing

In fall 2013 EcoTexNano started its exploration towards the safe use of Nanomaterials in textile finishing operations. By now the project has entered its third-, and final year. By the end of 2016 EcoTexNano will provide a support tool for the textile finishing industry, to assess the **risks for human health and the environmental impact of using nanomaterials in textile finishing operations.**

Pilot productions

The core of EcoTexNano consists of pilot scale productions. During these small scaled production runs, the fabrics have been treated by either "conventional finishing" or "nano-finishing", allowing the quantification of the difference in environmental impacts and risks for human health. The applied finishes have provided the fabrics with one of the following functionalities; Antibacterial, UV-protection, Soil release or Flame retardancy.

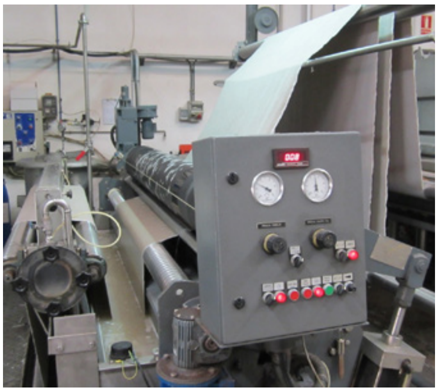
The data collected during the production trials serves as the baseline for the risk analyses (RA) and life cycle analyses (LCA) that are being performed throughout the project. Examples of such data are the number of nanoparticles in the air (Risk Analyses) and the raw materials used, energy consumption, water consumption, (hazardous) waste streams and air emissions for Life cycle assessment.

Pilot trials were performed at Piacenza, the manufacturer of luxurious woolen fabrics, and Vincolor, the subsidiary finishing department of Crevin (upholstery manufacturer)

Articles

Overview of the applied materials for each property				
Case Study 2				Case Study 1
PROPERTY	Antibacterial	UV protection	Soil release	Flame retardant
CONVENTIONAL	Silver Salt Dilution	-	Modified Polyester copolymer (27% in water solution)	Antimony trioxide and organic halogen
NANOMATERIAL	Nano dispersion silver particles	Nano dispersion of Titanium dioxide	**Hydrophilic** → Nano dispersion of perfluoroakyl acrylate copolymer in water **Hydrophobic** → Nano dispersion of acrylic copolymer in water	Montmorillonite nano-Clay

"Blade coating" performed at Vincolor



Padding performed at Vincolor

Drying and curing performed at Vincolor

The application of the finishing chemicals has been mostly performed by padding. For one property, flame retardancy, the finishing chemicals have been applied by coating. After the application of the finishing chemicals, the treated fabric has been led to a gas heated stenter, for drying and curing.

Coating

Coating is a method to confer a property onto textiles. However, unlike padding, the property remains only on the surface of the fabric. The functional agent is formulated as a paste with greater viscosity than water.

This technique applies a thin layer of finish with a controlled thickness on the fabric.

Padding

Pad-dry technique is commonly used in textile finishing processes. It consists of impregnating the fabric into a finishing solution, and then, the fabric is squeezed between two rolls, eliminating excess water or finishing product in the fabric.

Drying and curing in a Stenter

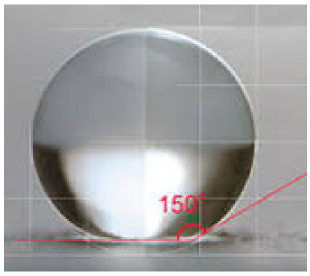
Finishing is mostly ended by temperature treatment of the fabric in a stenter, for drying and curing if needed. During this treatment the finishing solution is dried and polymerized onto the fabric.

Performance characterisation of the induced properties

Modifying wettability of textiles

Contact Angle: This methodology is based on the difference of interaction (wetting) between a droplet of fluid and the fabric. When the repellence is high, the droplet has a spherical shape – resulting in a high contact angle.

Treating the fabric with a Nano-based finish, resulted in a significant increase of the contact angle. Averagely, an increase was found from 90° (non-treated fabric) to 105° (fabric treated with nanofinishing).



