

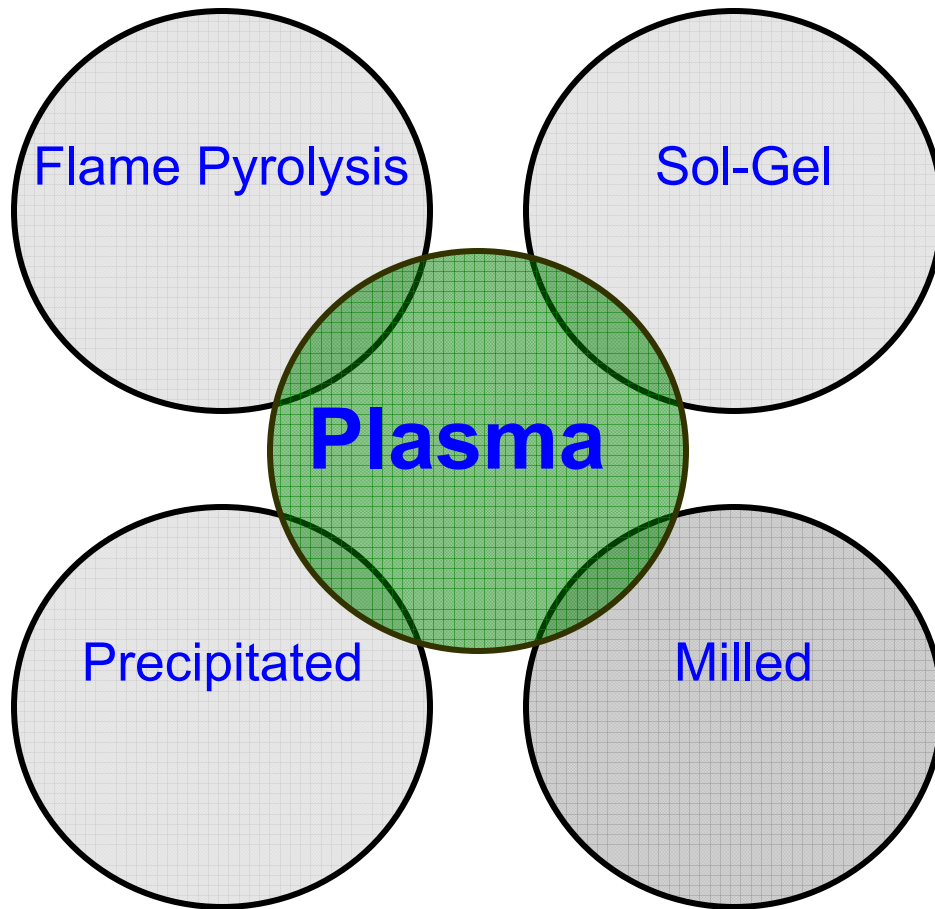
The use of dispersed nanosized functional materials in Coating applications

John Du
BYK USA

**2008 International Conference on
Nanotechnology for the Forest Products Industry**

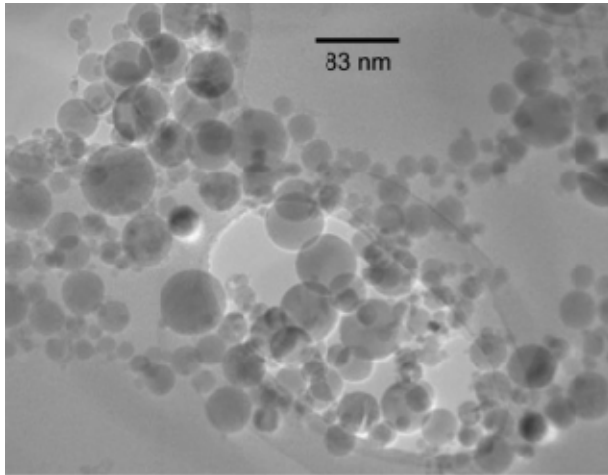
- Relationship between preparation and shape
- Why dispersion of nano particles is important.
- How Al_2O_3 and SiO_2 influence scratch resistance
- What types of coatings can benefit from nano.
- Improvement of UV protection in Paint and Plastic using nano

Unique Nanoparticles



- Nanoparticles from other methods may overlap, but do not share the same particle properties
- Plasma-produced nanoparticles have unique properties

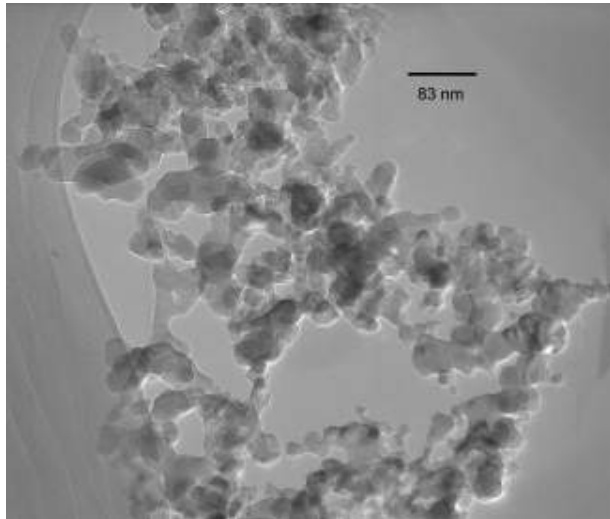
Comparative Processes → Alumina



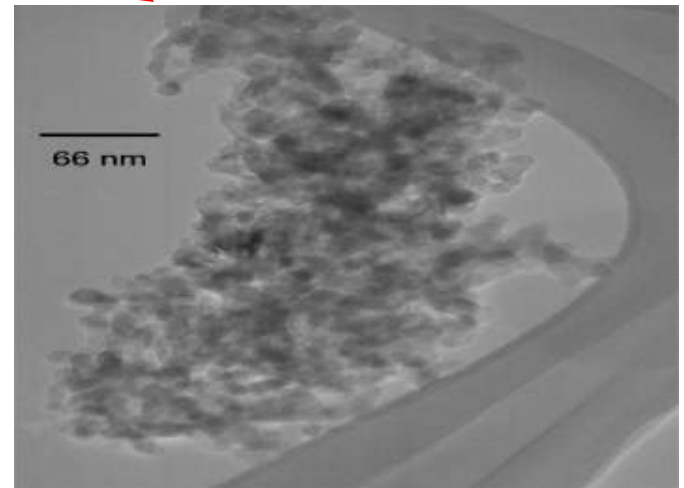
Plasma Vapor Alumina

← **Spherical & discrete particles**

Irregular, aggregated & agglomerated



**Flame
Synthesis
Alumina**



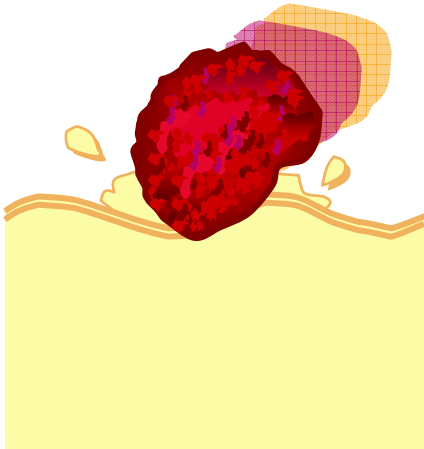
Precipitated Alumina

How to
Disperse?
Stabilize?
Functionalize?

