

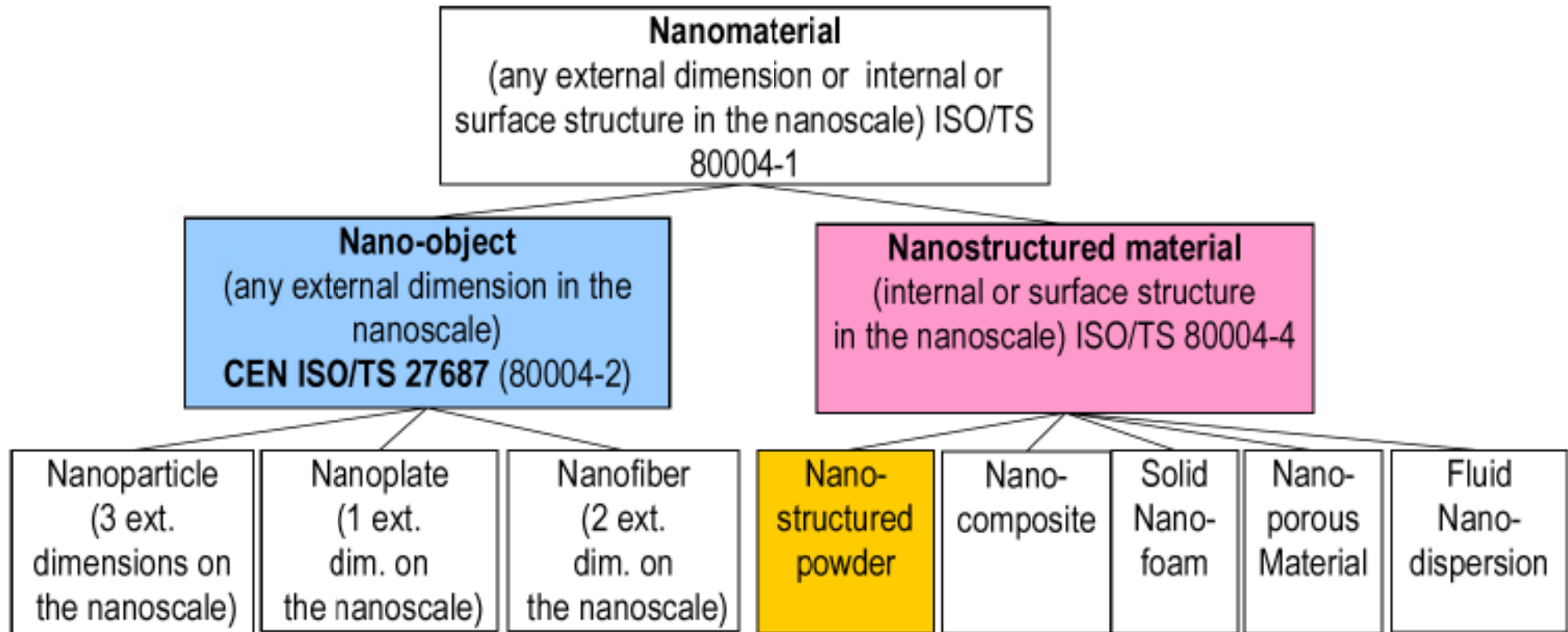


Abrasion induced nanoparticle release into air from surface coatings

Michael Stintz, Daniel Göhler

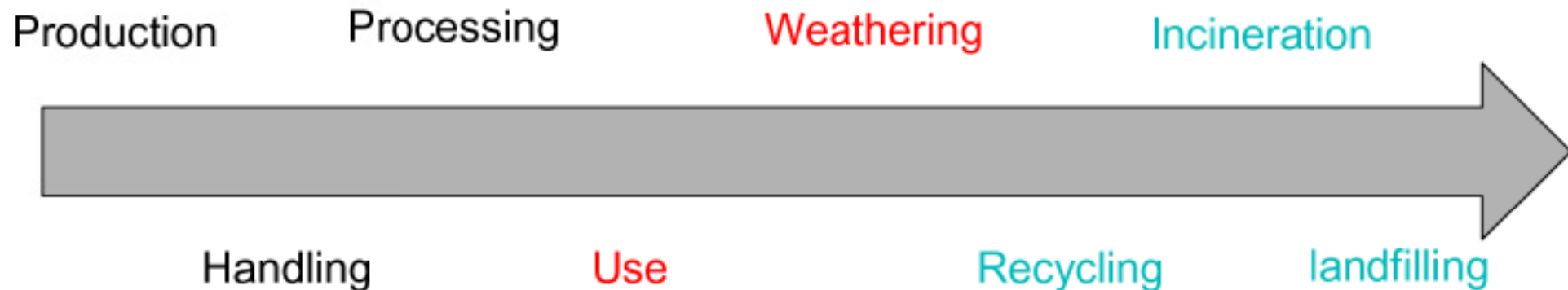
Institute of Process Engineering and Environmental Technology
TU Dresden, Germany

ISO/TC 229/JWG 1



Assemblies of nanoparticles or nano-objects, which extend the nanoscale, are covered by ISO/TS 80004-4 Nanotechnologies -Terminology and definitions for nanostructured materials

Lifecycle of Nanomaterial and Release Scenarios



Workplace Measurements with Nanoparticle measurement methods

Simulation of process with „zero-background“ presented here

Simulation of process in other Projects

Nanoparticle exposure at nanotechnology workplaces: A review

Kuhlbusch et al.; Particle and Fibre Toxicology 2011; 8:22 , doi:10.1186/1743-8977-8-22

Tiered Approach

- 1) Simulation of normal use of coatings - „walking“- with Taber-Test
- 2) Simulation of sanding processes
- 3) Simulation of weathering/ageing and subsequent sanding

**Sponsored by German Paint Industry Association (VdL)*

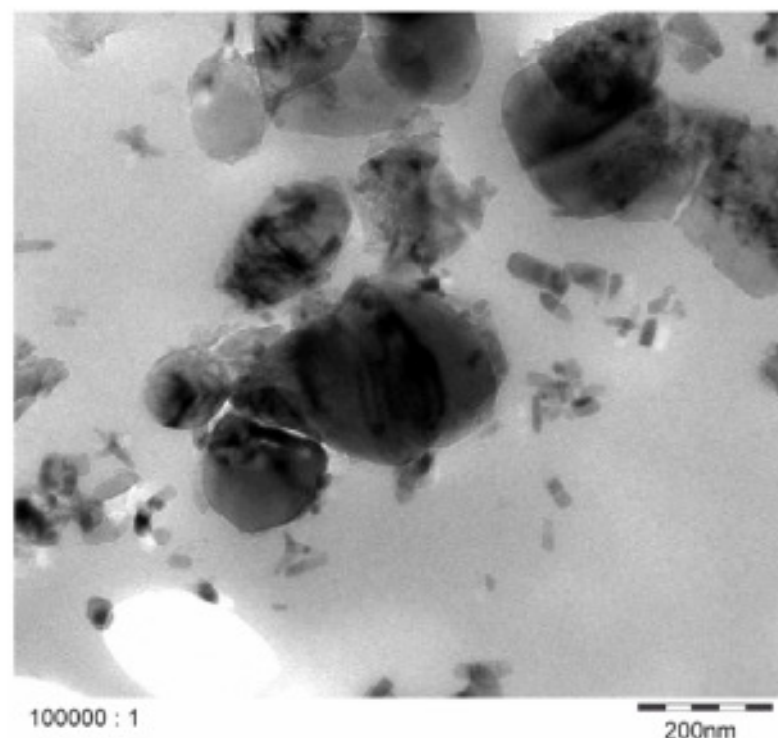


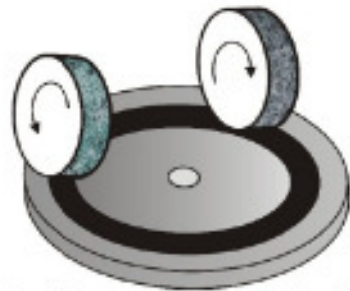
1) Simulation of normal use of coatings - „walking“