Contact angle between a droplet and a fabric

Increasing water-repellency of the fabric

Spray test: Fabrics with a hydrophobic surface will give high repellency towards water. During the spraytest the amount of water repelled by the fabric surface is measured and expressed as a percentage of the poured quantity.

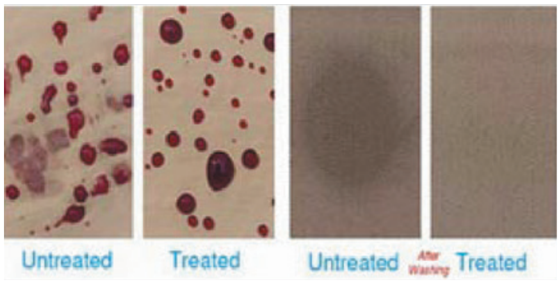
A significant increase of water repellency was provided to the fabric, respectively from 0 to 70-75 by Nano-treatment.


Performance of the Spray test

Soil release during washing

Soil release test: The washability of the fabric can be improved by treating it with a hydrophilic finishing agent. During the test, each fabric was stained with different substances such as, greace, Ketchup, ink and synthetic oil. After washing the removal of the stains was evaluated.

The test results indicated no conclusive difference between the untreated-, the conventionally treated- and the "nano-treated" fabrics.

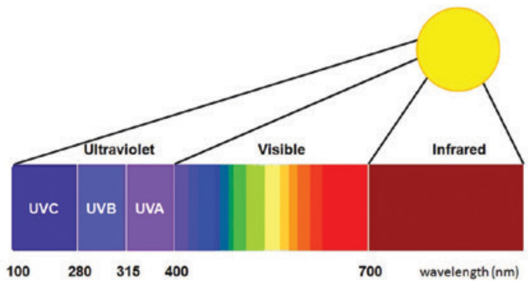


Demonstration of the soil release property

UV – protection

The ultraviolet protection factor (UPF) is a scale for rating the UV-protective capacity of fabrics. A UPF ~30 is typical for protective fabrics, while UPF ~6 is typical for standard summer fabrics.

The UV-protection factor of a fabric delivered by Piacenza was increased from 18.3 to 30, by treatment with Nano-Titanium dioxide.

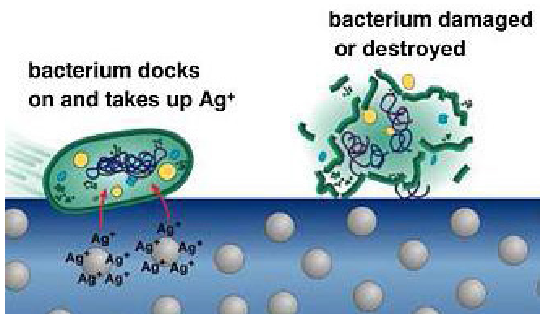


UV- spectrum

Anti-microbial property

The antimicrobial effectiveness of a fabric, treated with Nano-Silver, was measured and compared to the antimicrobial effectiveness of an untreated fabric.