NANOPARTICLES

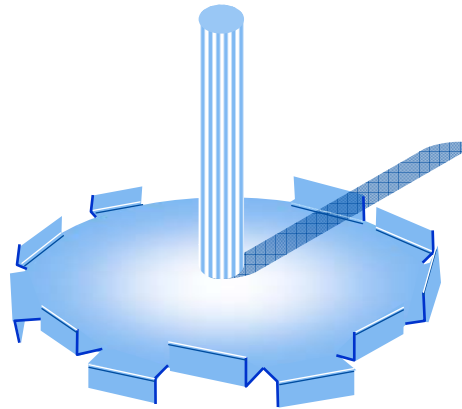
Wetting and Dispersing Process

1 Wetting



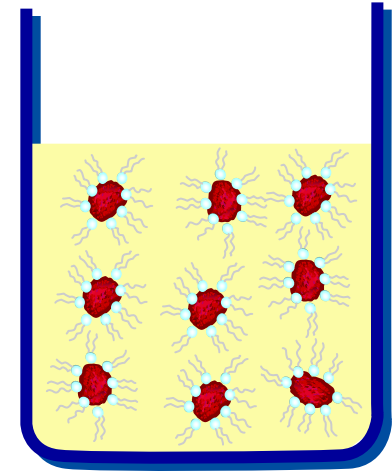
Displace air and
wet particle

2 Dispersion



Energy input

3 Stabilization



Prevent re-flocculation

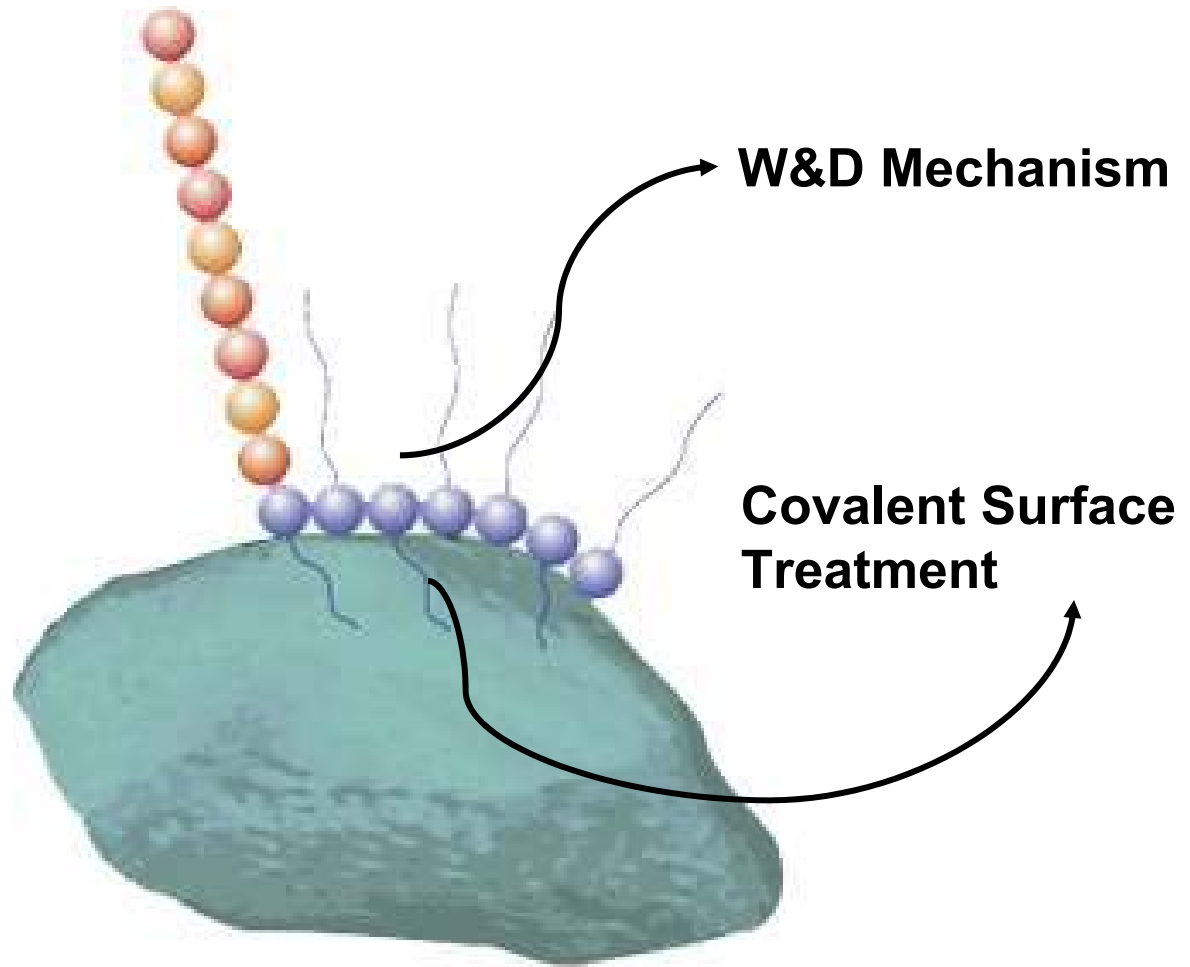


Wetting Additives

Dispersing Additives

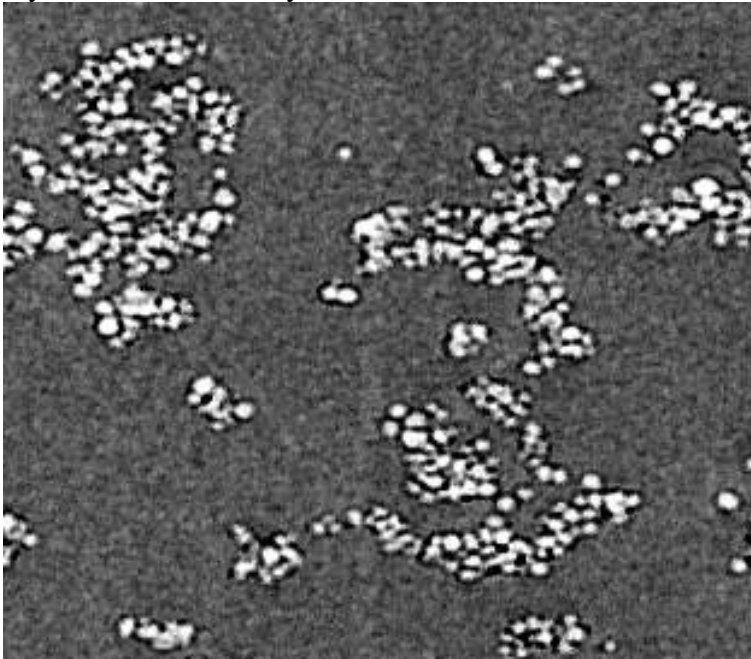


W&D Additives vs. Covalent Surface Treatment

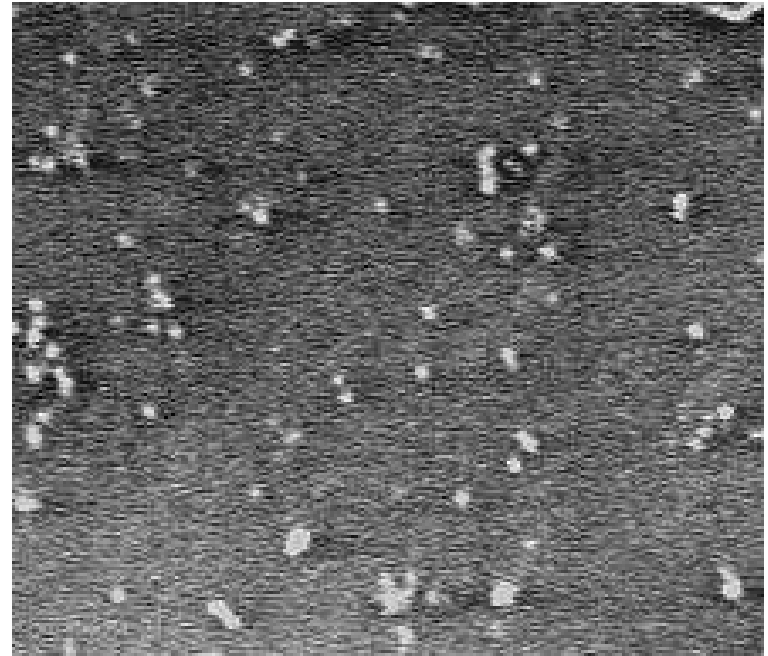


