Nano-sized oxide powders for UV applications

Presentation outline

1. Introduction
2. Umicore UV absorbers
3. The importance of stable dispersions
4. Conclusions

1. Introduction

Nano: Hype or future?

Some properties change dramatically with size

Some examples (where Umicore is active) :

- Chemical : from inert to active

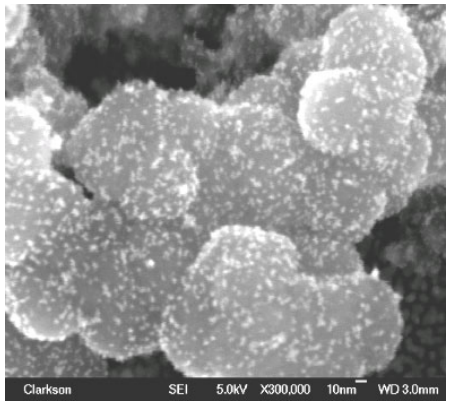
  ↪ catalysis (Precious metals , oxides)

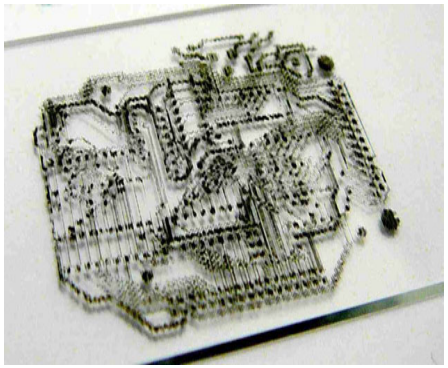
- Thermal: from stable to low temperature sintering

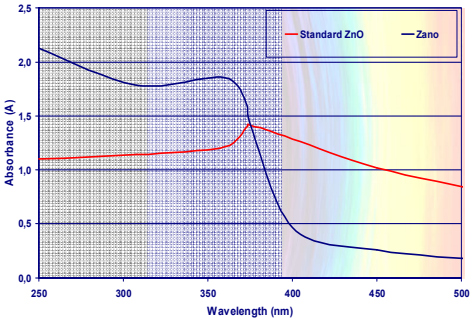
  ↪ printed electronics (nano Ag)

- Optical: from colored to transparent

  ↪ UV protection







Inorganic UV absorbers

- Some inorganic powders (as TiO_2, CeO_2, ZnO):
  - are broadband UV-absorbers
  - guarantee long-term protection
  - don't migrate out of or in the coating (environmentally friendly)
  - are heat resistant

- Inorganic pigments have relatively high refractive index, therefore:
  - Particle size distribution should be well below 100 nm
  - Particles should be well dispersed in application to maintain transparancy

Inorganic UV absorbers

- Umicore has a portfolio of UV-absorbing nanomaterials:
  - Nano TiO_2 (Optisol®)
  - Nano ZnO (ZANO®) and
  - NanoGrain® CeO_2

- Potential markets :
  - Coatings
  - Plastics
  - Cosmetics
  - Textiles

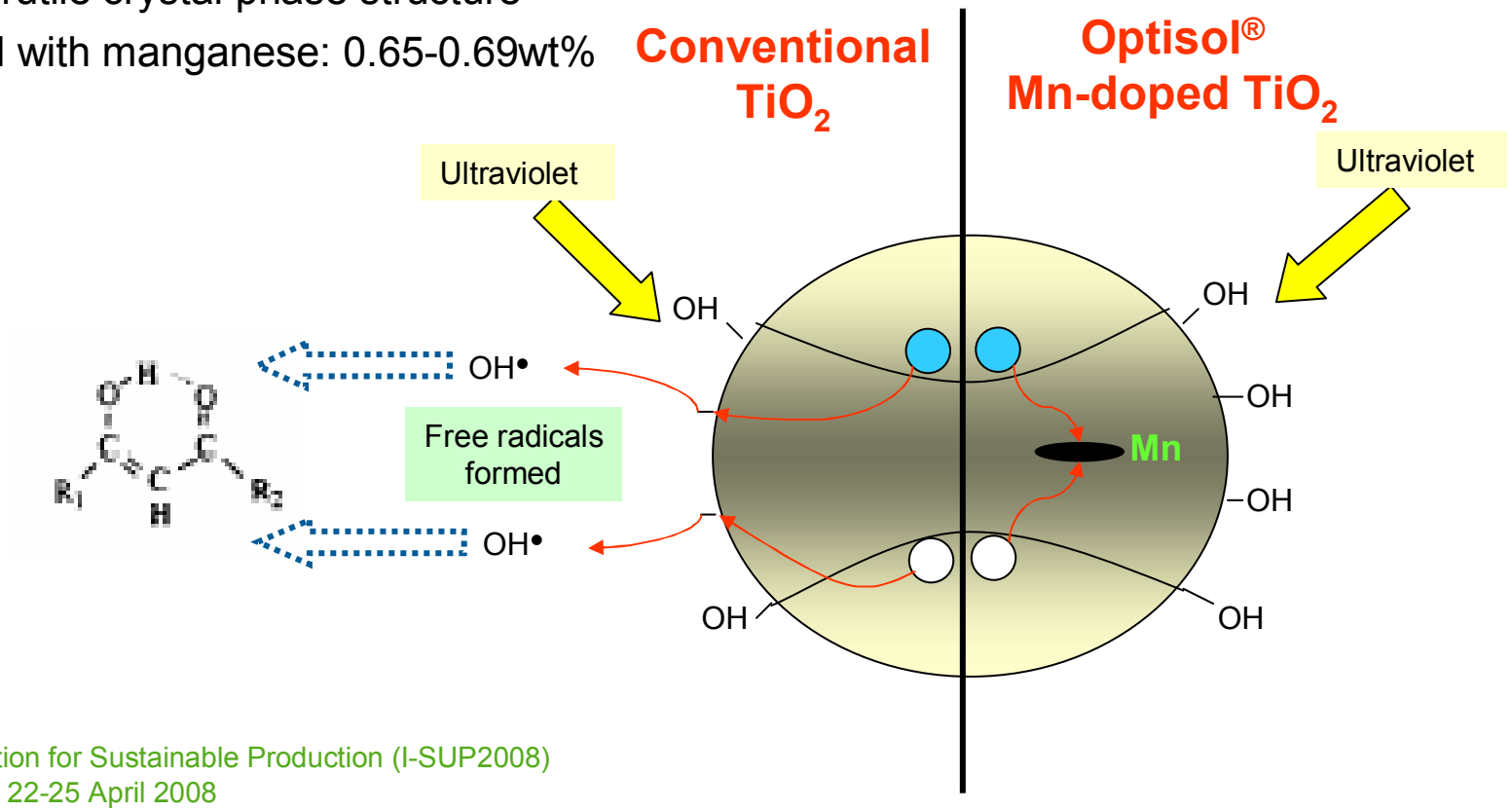
- Such UV-absorbers often have other synergistic properties