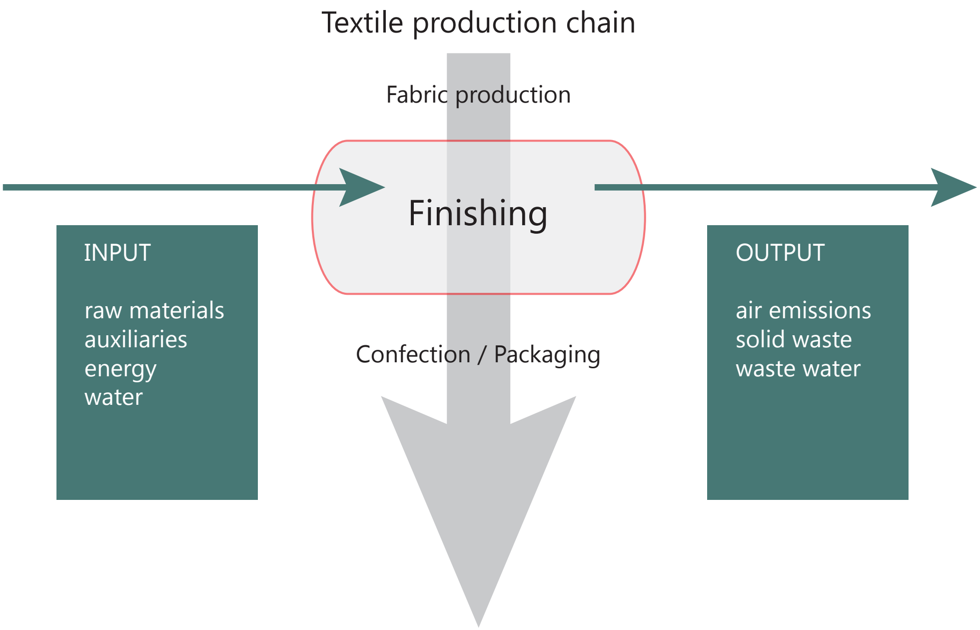
The untreated fabric showed no biocidal effect. For the treated fabrics however, a biocidal effectiveness was found of 60% for conventional and 99% for nano-based finishing.



Antimicrobial property

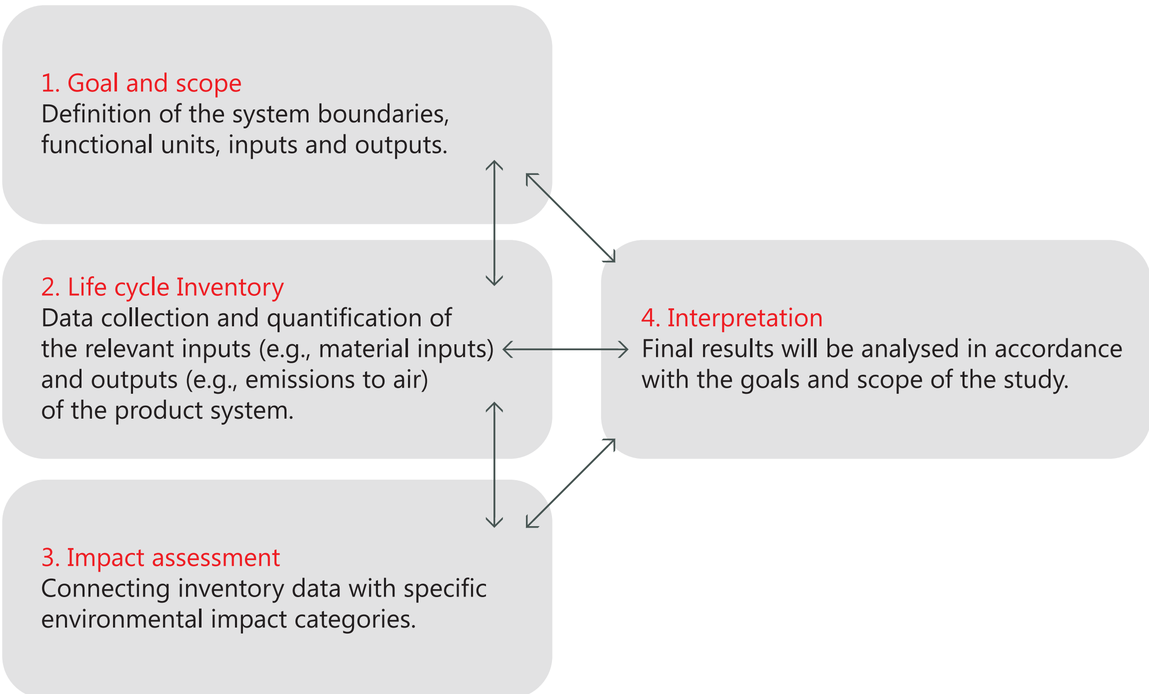
Life cycle assessment

Over the last years, questions have raised about the potential environmental impacts of nanomaterials. EcoTexNano studies the environmental impacts that nano-finishes present versus the conventional finishing technologies they replace. In the pilot scale productions both "nano-based-" and "conventional textile" finishing have been performed, resulting in real data to feed the lifecycle analyses and to quantify the difference in environmental impact between the conventional and traditional finishing processes.
LCA is being performed in accordance with the ISO standards (ISO 14.040 and ISO 14.044) and the International Reference Life Cycle Data System (ILCD) Handbook of the European Platform on Life Cycle Assessment. The software used for LCA is Simapro. The results will be presented in March 2016 and the final conclusions will support recommendations for potential updating of related legislation and standards, such as BREF for textile industry and Ecolabel.