Impact of W&D–additive on deflocculation / stabilization

System: 2 Pack Acrylate / NCO

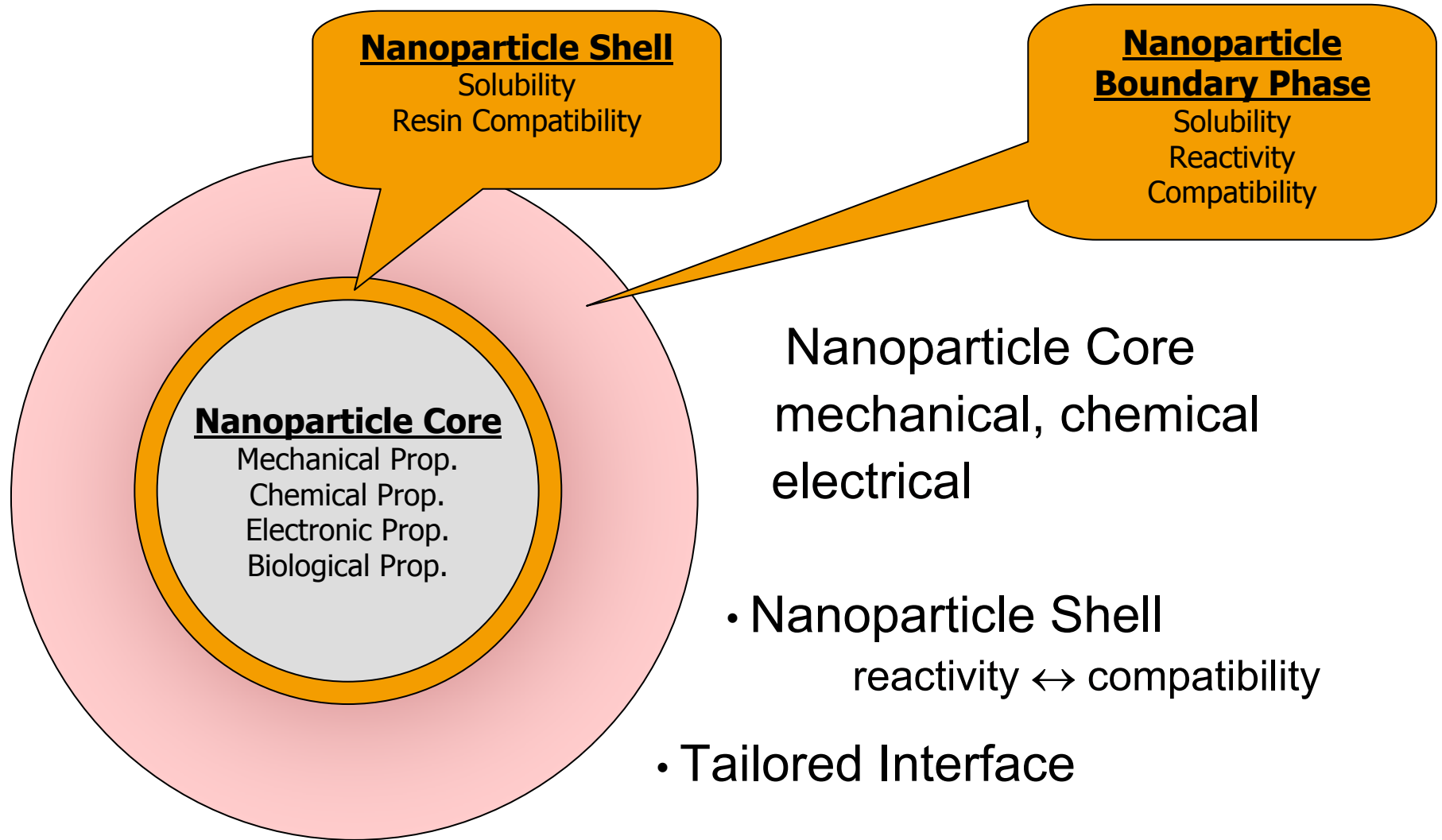


No W&D–additive

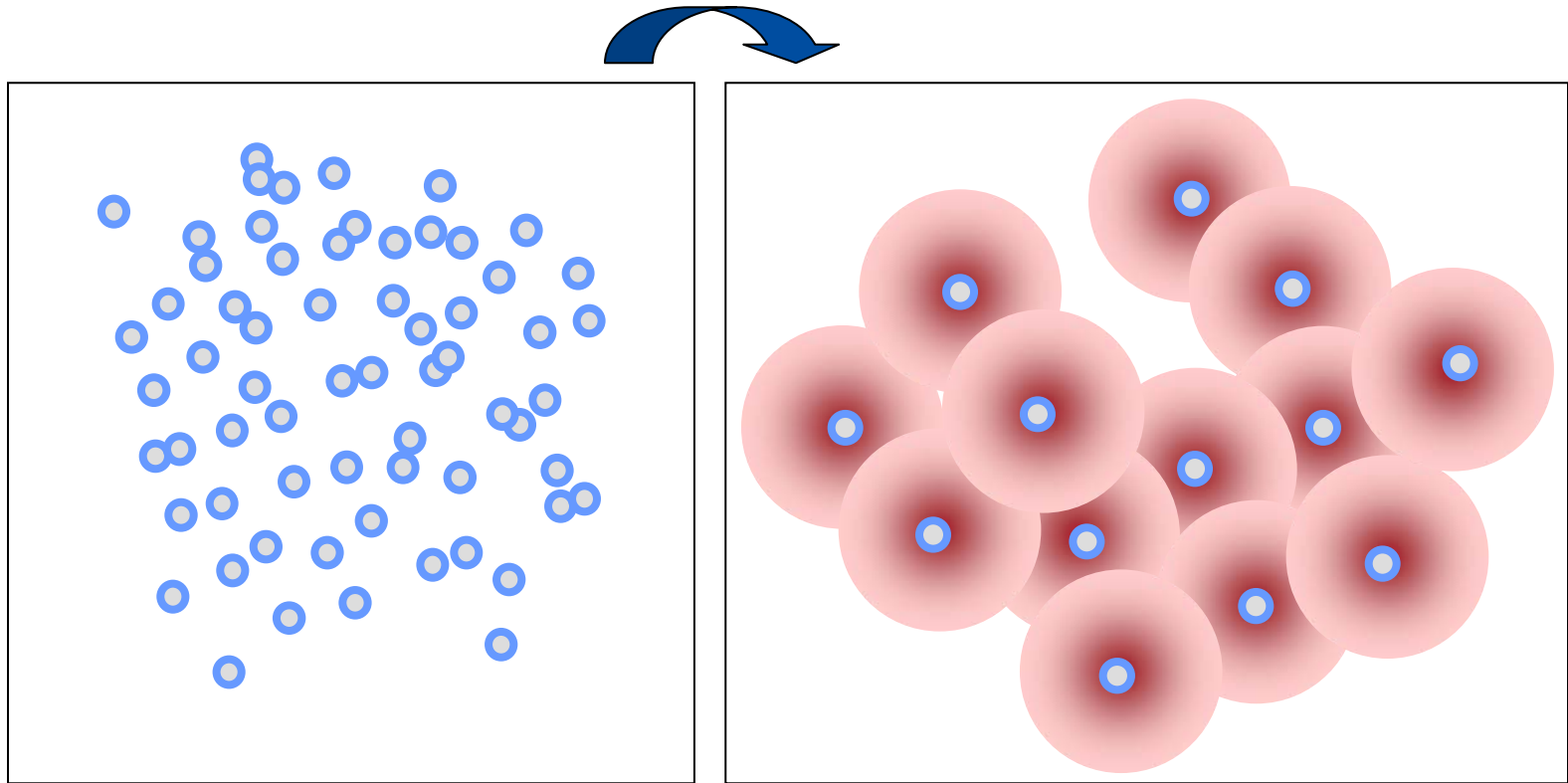


W&D–additive

Functionalized Nanoparticles



Role of Boundary Phase



Expansion of boundary phase on Nanoparticles provides

- **compatibility**
- **extends functionality** (e.g. scratch resistance)
- **lower loading requirements**

Dispersing Nanomaterials

Example “Baytubes®”

