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Materials Science & Technology

# Transformations of silver nanoparticles relevant to product use

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# **Project Goals**

#### Nanomaterials safer by design

- Correlate specific ENM properties to their aging, transformation, and behavior
- Relate specific characteristics to impacts
- Classify nanomaterials according to their impacts

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#### Presentation Outline

- Understand relevant, product specific Ag ENP transformations
- Laboratory washing of nano and conventional Ag fabrics
- Measure [Ag] release and define NM forms in wash water
- Correlate transformations to materials washed

# **Aging and Transformation Studies**



D. Mitrano

# **Particle Aging and Transformations**



"By exploring exposure potentials and characteristics across the life cycle of a product that utilizes new materials, it is, in principle, possible to flag up areas of risk concern that can be used to direct further research and action."

-- Maynard, Nature Nanotechnology 2014

# **Particle Aging and Transformations**



D. Mitrano









### Ag Release and Transformation after Laundering Fabrics



Nowack et al. 2013

(polymer / coating)

### Comparison of NP and Conventional Ag after Release



#### **Conventional Ag Additives**



Ag salts: AgCl, AgCl on TiO<sub>2</sub> carrier Ag ion exchange: AgZeolite Metallic Ag: Ag threads

### Comparison of NP and Conventional Ag after Release



# Comparison of NP and Conventional Ag after Release

- Make fabrics with known Ag additives (conventional and nano)
- Laboratory washing procedure with standardized detergent
- Collect wash solution and analyze [Ag] in various fractions
- TEM/EDX analysis of (transformed) particles after wash cycle

Washing Ag imbedded textiles forms similar Ag particulate material



# (nano) Silver Release from Textiles



- Commercial fabric released highest total [Ag], but had 100X more Ag added
- Prepared nano-textiles released lower total [Ag] into the wash water ( < 100 µg/L) than similar conventional treatments
- Most Ag was recovered in the > 0.45 micron size range (filter digest) for all prepared fabrics

#### Nanomaterial Release from Textiles



D. Mitrano et. al, ACS Nano 2014

### Nanomaterial Release from Textiles

			Starting Silver Form on Textile									
			Control Conventional					Nano				
			AgNO <sub>3</sub>	X-Static	AgCI	AgCI/TiO <sub>2</sub>	AgZeolite	NM 300	AGS-20			
			Α	В	С	D	E	F	G			
NP Forms in Washing Liquid	Ag	1		27	-	ND	<u>854</u>	there	ND			
	AgCI	2	<u>50 nm</u>	ND	ND	ND	ND	<u>20 nm</u>	ND			
	Ag/S	3	**	<u>m</u> .	ND	2 <u>8 ne</u>	33	22 mm				

D. Mitrano et. al, ACS Nano 2014

# **Ag Transformation After Release**



# **Transformation of Materials**



D. Mitrano et al, submitted

# **Experimental Outcomes**

- Aged and/or product released NM will have different qualities than pristine ENM
- Product use dictates relevant aging/transformation
- Initial form of Ag incorporated into textile is important to the size and concentration of released Ag
- "Conventional" additives to textiles, etc. may also release nano-sized materials
- Multiple, subsequent transformation possible and likely



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# **Thank You!**

Dr. Bernd Nowack (Empa St. Gallen) Elisa Rimmele (Currently: bluesign) Adrian Wichser (Empa Dubendorf; analytical chemistry) Rolf Erni (Empa Dubendorf; microscopy center) Dr. Murray Height (HeiQ AG Fabrics)



# Silver Treatments on Fabrics

	Silver Additive	Trade Name	Supplier	Silver Form	Particle Size	Fabric Construction	Treatment	Measured (mg Ag/kg fabric)
	AgCl	T25-25	Sanitized	Salt	> 100 nm	Woven	Surface, roll to roll	14.6
nal	X-Static (metallic Ag)	X-Static	Noble Biomater ials	Metal	Fiber	Knitted	Surface, electrolyti c deposition	14500
onvention	AgCl/TiO <sub>2</sub>	JMAC	Clariant	Salt	Composi te Ø ca. 1µm	Woven	Surface, roll to roll	19.5
C	Ag-Zeolite	#382280	Sigma- Aldrich	Ionic	Composi te +20 mesh	Woven	Surface, roll to roll	67.6
Nano	Ag/SiO <sub>2</sub>	AGS-20	HeiQ Materials	Metal	Composi te Ø ca. 1µm	Woven and knitted	Bulk and Surface	116 ± 1 (Bulk) 18.2 ± 0.3 (Surface)
	NM-300K	NM300K	EU JRC	Metal	< 20 nm	Woven	Surface	15.5 ± 0.6

D. Mitrano et al, ACS Nano 2014

### EDX Analysis of NP in Washwater

![](_page_23_Figure_1.jpeg)

#### D. Mitrano et al, ACS Nano 2014

#### Spike Recovery of Ag in Washing Liquid

![](_page_24_Figure_1.jpeg)

D. Mitrano et al, ACS Nano 2014

# (nano) Silver Release from Textiles

![](_page_25_Figure_1.jpeg)

D. Mitrano et. al, ACS Nano 2014