Tested Coatings with/without 20 nm zinc oxide :

- architectural coating
(white pigmented styrene acrylate copolymer dispersion)
- parquet coating
(UV curable clearcoat)
- furniture coating
(two-pack polyurethane)

Substrates: wood and metal

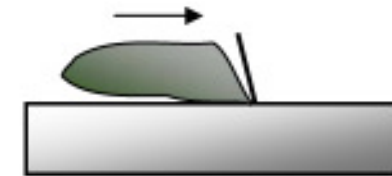




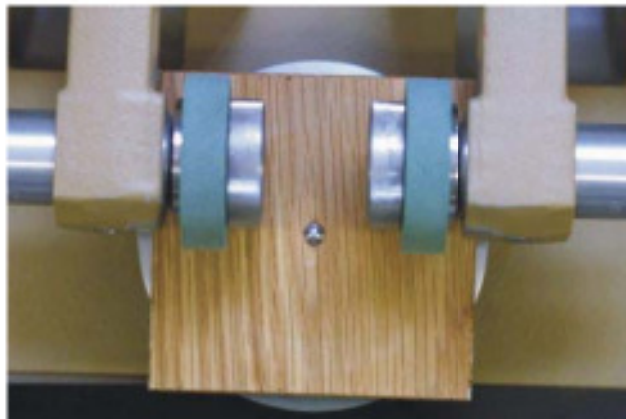
Rolling and friction of wheels from corundum



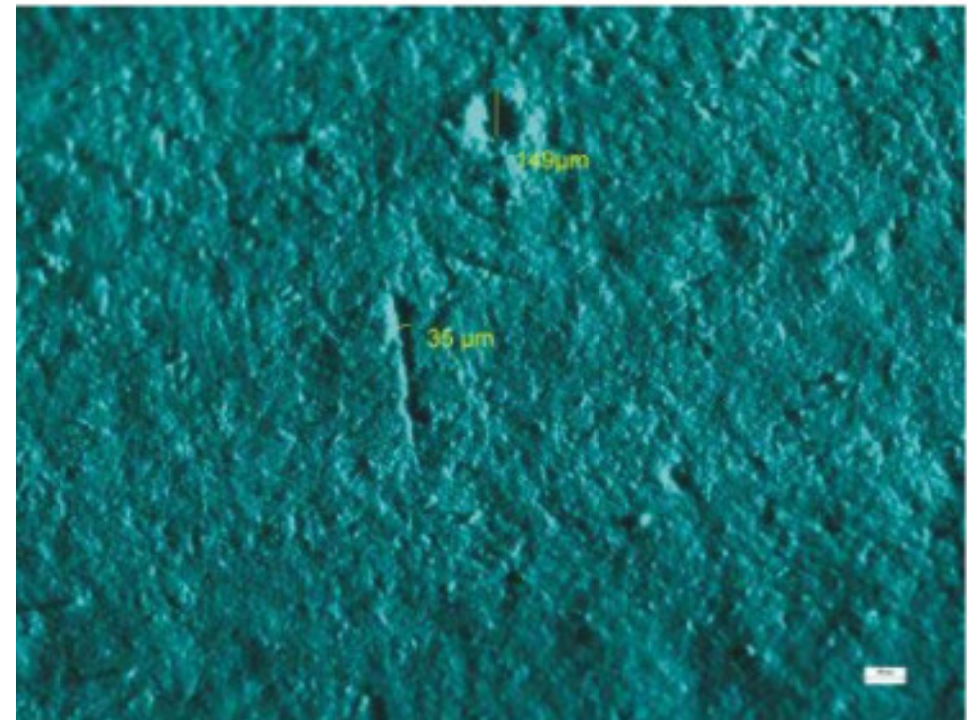
abrasion grain on coating



stress comparable with scratching move

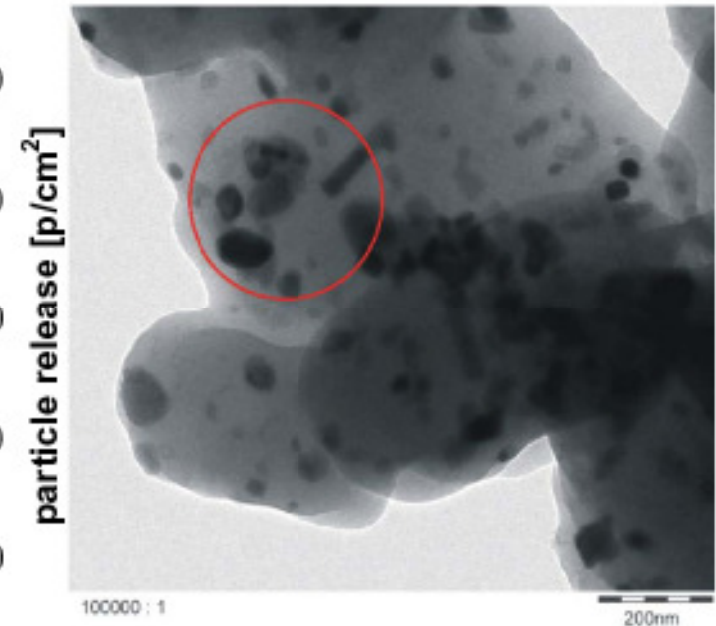
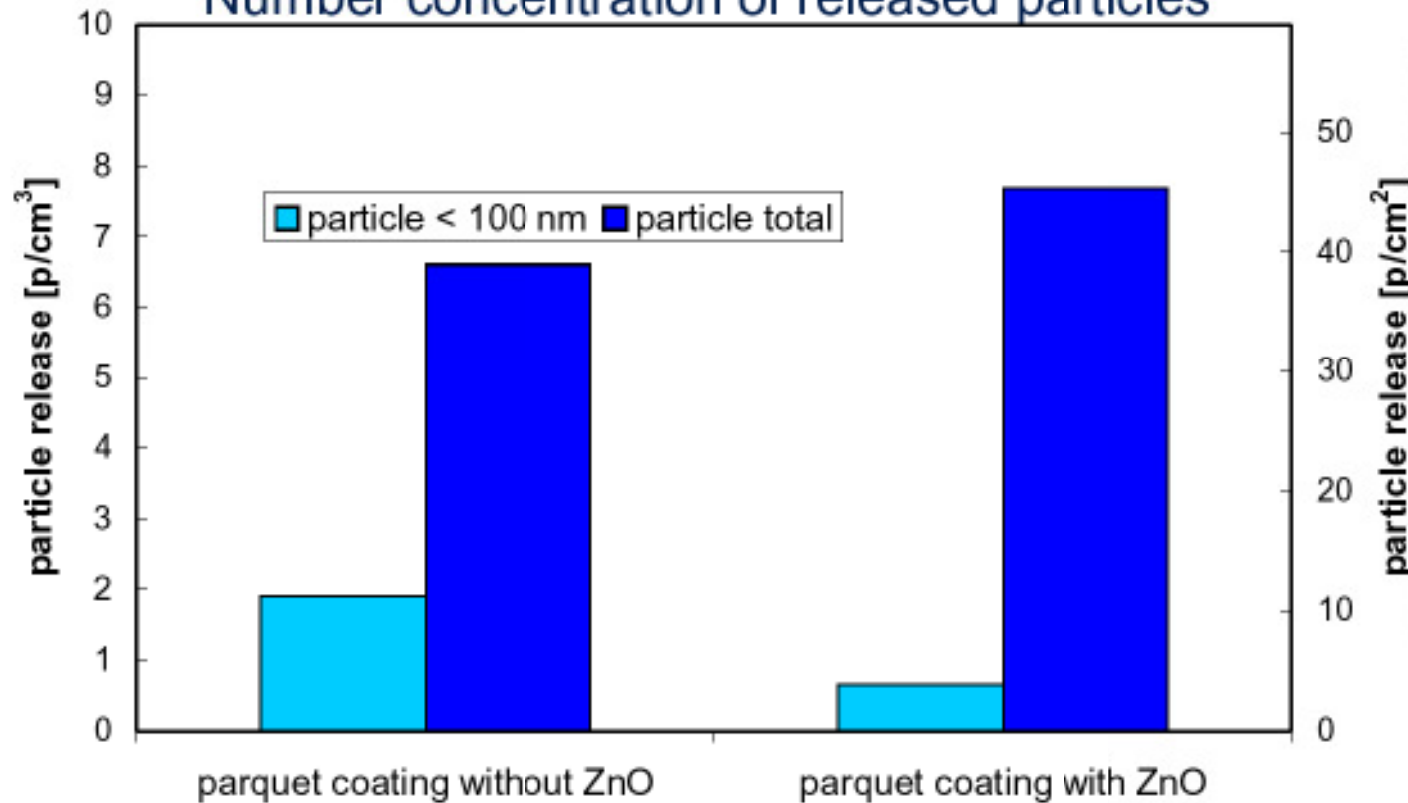