Dispersing Carbon Nanotubes

Cooperation with Bayer Material Science

1% MWCNTs in PMA

Without dispersant



1% MWCNTs in PMA

With dispersant



Wetting & Dispersing – Key Factor in Stabilization



**Microscopic
images**

Decreasing Agglomerate Size



Increasing Stability



**Pictures were
taken 2 months
after dispersing**

***0,1% CNT in PMA
0,05% W&D***

***0,1% CNT in PMA
0,1% W&D***

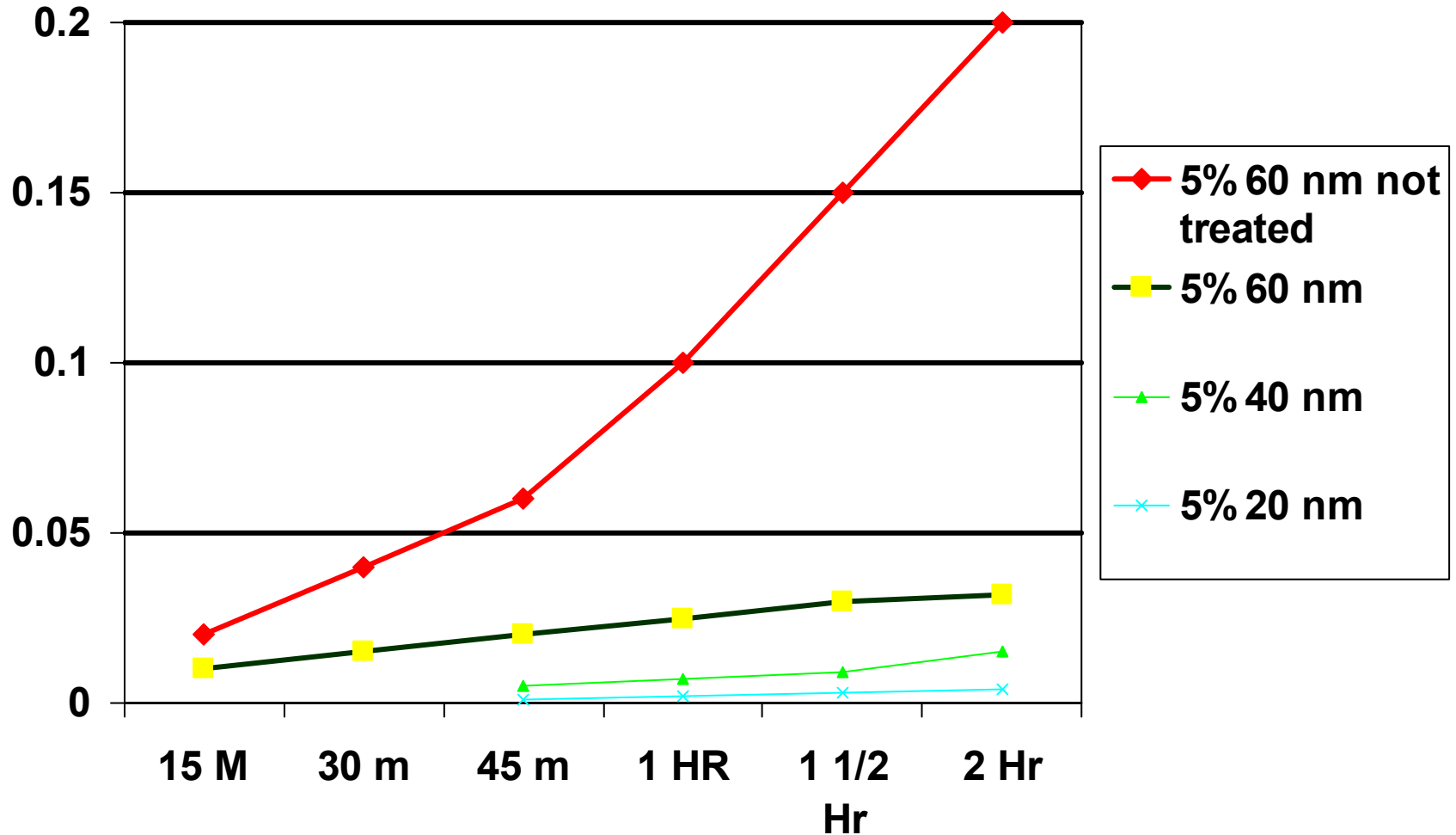
***0,1% CNT in PMA
0,15% W&D***

Dispersing Nanomaterials

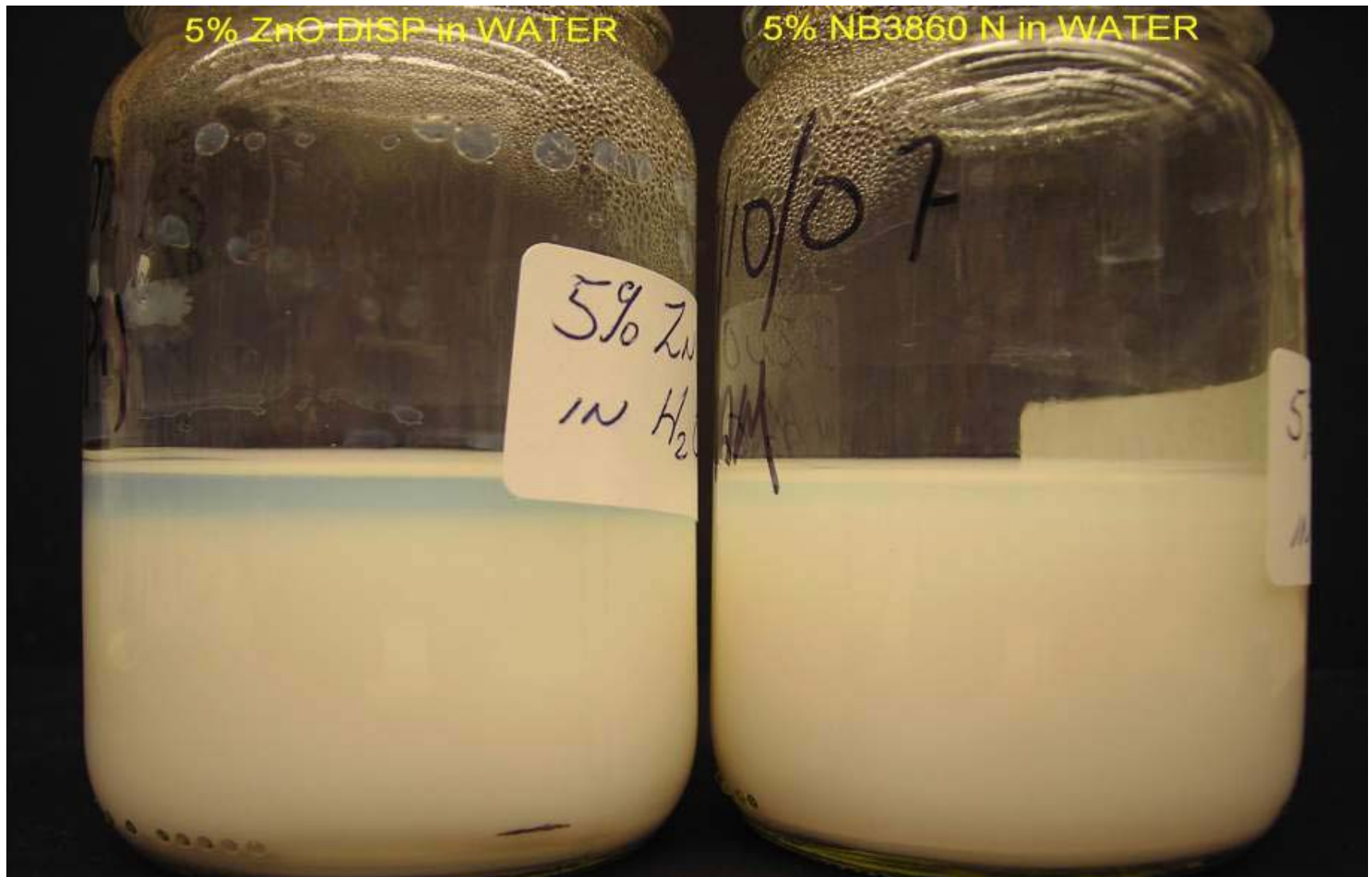
Example ZnO

Dynamometer Testing – 5% ZnO dispersions to estimate the time of settlement