2. Umicore UV absorbers

Umicore UV absorbers

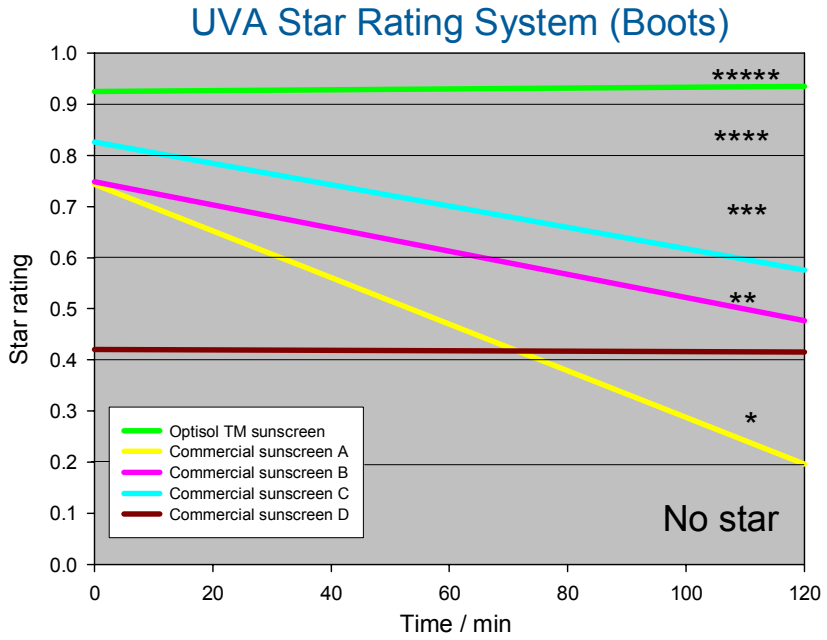
1) Nano Mn-doped TiO_2 (Optisol®) for cosmetic applications

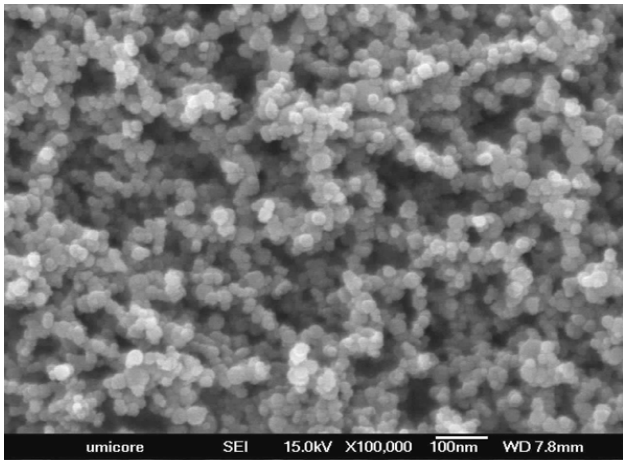
- Special modified TiO_2 powder:
  - Specific surface area: 20 m²/g (70nm)
  - 100% rutile crystal phase structure
  - Doped with manganese: 0.65-0.69wt%



Umicore UV absorbers

1) Nano Mn-doped TiO_2 (Optisol®)





Innovation for Sustainable Production (I-SUP2008)
Bruges 22-25 April 2008

Umicore UV absorbers

1) Nano Mn-doped TiO_2 (Optisol®)

Performance:

- Most sunscreens mainly protect UVB (sunburn), only slightly UVA (skin ageing, skin cancer)