architectural coating after the process with two scratches



1) Taber-Abraser results

Number concentration of released particles

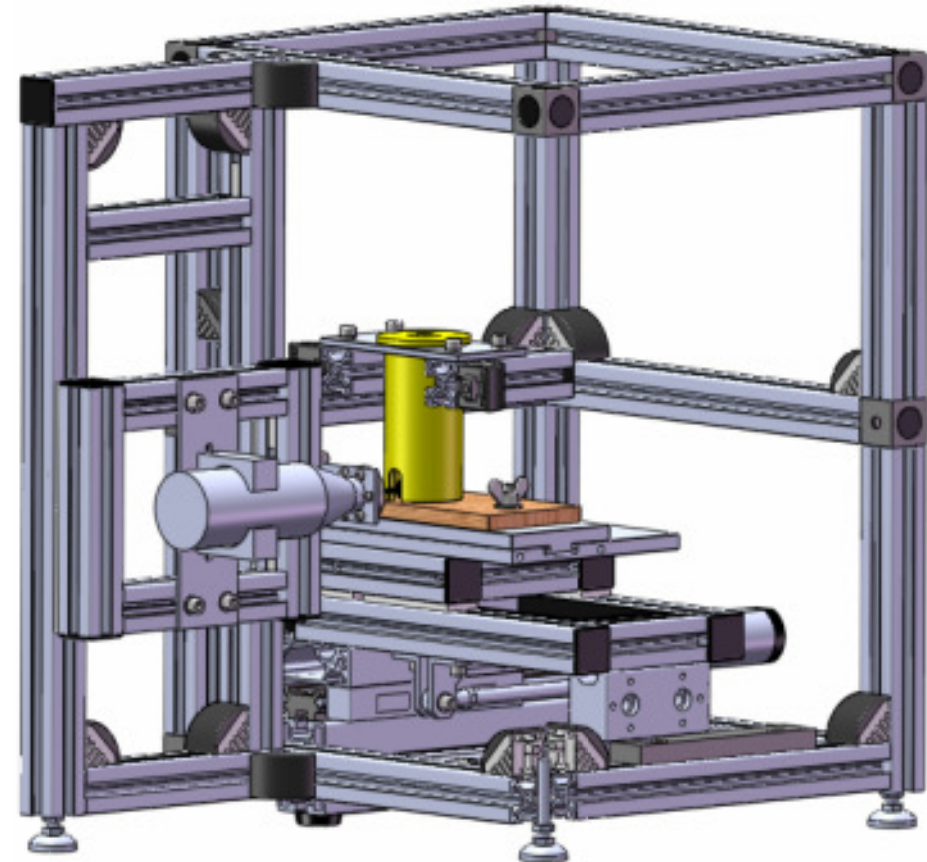


- particle concentration <100 nm too low for statistical certainty
- dosage of 20 nm ZnO should not increase the particle release <100 nm

Vorbau et al. (2009) *J. Aerosol Sci.*; 40(3): 209-217

2) Simulation of sanding processes

Test Setup



2) Surface coating conditions

□3 types of coatings

PU	two-pack polyurethane (furniture)
UV	UV curable clear coating (parquet)
AC	white pigmented (TiO_2) acrylate coating (facades)

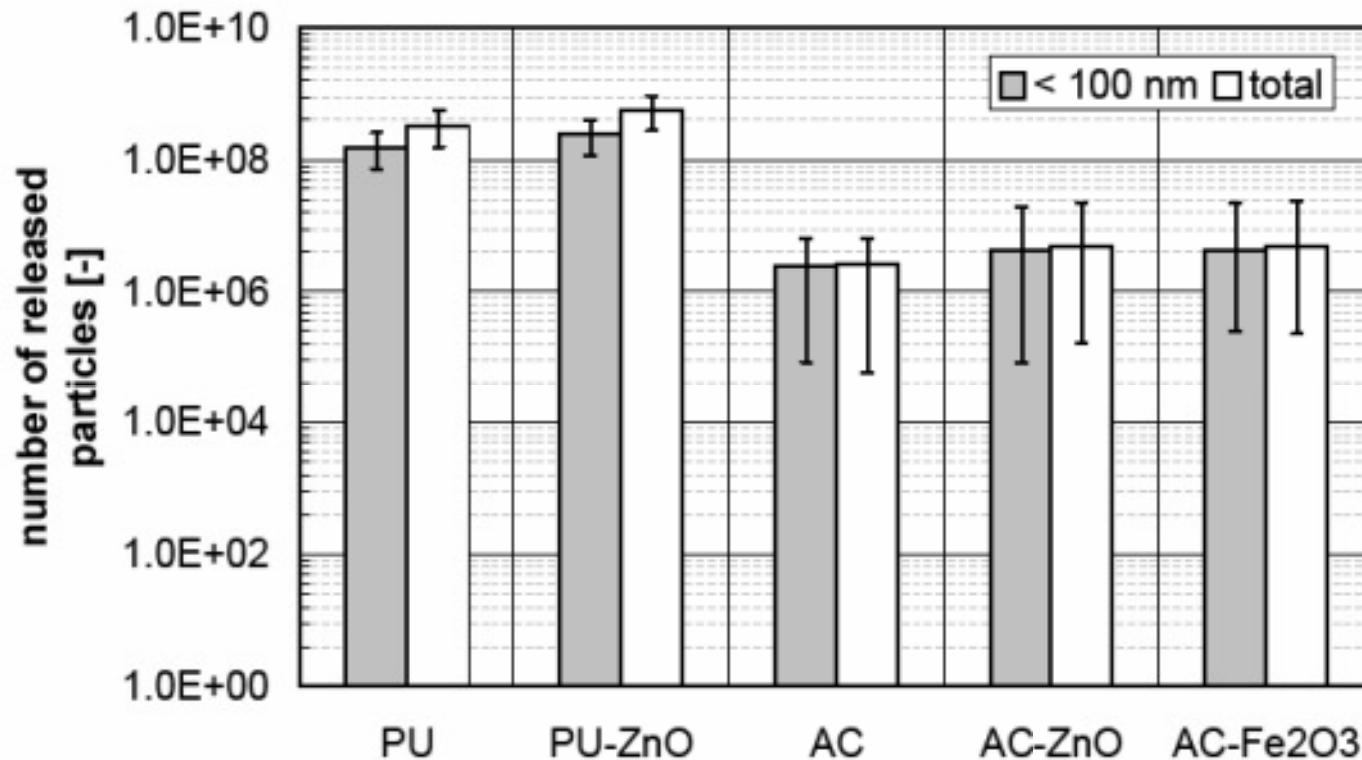
□2 types of metal oxide nanoparticle additives