Crystal density 5.6g/cc

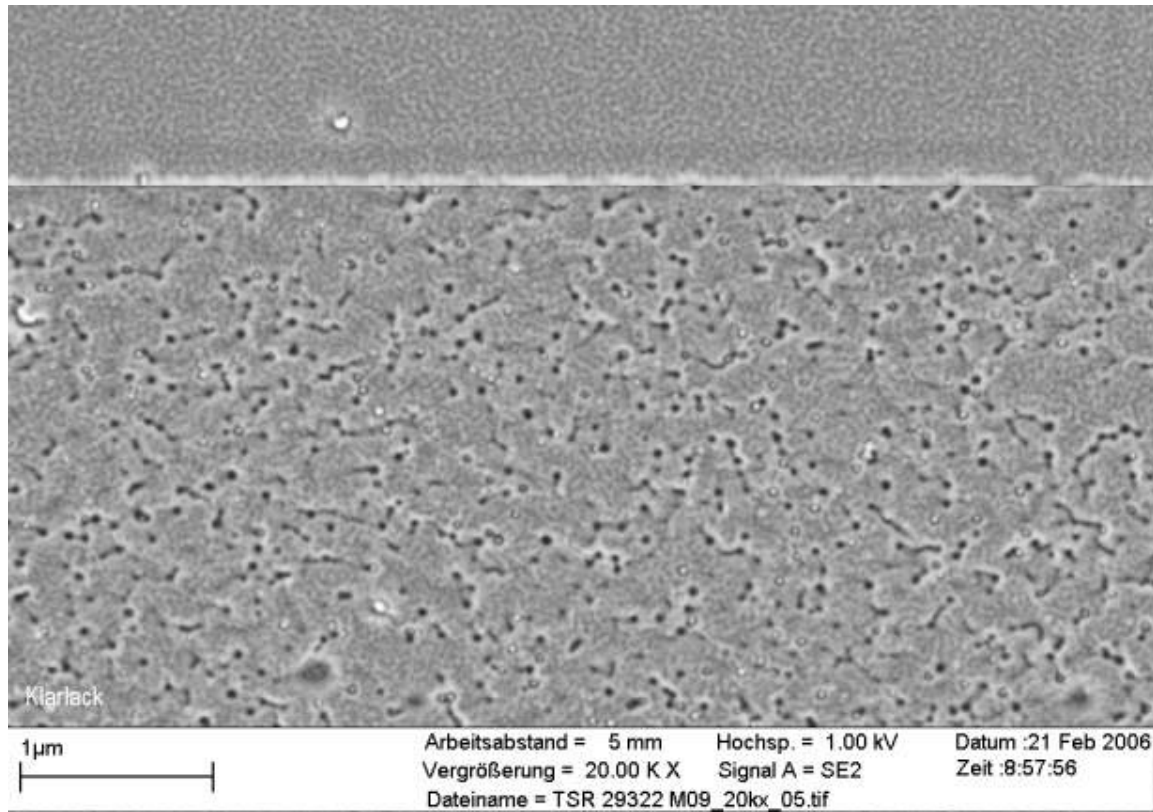


Hot box testing – 7 days at 140° F



Why Nano Dispersions Work for Scratch and Wear Resistance

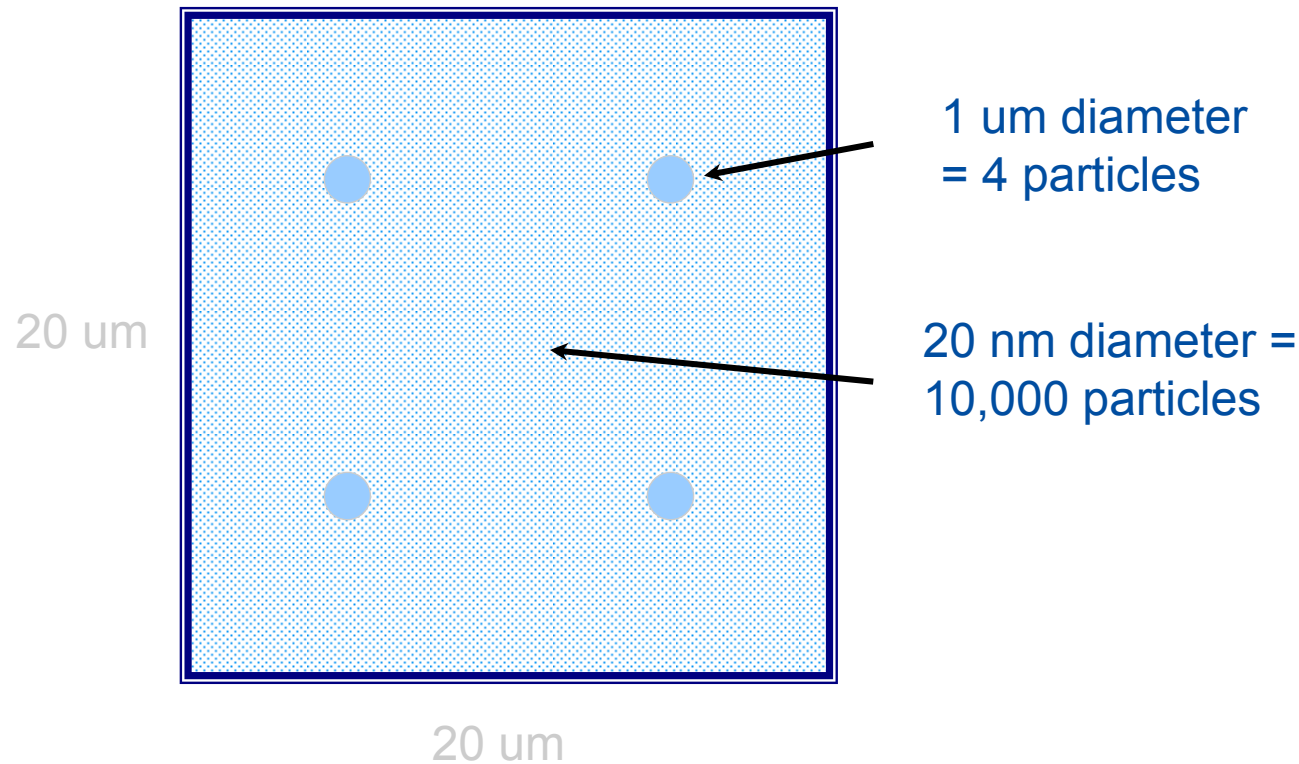
Mechanisms of Scratch Resistance - Boundary Phase Properties



- homogeneously distribution of NP in coating system
- good improvement of scratch resistance properties
 - good long time stability
 - good elasticity

Nanotechnology Advantage

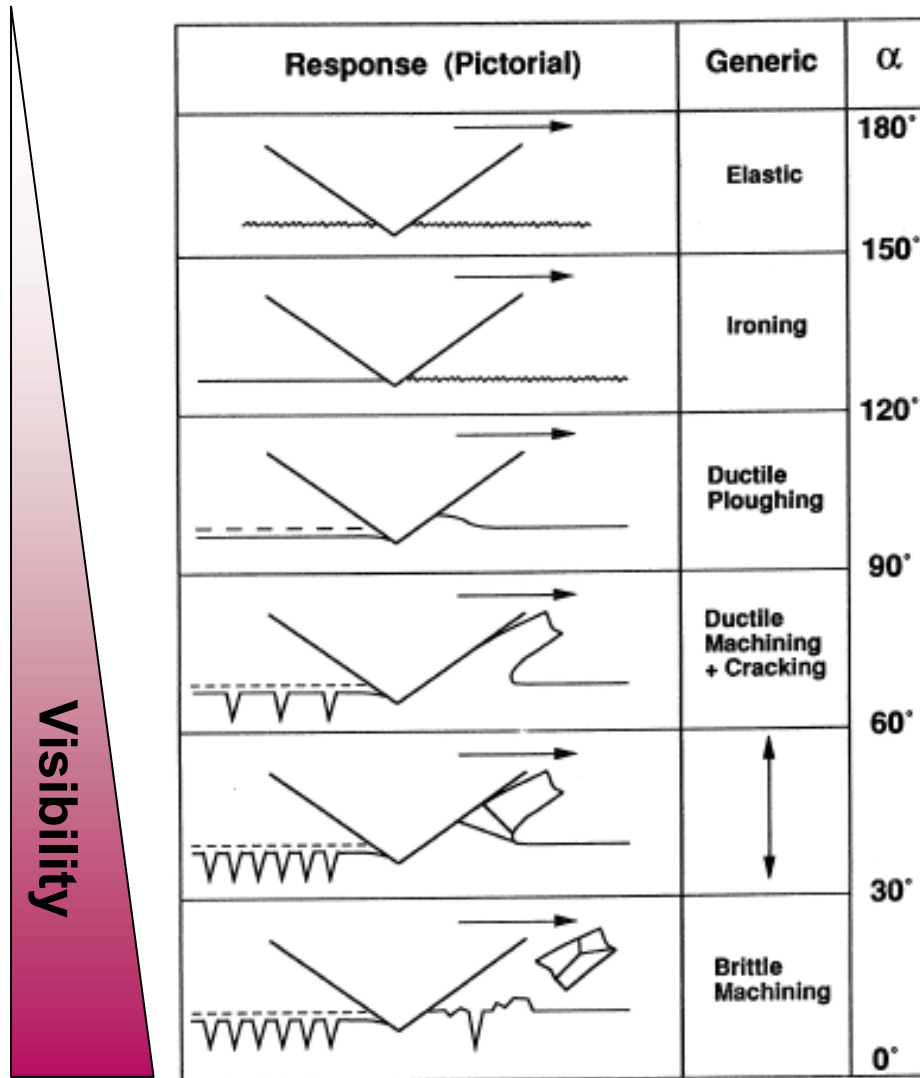
1 wt% particles dispersed in a coating:



Nanotechnology enables more particles per unit area,
and significantly decreases particle-particle separation