→ **Increased UVA protection (50% increase)**

- Most sunscreens only protect the skin for maximum a few hours

→ **Up to 6 hours protection**

- High Skin Protection Factors (SPF) result in a white-coloured sunscreen which can be hardly spread out

→ **Transparent sunscreen can be easily spread out**

Nano-ZnO (Zano) for personal care applications

- 2 available products:
  - Zano 10: uncoated zinc oxide
  - Zano 10 Plus: coated zinc oxide

- Coating on Zano 10 Plus will enhance dispersion and compatibility of Zano in oil phases of emulsions

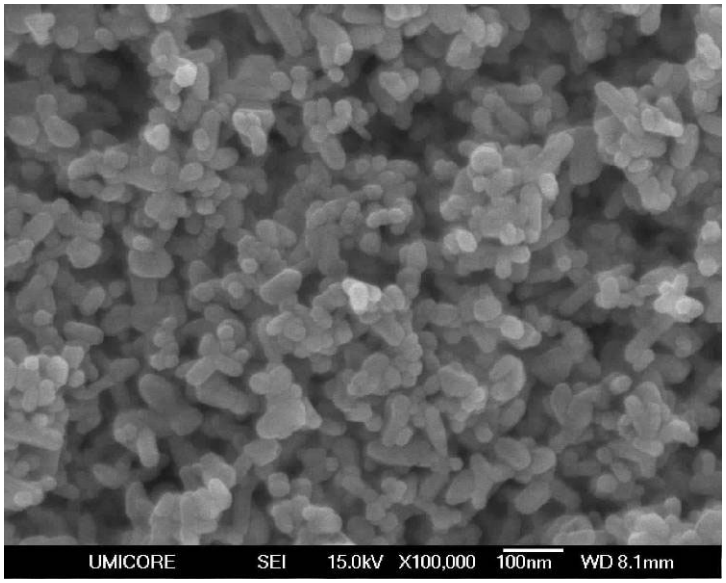
- Advantage of Zano as UV absorber in personal care applications:
  - Long-term protection
  - Broad band protection (UVA and UVB)
  - Non-whitening on the skin

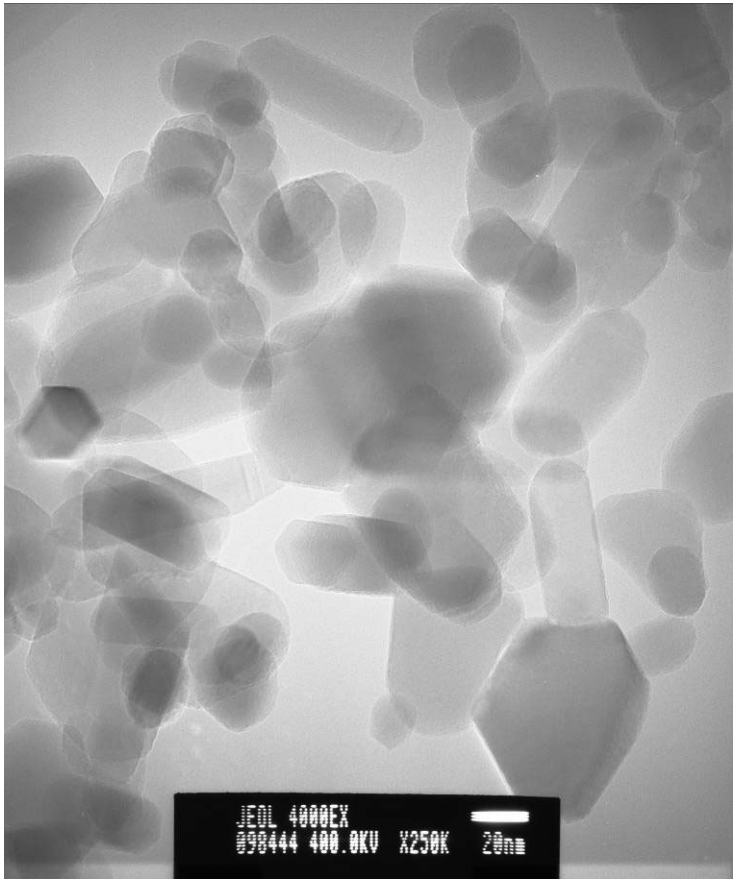
Umicore UV absorbers

2) Nano ZnO (Zano®)

- Typical physical properties:

  SSA (BET): 30 m^2/g - 35 nm



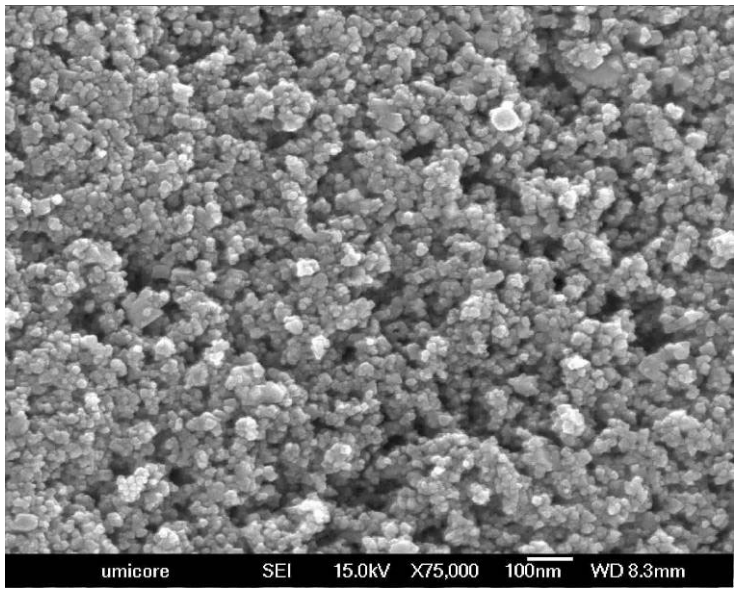


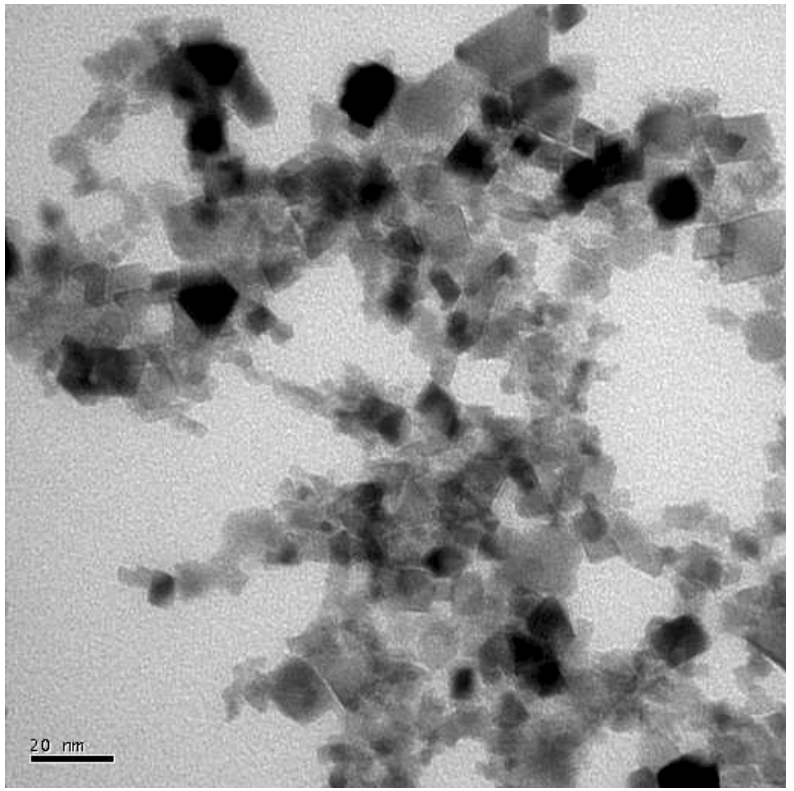
Umicore UV absorbers

3) Nano CeO_2 (NanoGrain® CeO_2)

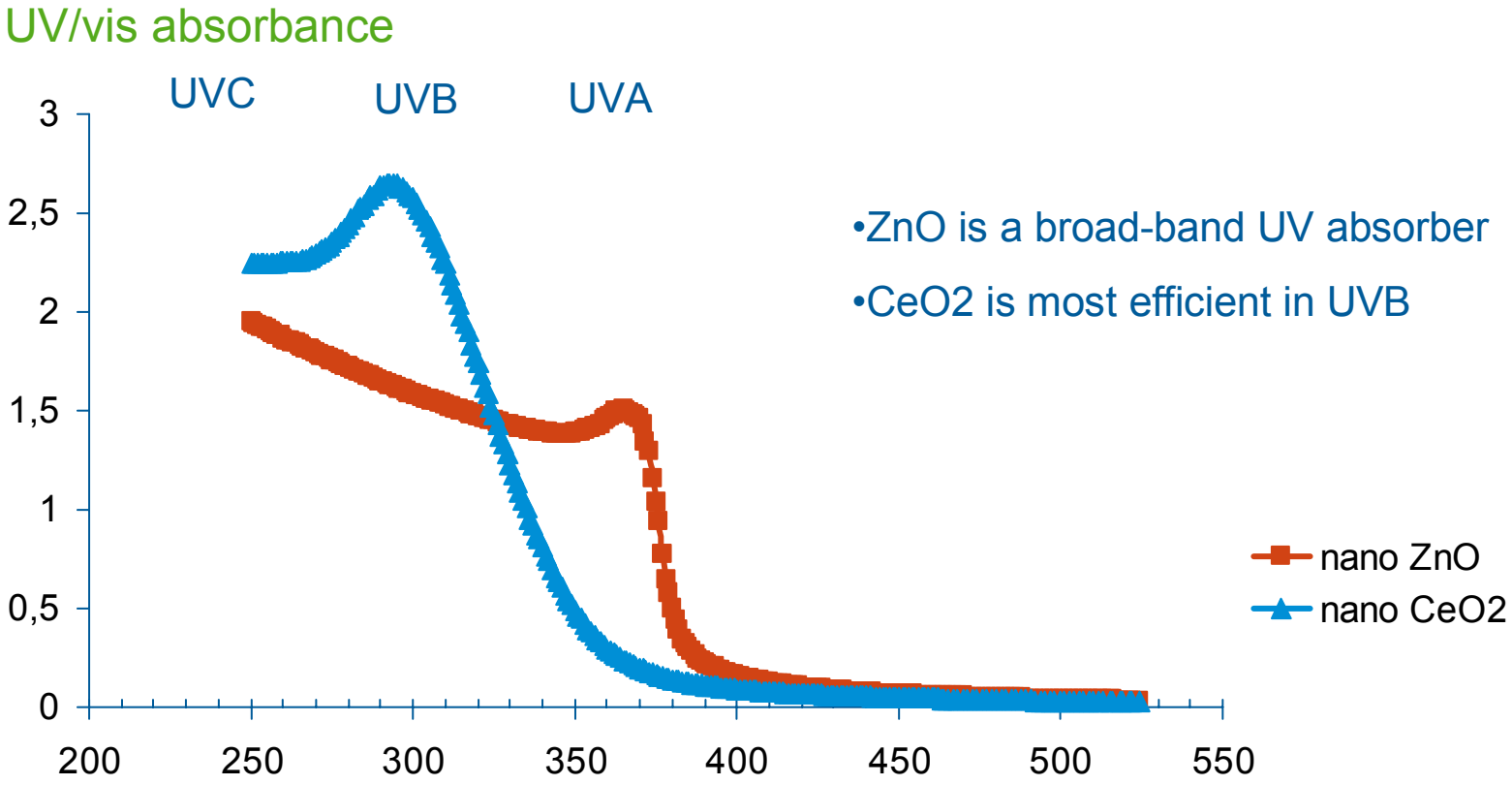
- Typical physical properties:

  BET: 60 m^2/g - 15 nm





Nano ZnO and CeO_2: excellent transparent UV absorbers



Why nano?

- Transparency, determined by:
  - Size of particles in a coating
  - Refractive index:

    ZnO: 2.0, CeO_2: 2.2, (TiO_2: 2.6)
  - Particle concentration in the system/film

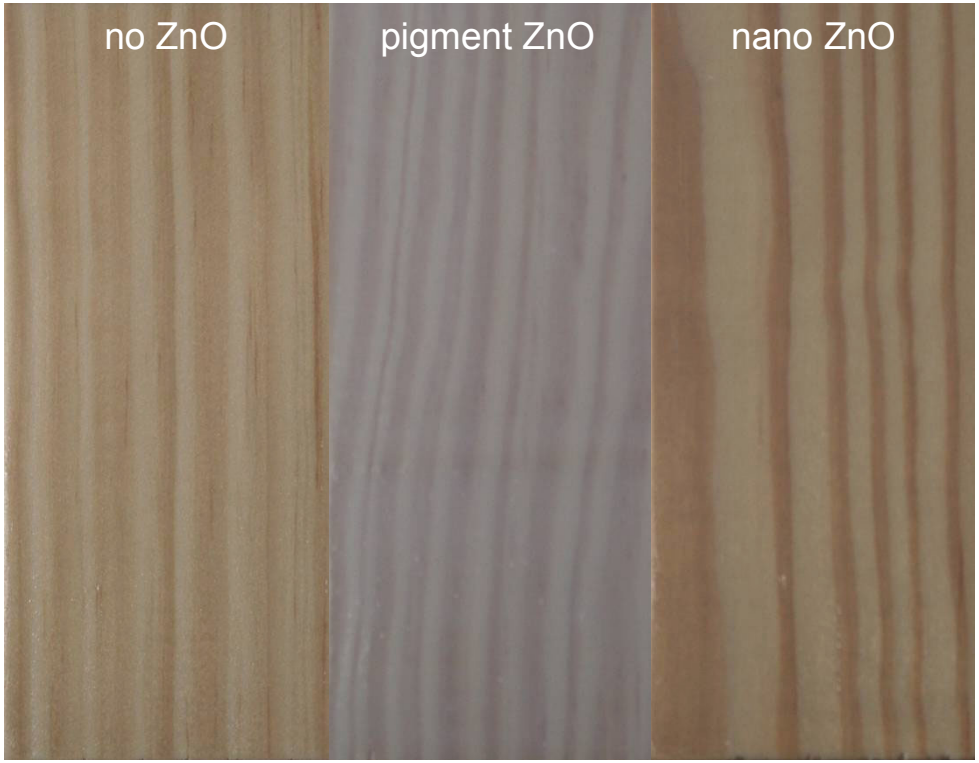
$$I = I_0 \frac{(1+\cos^2\theta)}{2R^2}\left(\frac{2\pi}{\lambda}\right)^4\left(\frac{\eta^2-1}{\eta^2+2}\right)^2\left(\frac{d}{2}\right)^6$$

Raleigh scattering

- Scattering determined by particle size to power 6 → nano particles to ensure transparency

Why nano?