ZnO	for all coatings
Fe_2O_3	for PU and AC

□3 types of substrate plates

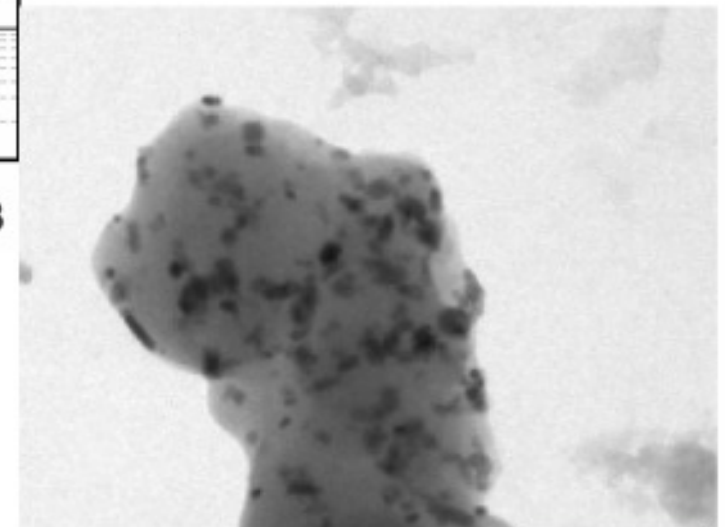
oak	for PU and UV
alumina	for PU (PU-Al)
fiber cement	for AC

2) Sanding processes - results



Nanoparticle additives do not increase the particle release <100 nm

Göhler et al. (2010) *Ann. Occup. Hyg.*; 54(6): 615-624



500nm

Experimental setup and procedure

Surface coating materials

□ 3 types of coatings

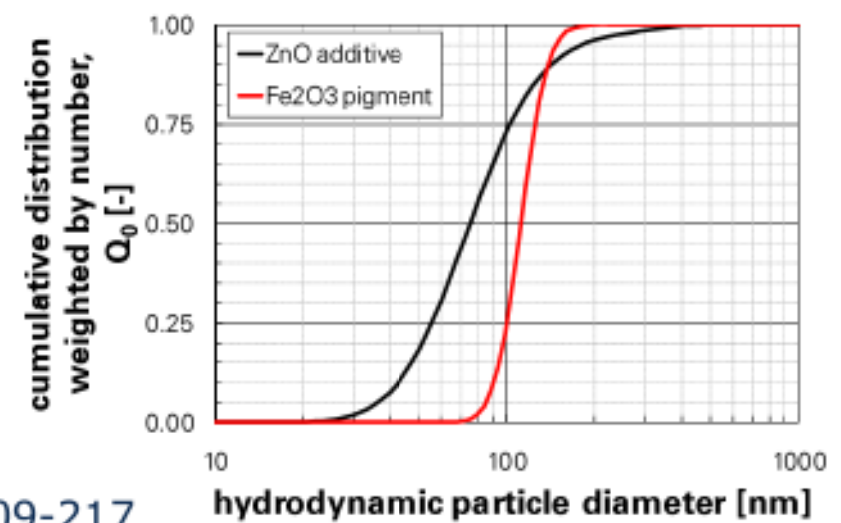
- PU two-pack polyurethane (furniture)
- UV UV curable clear coating (parquet)
- AC white pigmented (TiO_2) acrylate coating (facades)

□ 2 types of metal oxide nanoparticle additives

- ZnO for all coatings
- Fe_2O_3 for PU and AC

□ 3 types of substrate plates

- oak for PU and UV
- alumina for PU (PU-Al)
- fiber cement for AC



▮ Vorbau et al. (2009) *J. Aerosol Sci.*; 40(3): 209-217.

▮ Göhler et al. (2010) *Ann. Occup. Hyg.*; 54(6): 615-624

Experimental setup and procedure

Surface coating conditions

- ❑ **sample preparation** (ILF e.V., Magdeburg)
 - ❑ **squeegee application**
 - ❑ PU, UV $\approx 40 \mu\text{m}$ dry thickness
 - ❑ AC $\approx 125 \mu\text{m}$ dry thickness
 - ❑ **artificial aging (EN 927, dry)**
 - ❑ UV-A radiation, light wavelength of 351 nm
 - ❑ temperature of 50°C, 2000 h
- ⇒ darkening of non-doped PU and UV coatings
- ⇒ brightening of ZnO-doped coatings
- ⇒ no visible effect on Fe_2O_3 doped coatings
- ⇒ no visible effect for AC, AC-ZnO, AC- Fe_2O_3
- ⇒ no chalking observed



Experimental setup and procedure

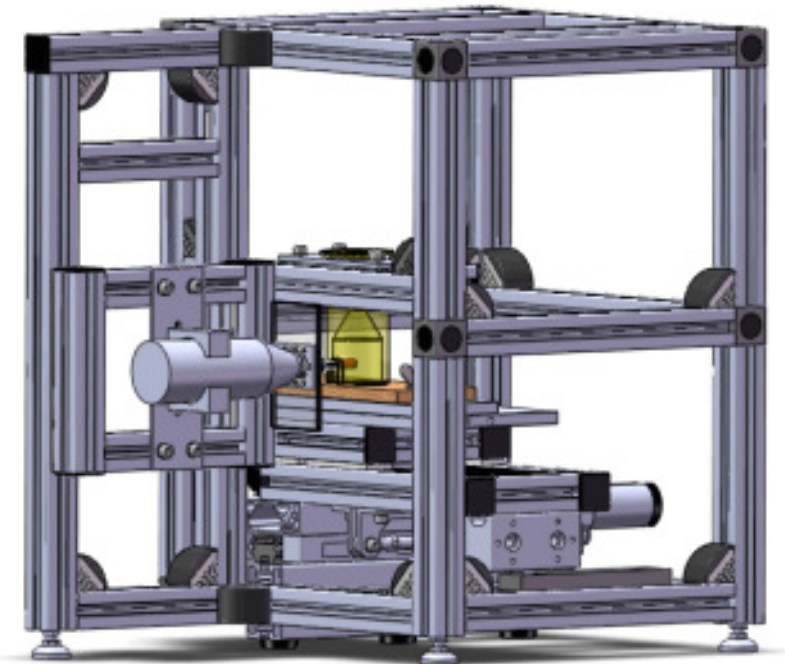
Experimental apparatus

❑ sanding process parameters

- ❑ contact force (0.5 N)
- ❑ contact pressure (≈ 150 kPa)
- ❑ peripheral speed ($1.8 \text{ m}\cdot\text{s}^{-1}$)
- ❑ grain size ($\approx 18 \mu\text{m}$, P600)