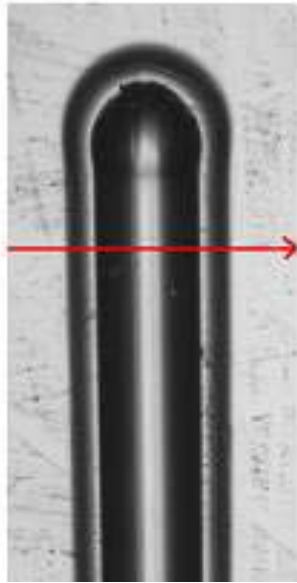
Scratch Damage of Polymeric Materials



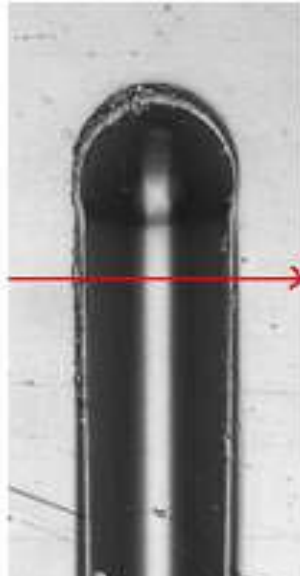
Scratch Profiles at 49 mN for Filler B system

NB-3610 / 20 nm Alumina / ST 2

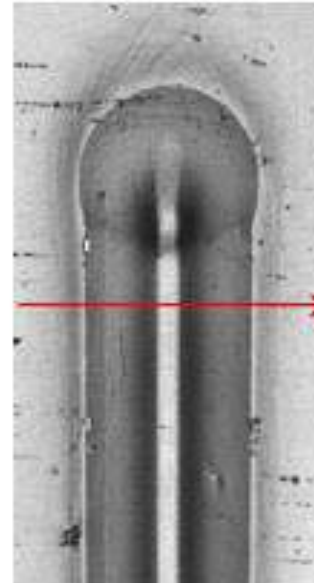
0 %



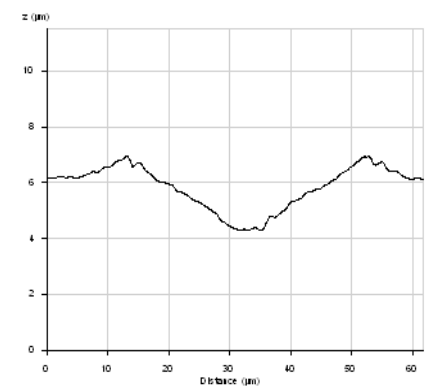
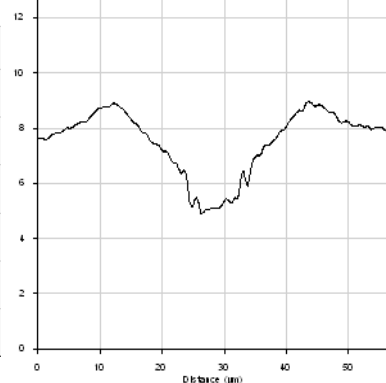
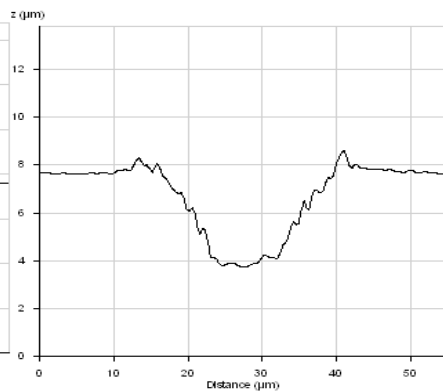
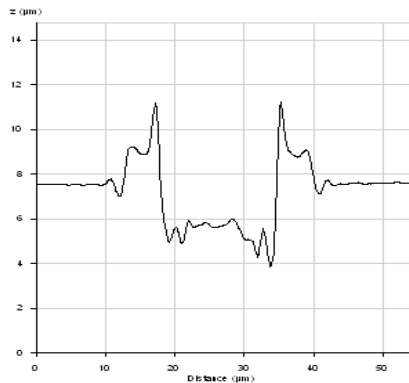
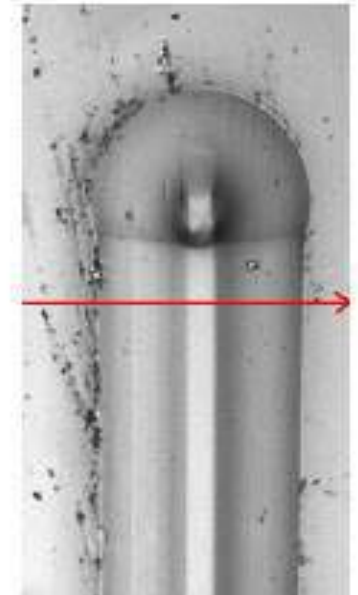
0.75 %