Schematic representation of the LCA scope within EcoTexNano

The environmental analysis is performed in the following four interrelated stages:



Risk assessment

The textile finishing industry uses a broad range of chemical substances for its finishing processes. These substances could be pure or in the form of a mixture. The human- and environmental risk entailed from the use of these substances depends on the specific physicochemical and (eco)toxicological properties, the likelihood of exposure under the specific operative conditions and the risk management measures implemented in the workplace.

As in other industries, **a high level of human health protection needs to be ensured by employers at all stages of the life cycle**. The main stages include production, use, accidental spills, consumer use and "end-of-life treatments." In this regard EcoTexNano addresses a comparative study of the potential health impact on workers and the environmental impact for the nano-finishes and conventional finishing technologies. The study has included a thorough evaluation of the toxicological profile of the most relevant nanomaterials that can be applied for the functionalization of textiles, as well as a quantitative assessment of the levels of exposure to nanomaterials during the application of nanobased finishing chemicals. This risk assessment has included the following stages:

1. Compilation of data on the physicochemical and (eco)toxicological properties of the ENMs studied under the scope of the Project.
2. Identification of the mode of use of each nanomaterial and if applicable the related formulation. The data needed to create an exposure scenario in accordance with REACH regulation requires, among other elements, the operative conditions (process), frequency of use, amounts, and specific risk management measures applied on site.
3. Analysis of data retrieved from the literature, to define the proper Derived no-effect level (DNELs) and predicted no-effect concentration (PNECs).
4. Estimation of the exposure levels using state of the art modeling approaches.
5. Quantification of the exposure levels in those scenarios represented in real case studies.
6. Risk assessment based on the quantitative and qualitative data.

The scope of the risk assessment is limited to the ENMs used in textile finishing processes. A critical set of exposure scenarios has been identified for each company and finishing application on the basis of on-site observations and information retrieved from dedicated questionnaires. The hazard characterization has been focused on the compilation of data from relevant sources of information, including peer reviewed publications, public reports from EU funded projects, as well as databases containing reliable data on the physicochemical, toxicological and ecotoxicological properties of ENMs.

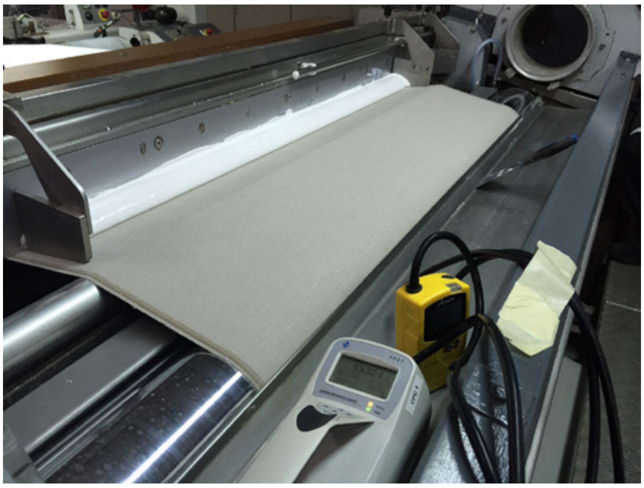
The table below includes information on the (eco)toxicological threshold limit values selected to perform the risk assessment of the nano-based products used in finishing process.