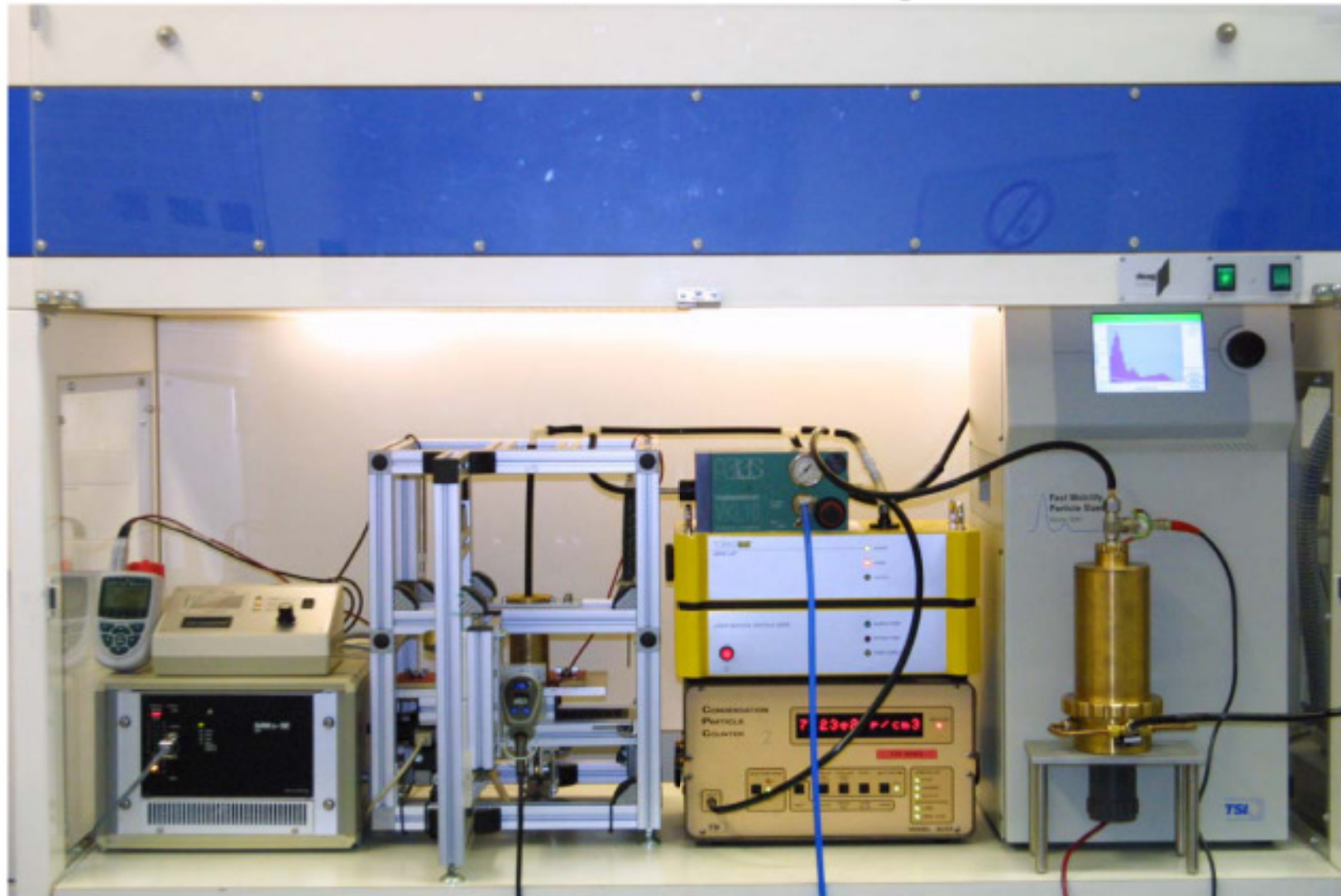
❑ construction

- ❑ vertically-movable sander
- ❑ horizontal sample supply
- ❑ encapsulated sanding zone
- ❑ spark particle flow deflection
- ❑ operation in laminar flow bench



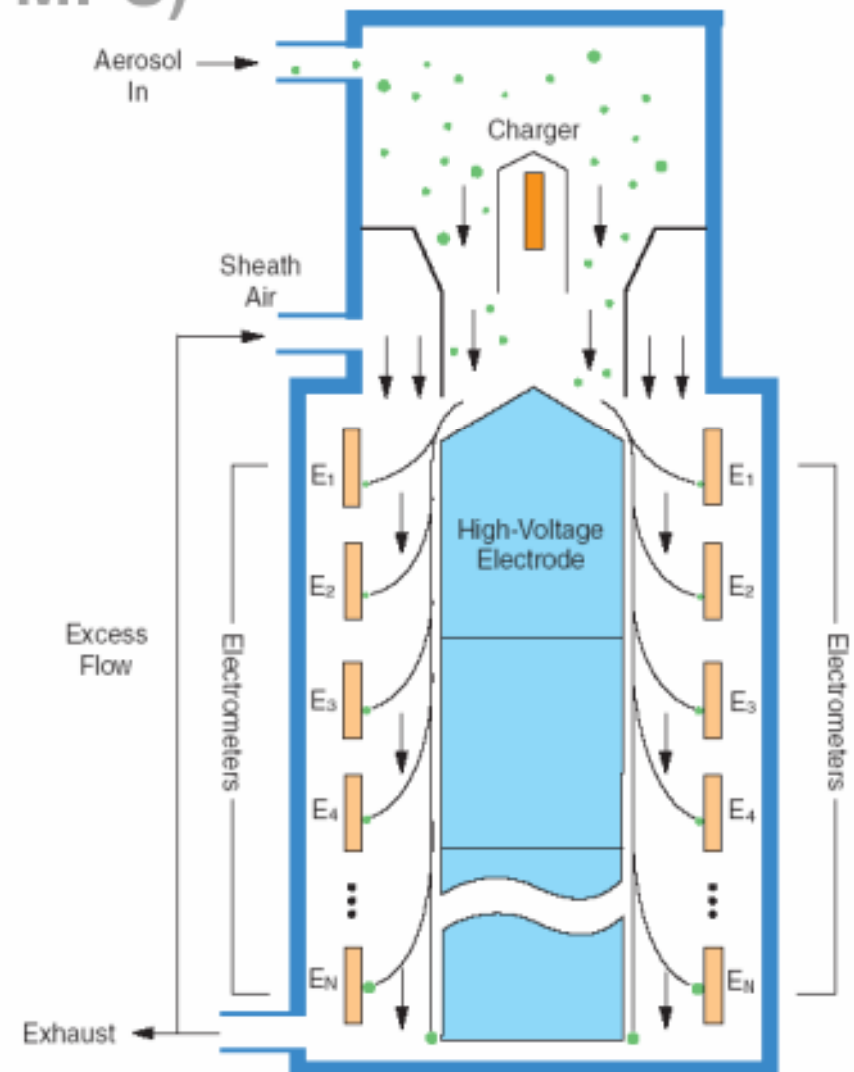
☰ Göhler et al. (2010) *Ann. Occup. Hyg.*; 54(6): 615-624.

Test Setup – without particle background

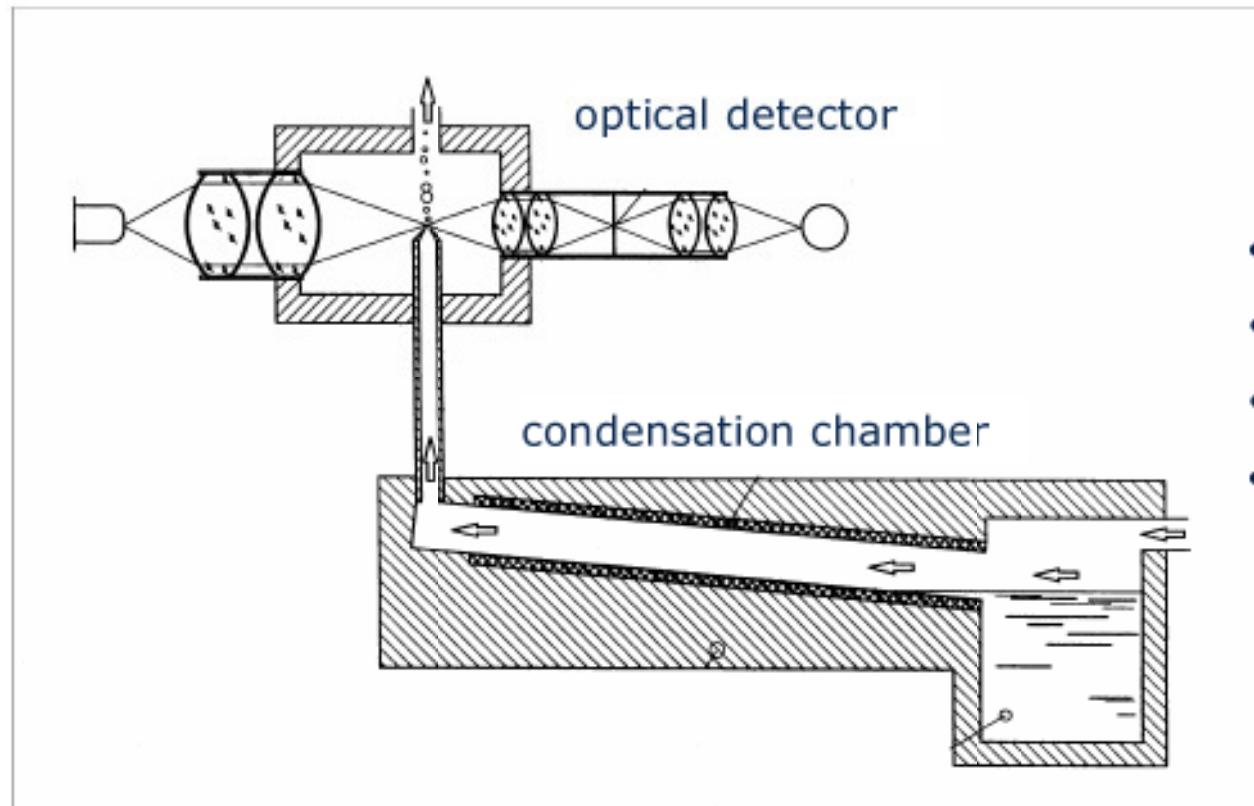


Fast Mobility Particle Sizer (FMPS)