1.75 %



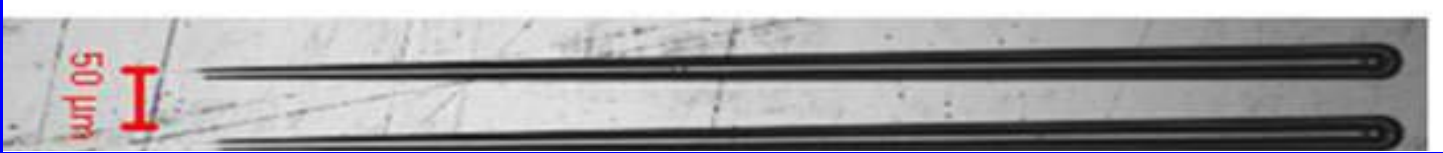
3 %



Scratch Results – Images

~ 2 % Nanoparticles

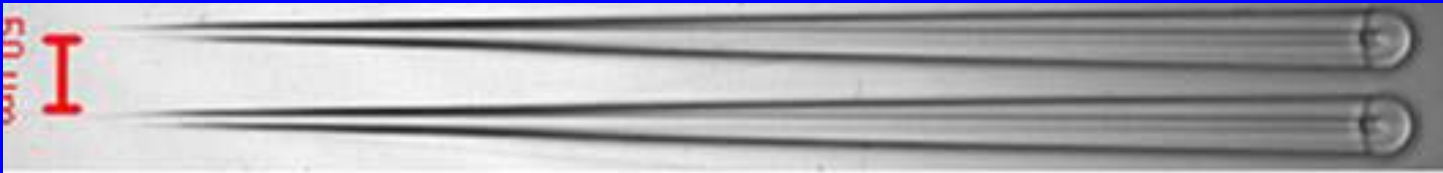
Unfilled



NB-3610



NB-3650



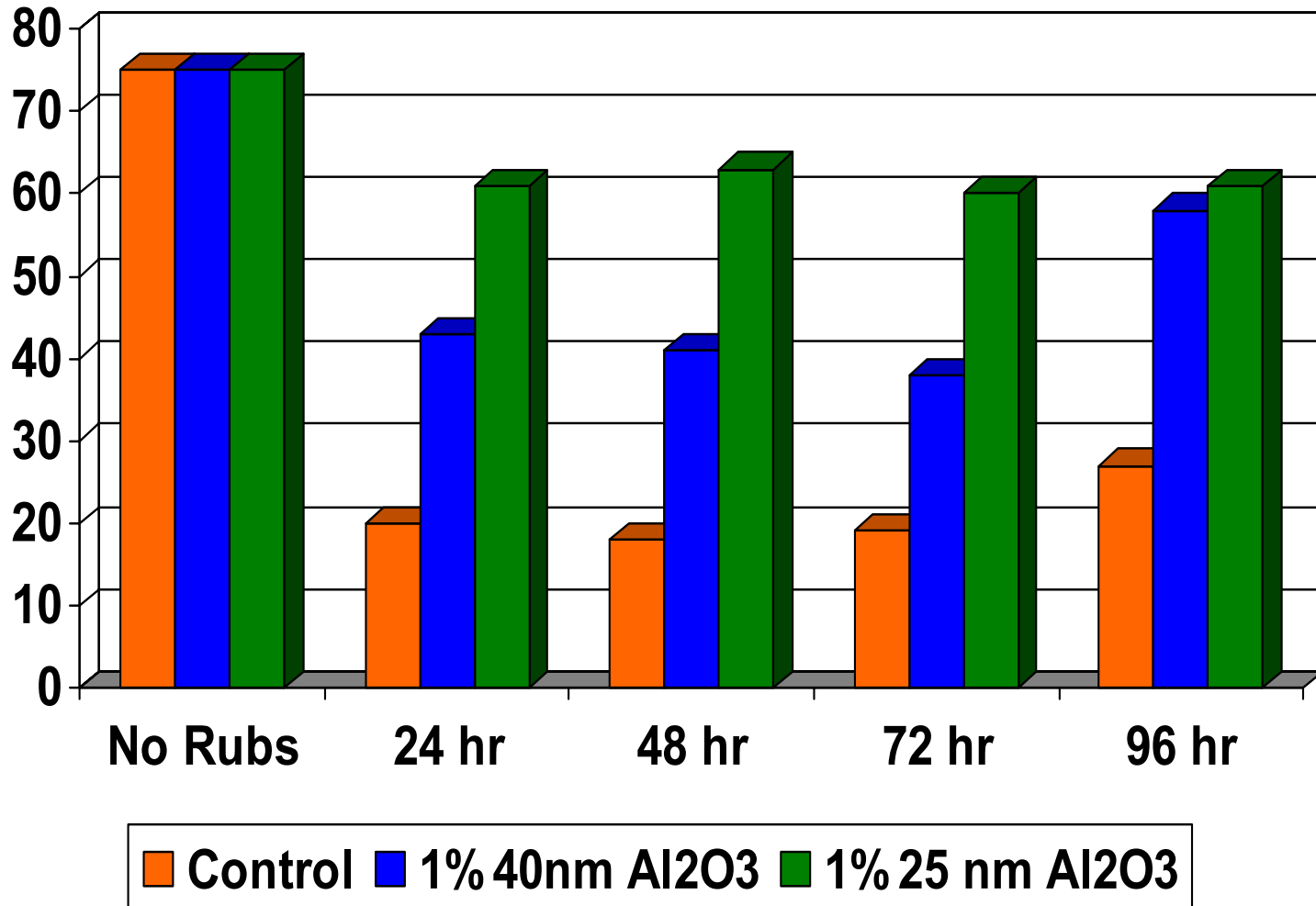
Control

25 nm Al_2O_3

Scratch Resistance of Aqueous Acrylic AD Coating

High Gloss over time

Gloss 20 ° [%], ASTM D 2486 abrasion tester, 100 cycles 00 steel wool



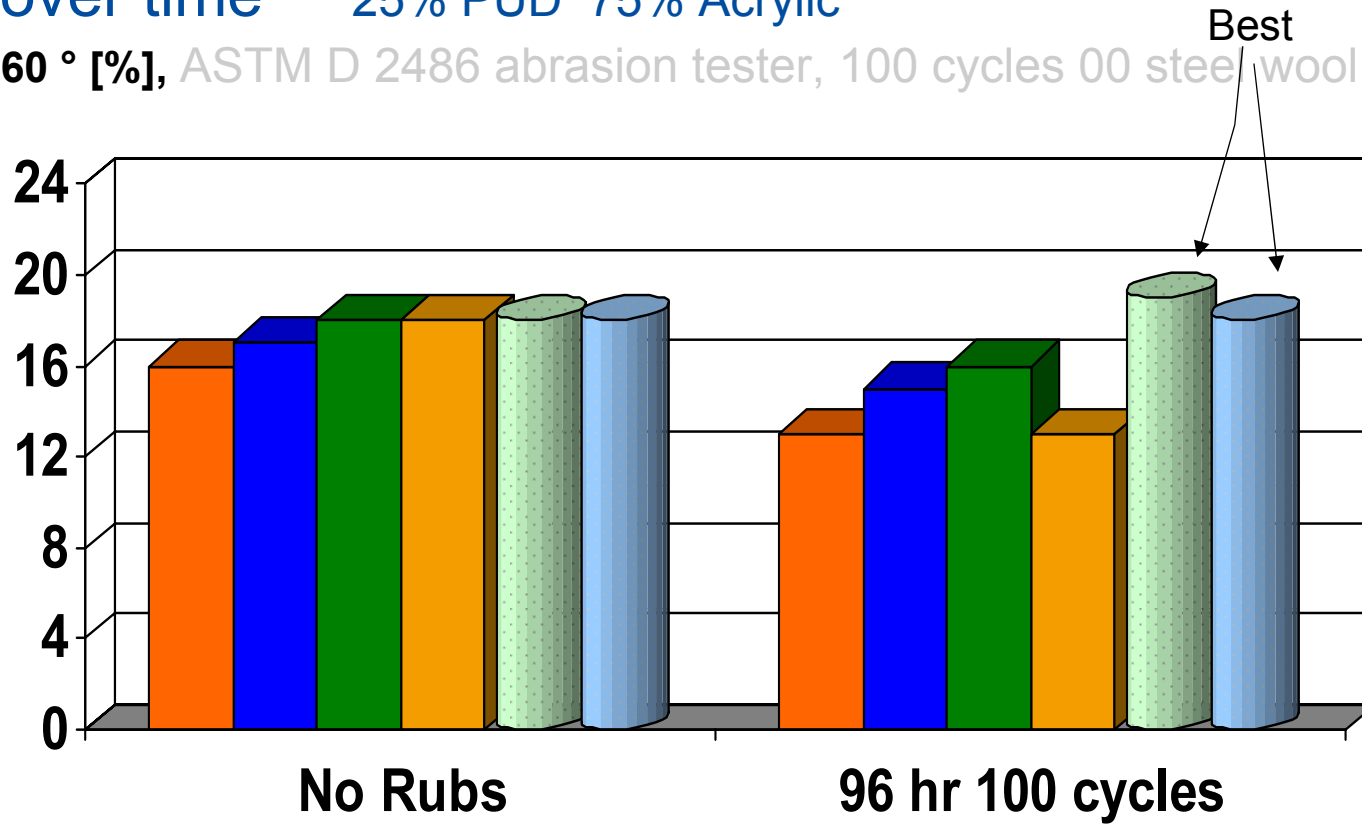
Effect of Nano-particles in Aqueous AD Coatings

1.0% Loading of Nano Alumina

- improves scratch resistance (gloss retention)
- 20nm alumina imparts early resistance properties (24 hrs)
- 40 nm requires longer dry time 96 hours for same properties

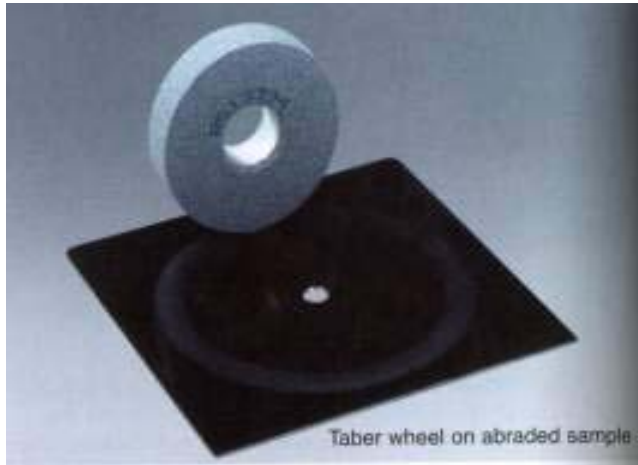
Scratch Resistance of Aqueous Acrylic/Urethane AD Satin over time 25% PUD 75% Acrylic

Gloss 60 ° [%], ASTM D 2486 abrasion tester, 100 cycles 00 steel wool



- Control
- Wax
- 1% 40nm Al2O3
- 1% 60 nm Al2O3
- 1% 60 nm Al2O3 + wax
- 1% 40nm Al2O3 + wax