- Transparency of wood coating with nano and pigment grade ZnO

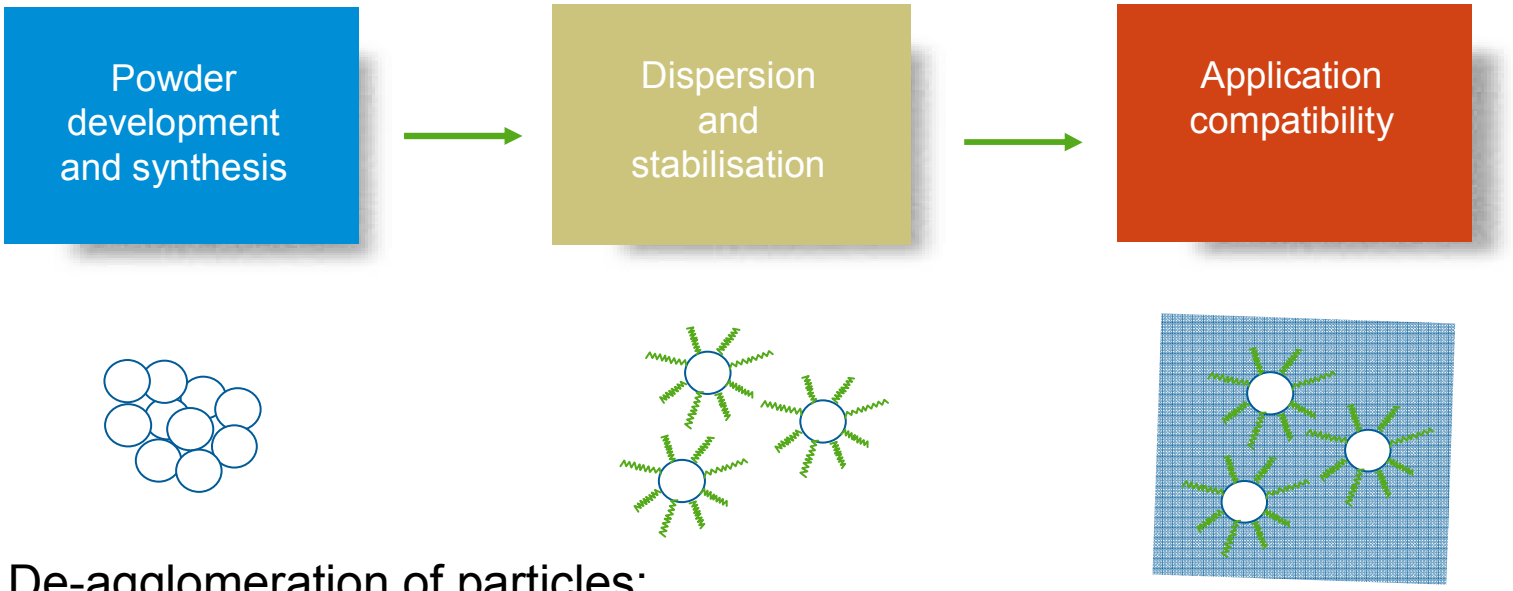


- Pigment grade ZnO: 150-300 nm
- Nano ZnO: ~35 nm

3. Importance of stable dispersions

Dispersion and stabilization

- Agglomerates of nano particles will behave as micron sized particles and needs to be prevented at all times → development steps:



- De-agglomeration of particles:
  - Overcome the Van der Waals interactive forces

Dispersing nano particles

- De-agglomeration of particles:
  - Apply the right amount of energy to obtain desired results

Low

- Used to prepare pre-mixes
- De-agglomeration not optimal
- Examples:
  - dissolver

Intermediate

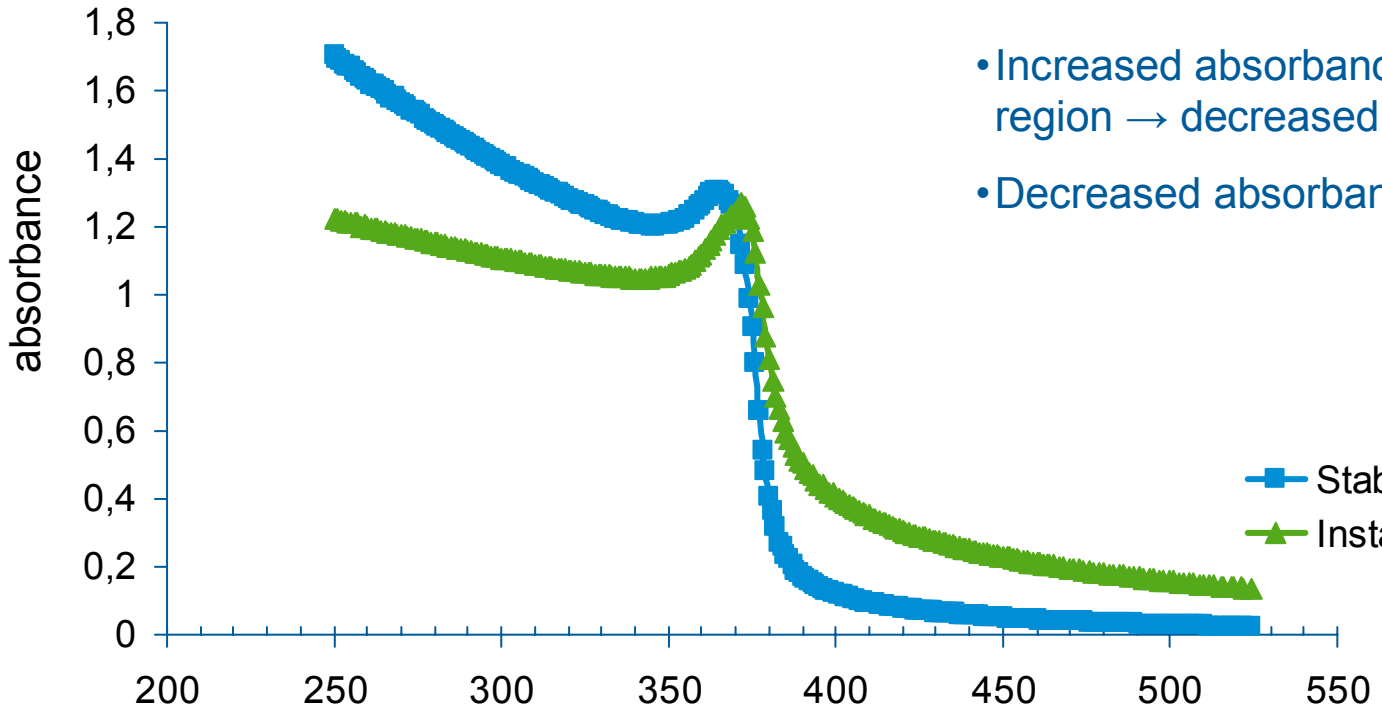
- Low solids loading
- De-agglomeration
- Examples:
  - ultrasone
  - rotor-stator