Number concentrations of
 the size distribution,
 based on electrical current
 measurement



Condensation Particle Counter (CPC)



- total concentration
- 7 nm - > 10 μm
- 0,01 - 10.000 p/cm³
- 0,3 l/min

Mass of a 20 nm ZnO-sphere:

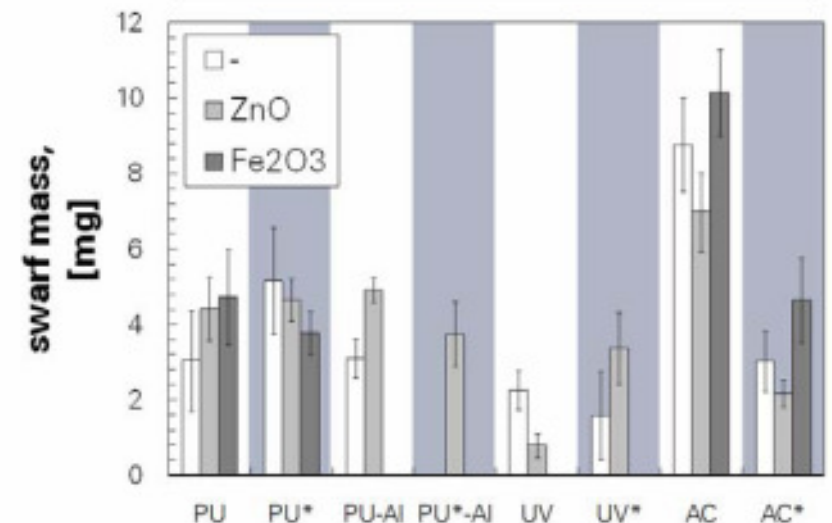
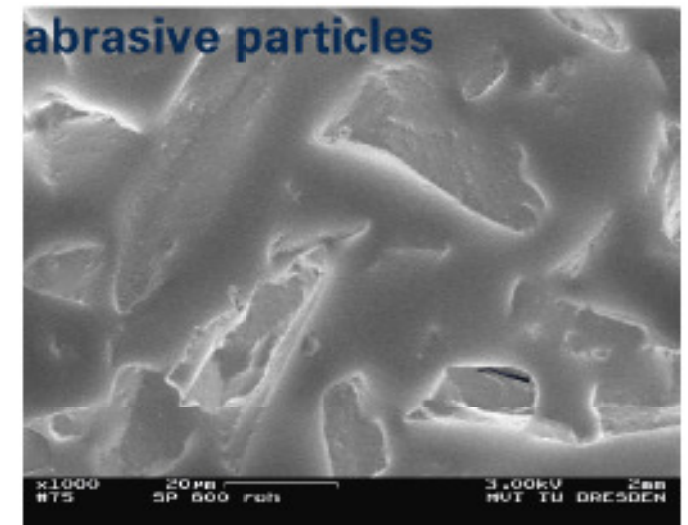
$2,35 \cdot 10^{-17}$ g

NO GRAVIMETRIC measurement applicable!

Results

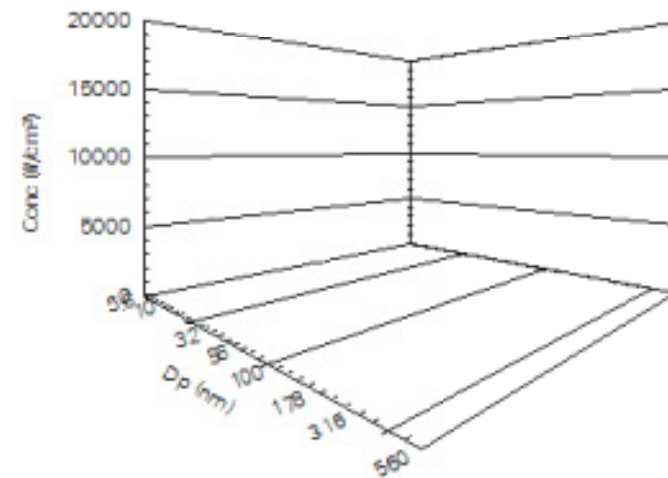
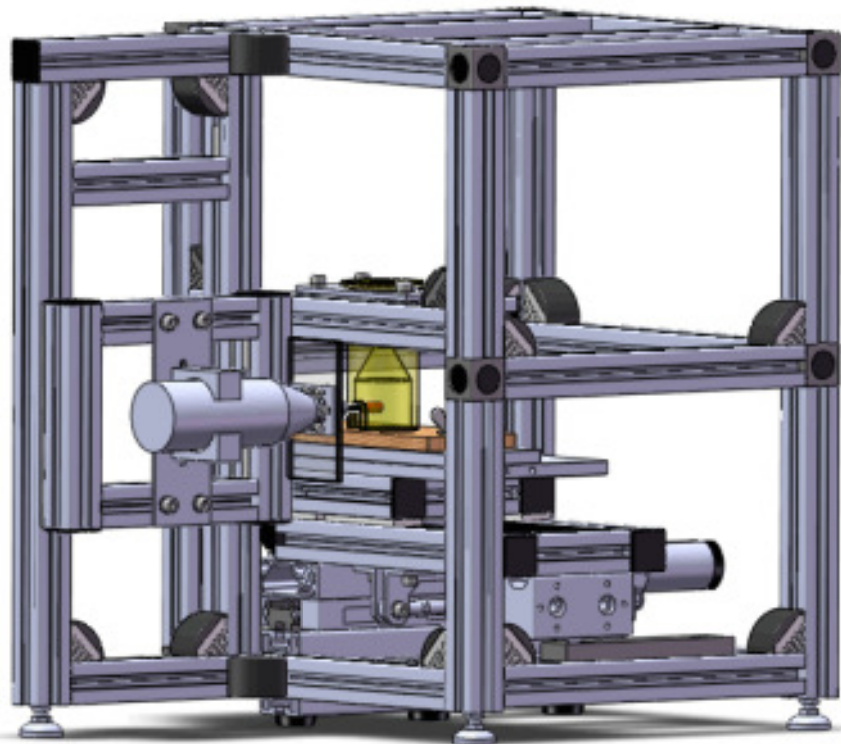
Quality of the sanding process

- ❑ **groove depth and distribution**
 - ❑ groove depth between 1 μm - 15 μm
 - ❑ homogeneously distributed grooves
- ❑ **cross-contamination ?**
 - ❑ no substrate particles
 - ❑ no particle-release from abrasive paper
 - ❑ background aerosol $c_n < 0.001 \text{ cm}^{-3}$
 - ❑ no spark particles from the cooling fan
- ❑ **repeatability**
 - ❑ example: wear mass
 - ⇒ $CV_{\text{mass}} \approx 10 \% - 40 \%$
 - ❑ CV over aerosol measurement devices
 - ⇒ $CV_{\text{MD}} \approx 20 \% - 40 \%$