Selected toxicological and ecotoxicological threshold limit values				
Active Substance in nanoform	Effect	Classification / labelling	Threshold limit value (OEL/DNEL)	Threshold limit value (PNEC)
PFHxA (C6)	Soil-release	Eye Irrit. 2 Skin Irrit. 2	Non-regulated Estimated > 5 mg/m3	$PNEC_w$: 97 µg/L $PNEC_s$: n.a
TiO_2 (< 5%)	UV protection	Non-hazardous	OEL: 0.3 mg/m3	$PNEC_w$: 15.7 µg/L $PNEC_s$: 91.1 mg/kg
Silver salts (< 0.1 %)	Antibacterial	Acute Tox. 4 Eye Irrit. 2 Skin Irrit. 2	OEL: 0.01 mg/m3	$PNEC_w$: 3 µg/L $PNEC_s$: 44 mg/kg
Nanoclay (< 2 %)	Flame retardant	Non-hazardous	OEL n.a REL*: 40.000 pt/cm3	$PNEC_w$: 400 µg/L

**It should be noticed that the active substances are incorporated into textile finishing products in quantities below 5%. This implies a critical reduction of the potential hazards.

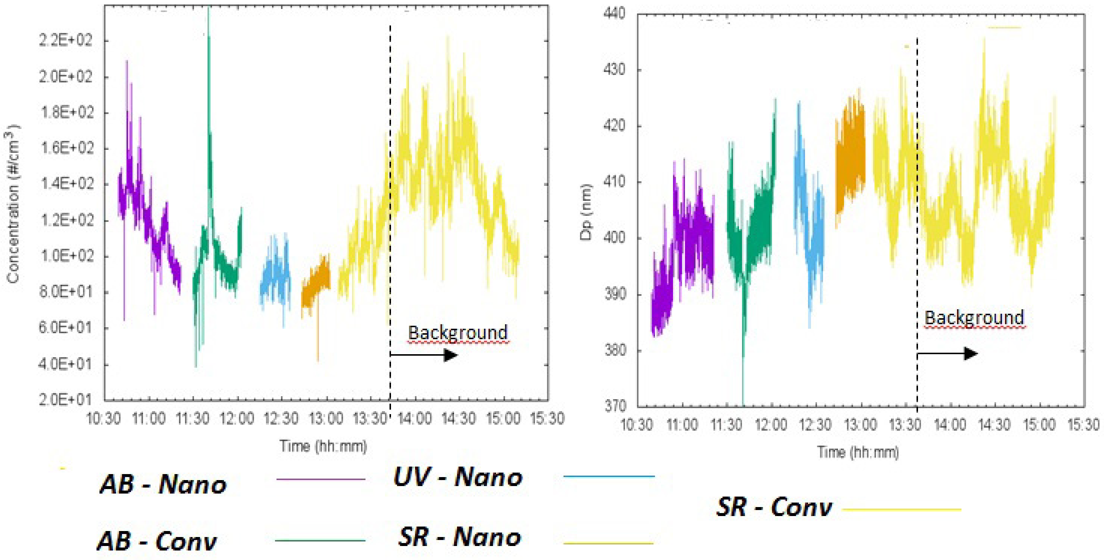
In accordance with the obtained data, the toxic effects on the environment and human health can be ranked as follows: **Antibacterial (Silver Salts) > UV protection (TiO_2) > PFHxA (C6) > Nanoclay based formulations.** However, under the operative conditions studied within the project, **only effects derived from the contact with skin and eyes are expected**. More elaborate data will be made available in the EcoTexNano Tool on the EcoTexNano website. It should be noticed that the active substances are incorporated into textile finishing products in quantities below 5%. This implies a critical reduction of the potential hazards.

For the exposure assessment, several monitoring campaigns have been conducted in case studies 1 and 2. The data has revealed that although measured concentrations of particles generally are quite high, there are no significant differences between the application of the conventional- and the nano-product in respect to the concentration of airborne nanoparticles. Therefore no relevant release of particles from the nanobased dispersions is expected. This has been supported by the fact that the air samples collected on polycarbonate filters do not show a significant presence of the nanoparticles applied in the nanobased dispersion.



Measurement during "Coating".

Concentrations (left) and Diameter distribution (right) over time during padding process registered by the OPS in the FF for case study 2.