High

- High solids loading
- De-agglomeration and milling
- Examples:
  - bead mills
  - ball mills

Importance of dispersion stability

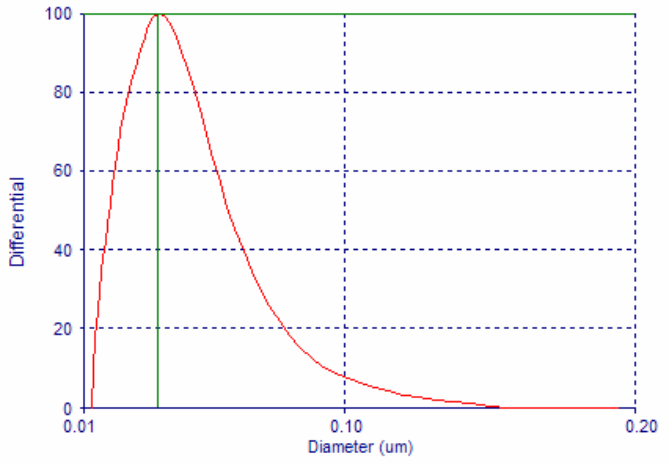
- UV/vis spectrum upon dispersion instability



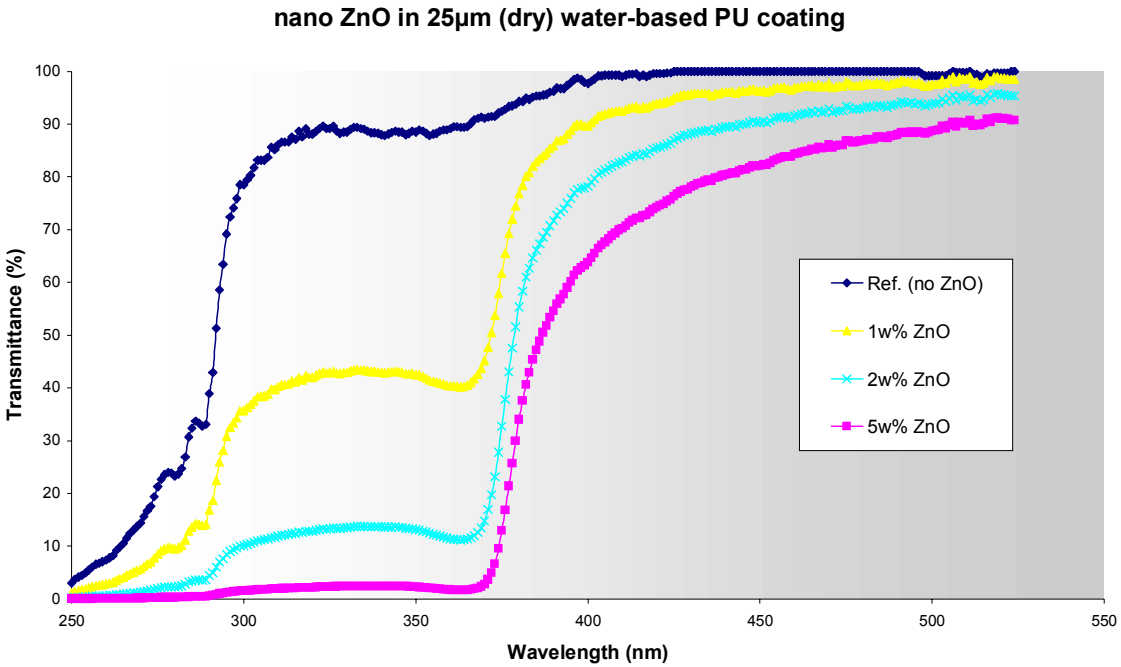
- Increased absorbance in visible light region → decreased transparency
- Decreased absorbance in UV region