Results

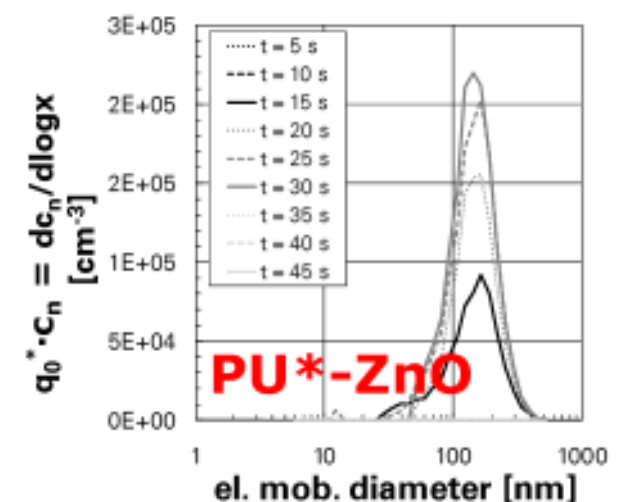
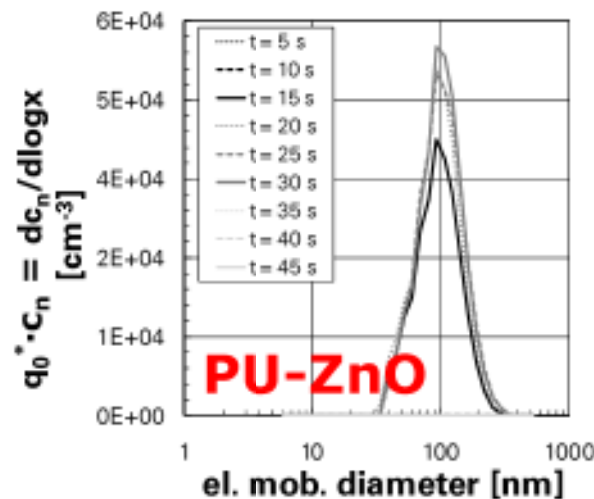
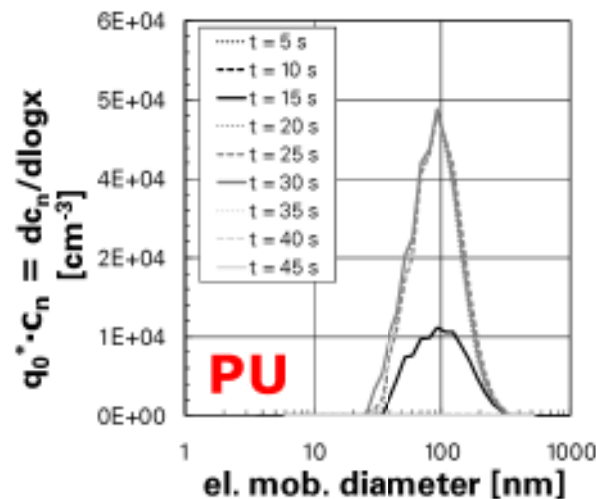
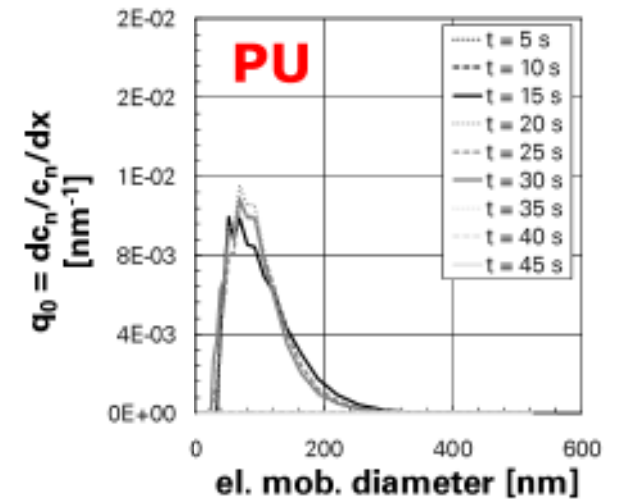
Time resolved particle size and concentration



Results

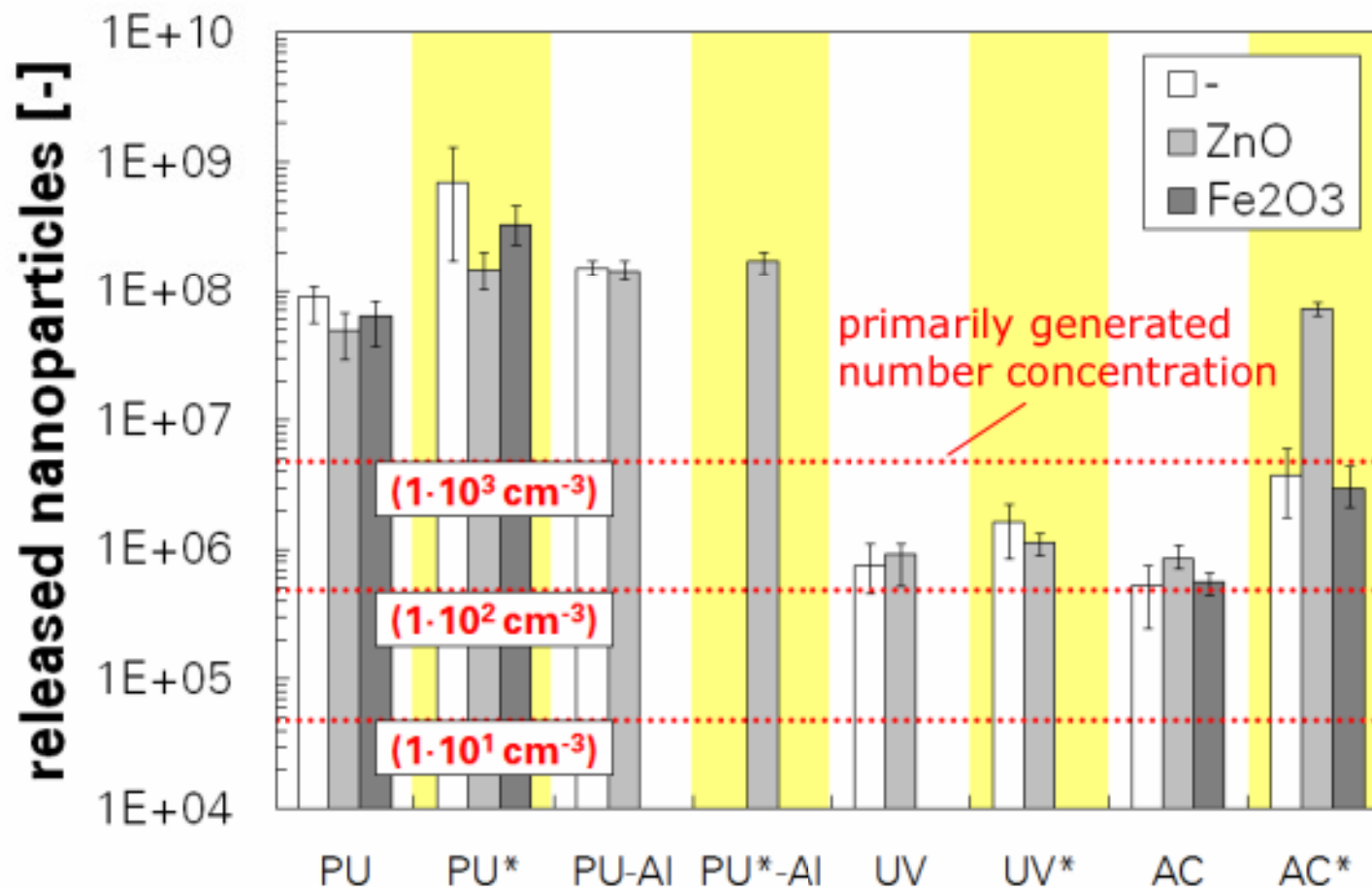
PSD and NC (EEPS)

- ❑ sanding process itself
 - ❑ q_0 constant in time
- ❑ effect of the NPA addition
 - ❑ no sig. differences in q_0 , slight differences in NC
- ❑ effect of the aging process
 - ❑ slight coarser PSD with significant increase in NC