The graphical representation of the data retrieved from the monitoring campaigns illustrate the fact that similar concentrations of particles in the nanorange during the application of conventional and nanobased finishing chemicals are expected. Moreover, a high level of particles in the background was measured due to the presence of process generated nanoparticles.

The monitoring campaigns, performed at the pilot sites have been complemented with the data estimated using state of the art exposure estimation models in order to obtain a risk characterization for all relevant exposure scenarios. These scenarios have been defined based on literature and scoping visits at the pilot-sites. The modeling software has been used for inhalative exposure was **ART Tool**. For the modeling of dermal exposure **RISKOFDERM** has been used. All defined exposure scenarios are listed in the table below. Subsequently a dose-response relationship has been defined for each exposure scenario.

The complete risk characterization has been completed in conformity with the ECHA defined methodology.

exposure scenarios		
	Contributing ES	Description
Case Study 1	CES 0. Filling finishing machine	Formulation flows to the padding machine bath. Automatic process (closed)
	CES 1. Textile finishing application	Textile is coated with the finishing in the bath and passed by several rollers
	CES 2. Drying	Closed own ventilated furnace
	CES 3. Cutting	Cut of pieces of the dried fabric with an automatic blade
	CES 4. Cleaning and maintenance	Of product formulation in the bathtub
Case Study 2	CES0. Filling portable packaging	Worker fills portable recipient and takes it to the machine mixing tank
	CES1. Filling mixing tank	Worker fills mixing tank
	CES 2. Mixing products	Automatic mixing of formulation. Closed process half of task time.
	CES 3. Filling finishing machine	Formulation flows to the padding machine bath. Automatic process (closed)
	CES 4. Textile finishing application	Padding process
	CES 5. Drying	Closed oven
	CES 6. Sampling	Of product formulation. PH measurement
	CES 7. Cleaning and maintenance	Of product formulation

The exposure estimations calculated for the dermal route has revealed that the **most critical process is the cutting of fabrics**. In this step, there is direct contact with the dried material and precisely the fact that fabric is dried, may contribute to the release of the nanomaterials included in the finishing.

In the case of the inhalatory route, the **most critical activities are the ones that involve the manipulation of the liquid solution for padding**. For drying and cleaning inhalatory exposure is less likely, because they are usually performed in a closed furnace with its own ventilation system (drying) or in a semi-automatic way with water, causing a high humidity (for washing).
The results from the risk characterization calculated as the ratio "Exposure level and the Derived No-Effect Level (Exposure/DNEL") are depicted in the tables.

Risk characterization ratios for the selected "nano-finishes"								
Case Study 2	Contributing ES							
	CES0	**CES1**	**CES2**	**CES3**	**CES4**	**CES5**	**CES6**	**CES7**
Antibacterial	0,3	**1,6**	**1,6**	0,02	0,5	2E-05	**1,6**	0,02
Soil release	3,8E-03	2,4E-02	2,2E-02	2,6E-04	2,4E-03	2,8E-07	2,2E-02	2,4E-04
UV Protection	1,3E-02	7,7E-02	7,3E-02	9E-04	7,7E-03	9E-07	7,7E-02	7,7E-04

Case Study 1	Contributing ES				
	CES0	**CES1**	**CES2**	**CES3**	**CES4**
Soil release	8,2E-03	1,2E-02	8,4E-08	4,4E-05	2,4E-06

- 0-1: no risk
- 1-5: moderate risk, precautions must be taken
- >5: high risk, substitution

EcoTexNano project meeting

On the 2nd November 2015, the EcoTexNano team came together for a full day meeting. During the meeting, the team discussed the latest developments in the pilot production trials and the outlooks for the final year of the project, 2016.

The picture above portrays the members of the EcoTexNano team, starting from the left, Jordi Mota (LEITAT) Carlos Fito and Jorge León (ITENE), Erik Wuyts (CENTEXBEL), Eva Araque (ITENE), Vincent Jamier (LEITAT), Alessandro Canepa (Piacenza) and Raquel Villalba (LEITAT)

EcoTexNano partners

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