Example: Water based Zano® 30 dispersion

- Solids content 50 wt%
- Mean particle size ~35 nm
- Introduced into water-based PU wood coating



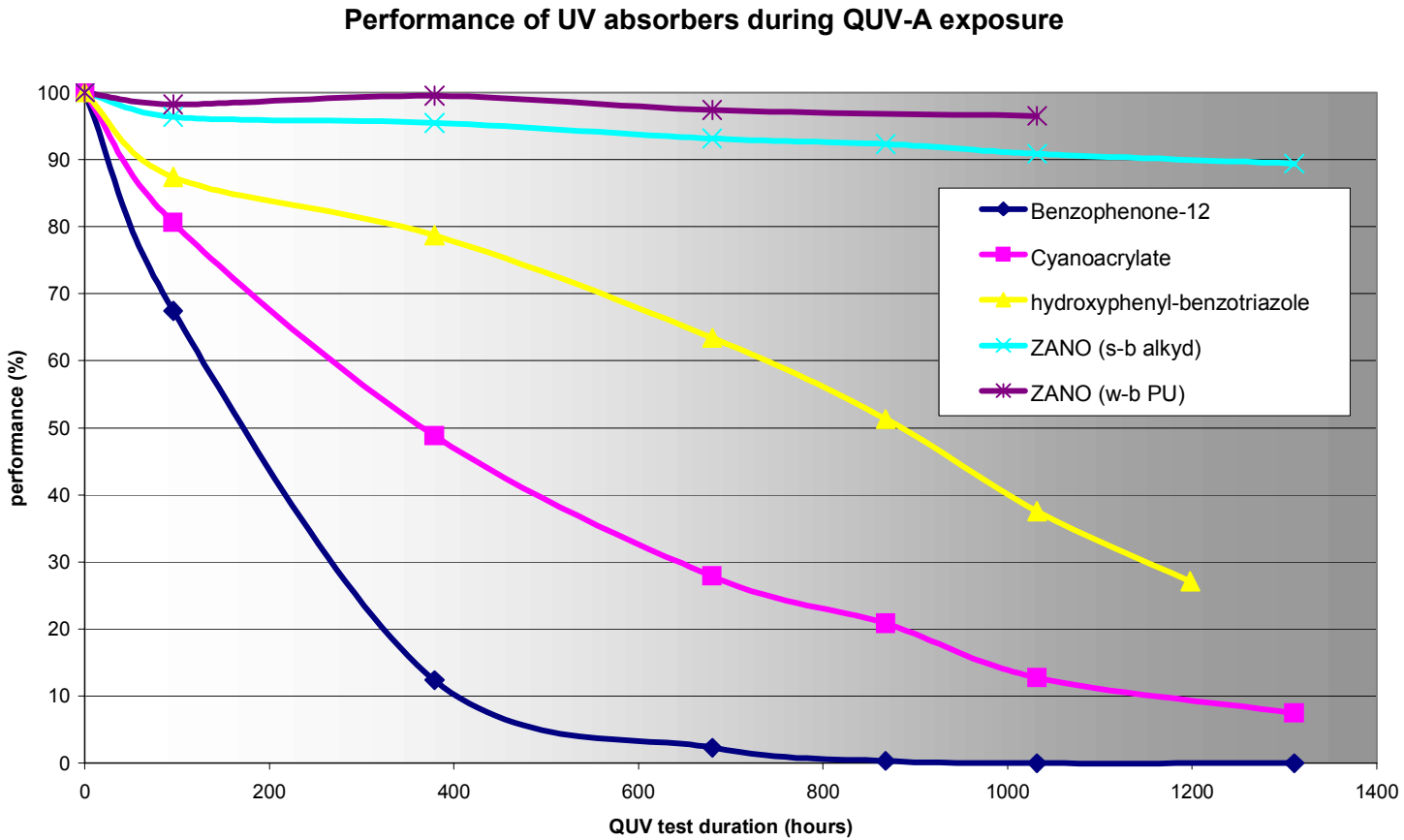
PSD measured via XDC



UV/vis transmission

Degradation of ZnO versus organic UV absorbers

- degradation overview



4. Conclusions

Conclusions

- All TiO_2, ZnO and CeO_2 are efficient UV absorbers:
  - TiO_2 (Optisol®) used in cosmetic sunscreen formulations
  - ZnO is a true broad band UV absorber
  - CeO_2 is most effective in UV-B

- Optisol Mn:TiO_2 offers:
  - Increased UVA protection (50% increase)
  - Up to 6 hours skin protection
  - Transparent sunscreen xhich can easily spread out

Conclusions

- Stable dispersions and full compatibility with coating system are important to ensure:
  - Transparency of the clear coating
  - Most efficient protection against UV radiation

- Inorganic UV absorbers truly provide long-term protection:
  - After 1300 hours QUV ZnO still provides more than 90-95% effectiveness
  - Most of the commonly used organic UV absorbers degrade fast over time

- Recommended level: 2-3w% of ZnO or CeO_2 relative to the dry coating film