Results

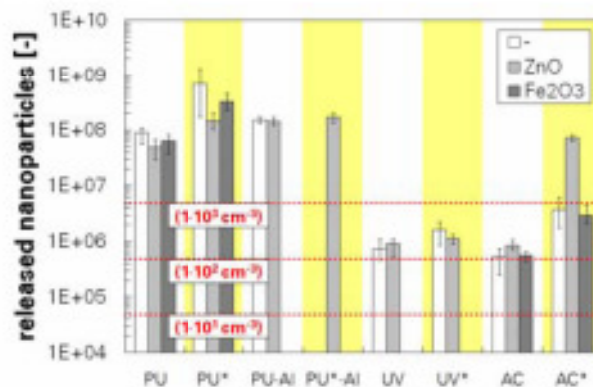
Nanoparticle release (5.6 nm – 100 nm, 10.4 cm²)



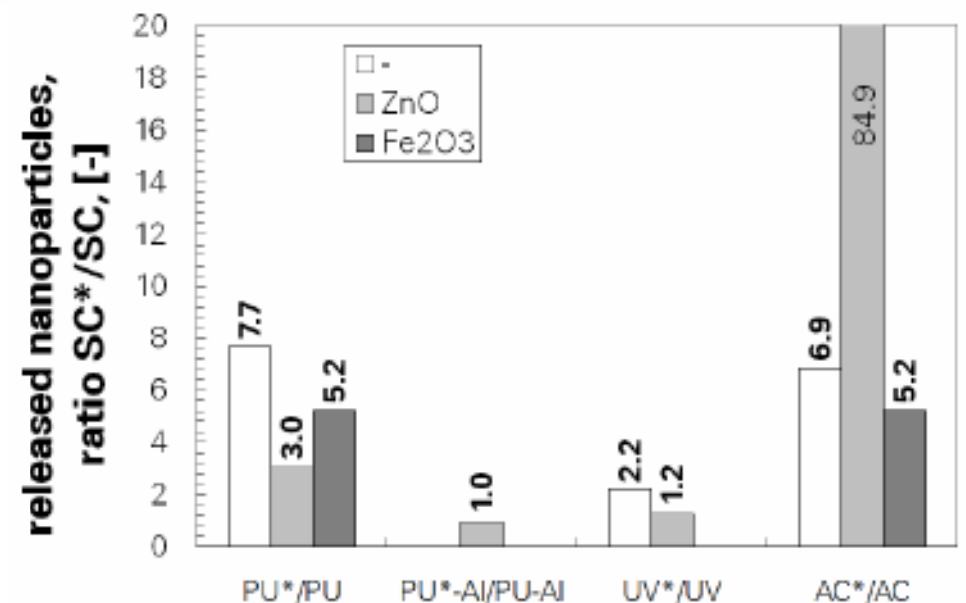
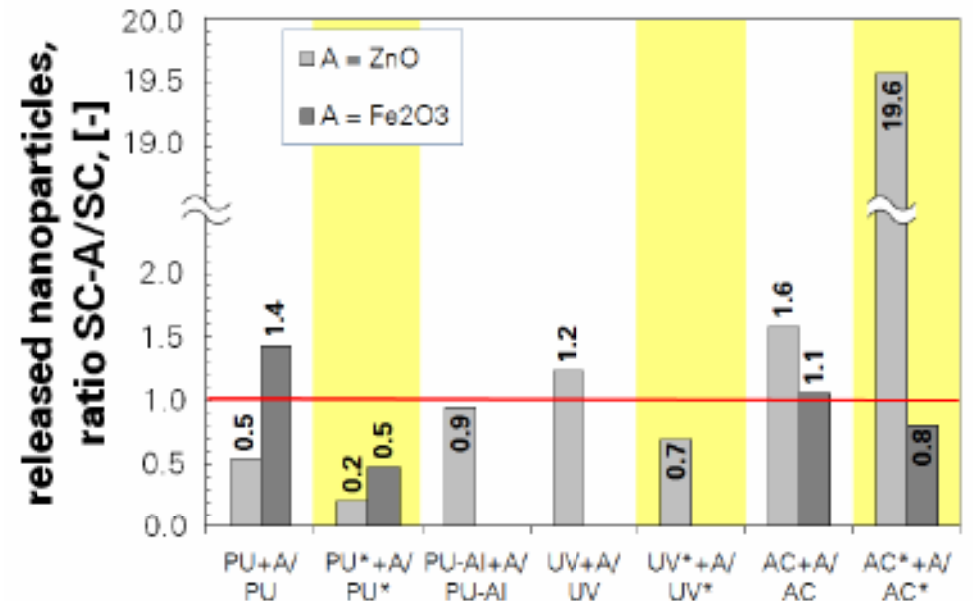
Results

Nanoparticle release

- addition of NPA
 - no systematic impact



- aging process
 - significant increase



Results

Nanoparticle identification

□ SEM-Analysis

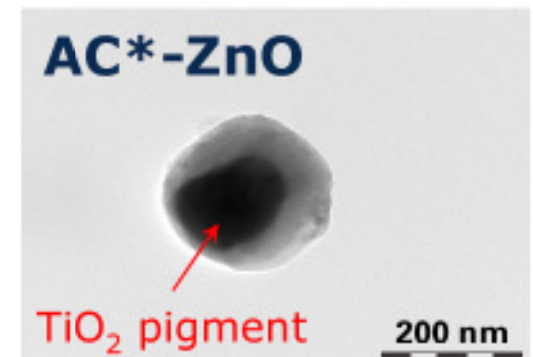
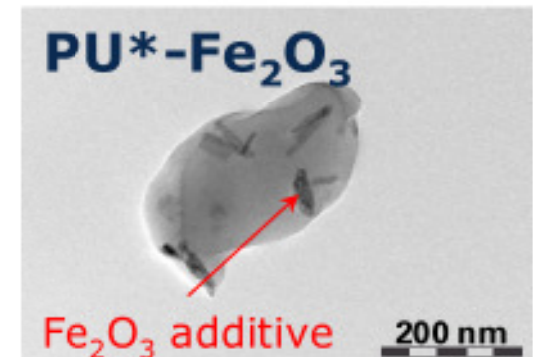
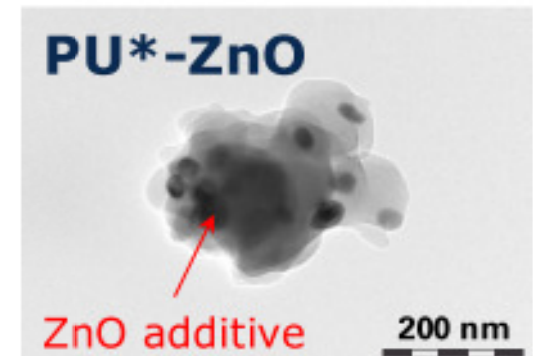
- NPA identification by morphology
- no free NPA observed
- ⇒ firmly embedded in the matrix material
- no differences between SC and aged SC*

□ TEM-Analysis

- NPA identification by morphology
- no free NPA observed
- ⇒ firmly embedded in the matrix material
- no differences between SC and aged SC*

□ EDX-Analysis

- ZnO & F_2O_3 & TiO_2 clearly identified
- particles < 100 nm made up of matrix material



Summary and Outlook

❑ findings on the nanoparticle release

- ❑ sanding of coatings produces nanoparticles

- ❑ effect of NPA in surface coatings:

- ⇒ no significant change in the PSD of the swarf aerosol

- ⇒ no systematic impact in the amount of nanoparticle release

- ⇒ no free nanoparticle additives and pigments observed

- ❑ effect of aging (2000 h UV-radiation):

- ⇒ significant impact in the PSD to coarser PSD

- ⇒ systematic increase in the nanoparticle release

- ⇒ no free nanoparticle additives and pigments observed

- ❑ **outlook:** investigations with pigment paints and composites

Thank you for your attention !

Acknowledgement:

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sample preparation/aging

TEM and EDX analysis