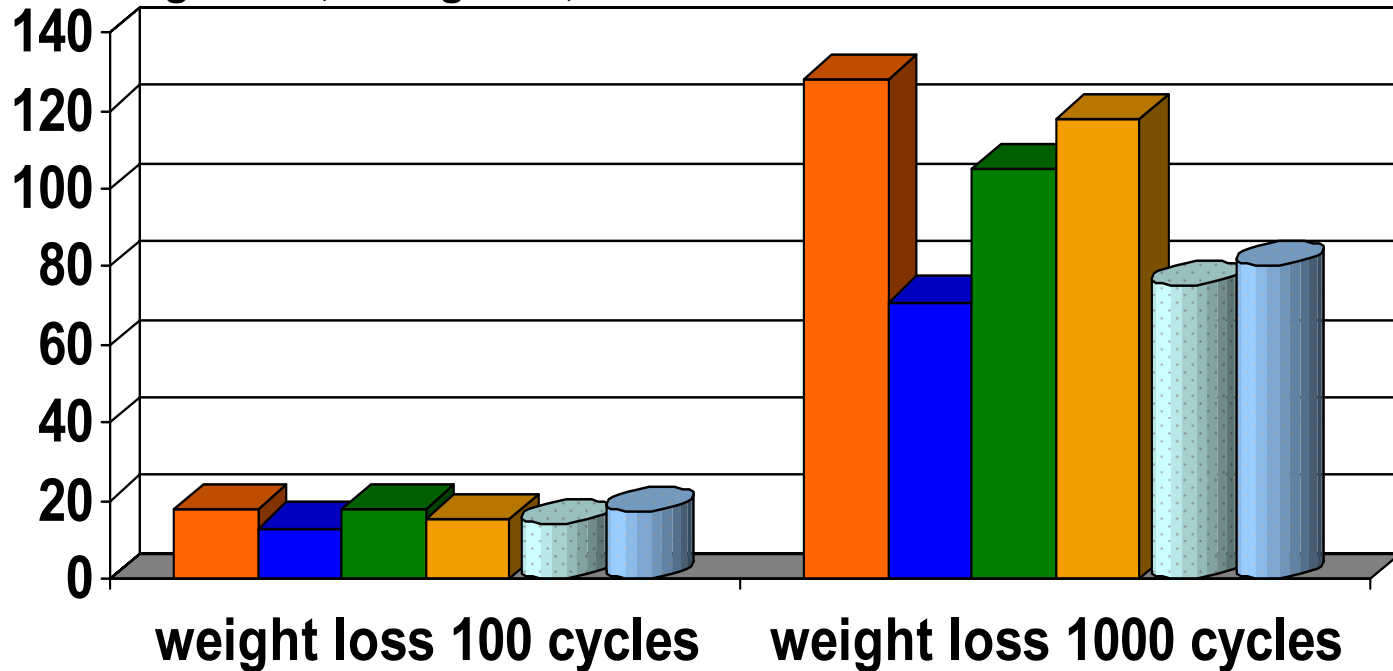
Taber Abrasion



Abrasion Resistance of Aqueous Acrylic/Urethane AD Satin Finish

25% PUD 75% Acrylic

CS 10 Abrading wheel, 1000g load, 3X4 mil WFT coats



Control

Wax

1% 40nm Al2O3

1% 60 nm Al2O3

1% 60 nm Al2O3 + wax

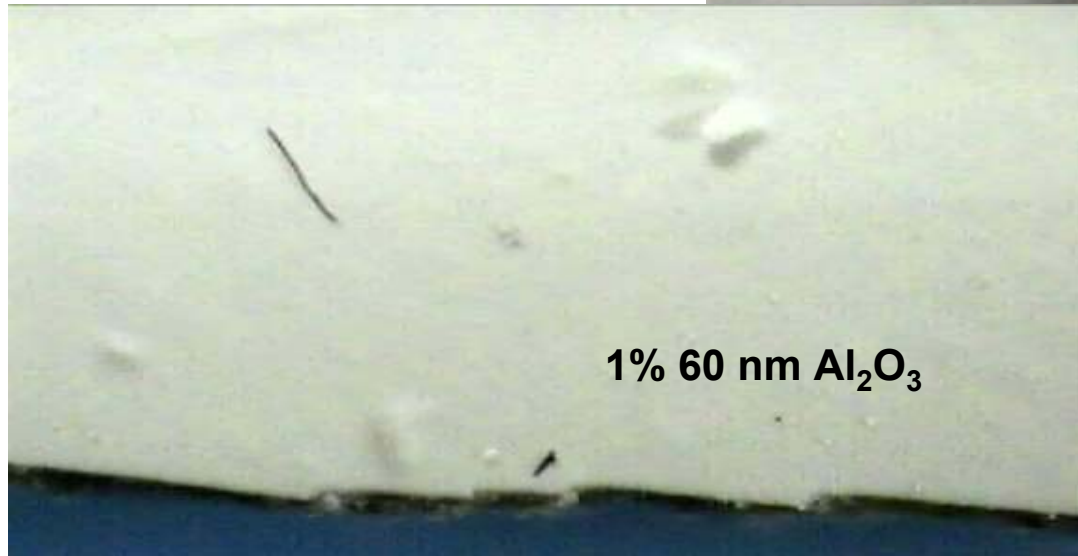
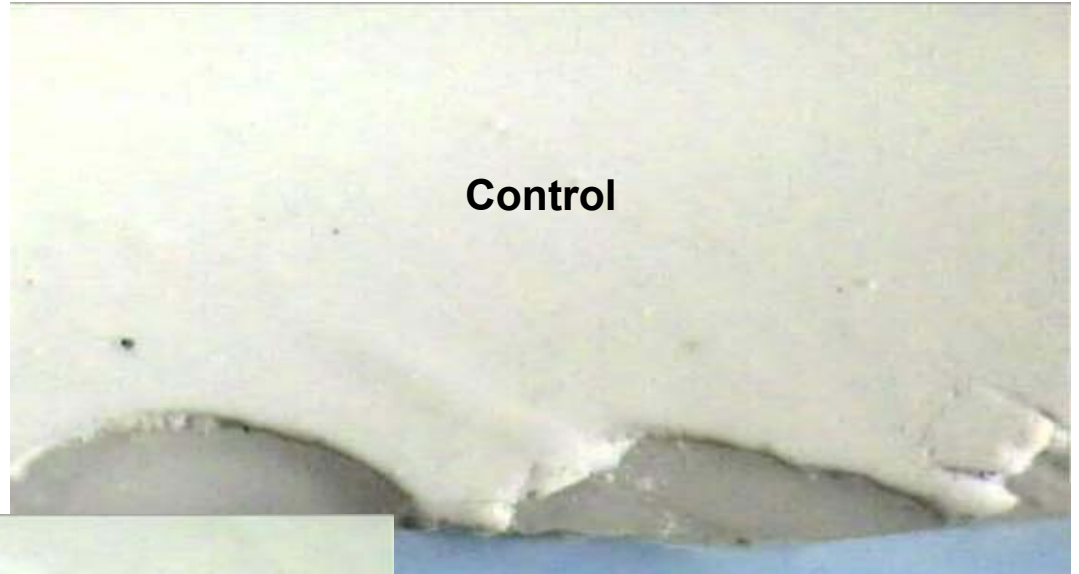
1% 40nm Al2O3 + wax

Effect of Nano-particles in Aqueous AD Coatings

1.0% Loading of Nano Alumina

- improves scratch resistance (gloss retention)
 - 20nm alumina imparts early resistance properties (24 hrs)
 - 40 nm requires longer dry time 96 hours for same properties
-
- Improves burnish resistance of matted coatings
 - Nano-Alumina with wax for best burnish resistance
 - Nano-Alumina with wax for best Taber Abrasion resistance

Adhesion and Scratch Resistance of Acrylic Water borne Coating to Fiberglass



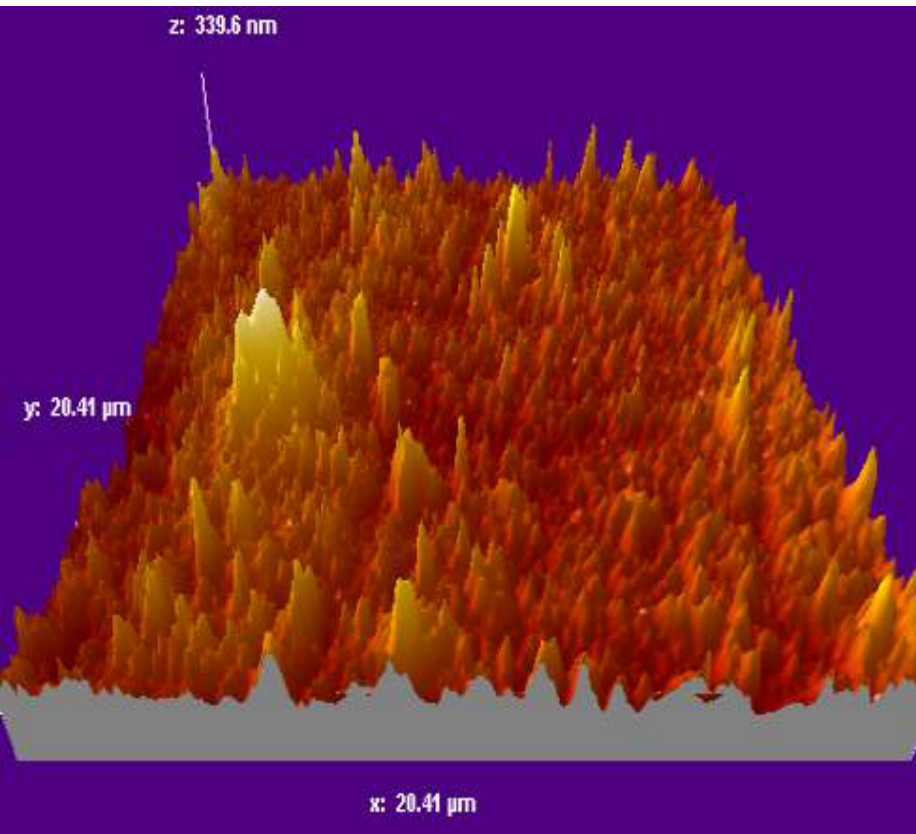
Effect of Nano-particles in Aqueous AD Coatings

1.0% Loading of Nano Alumina

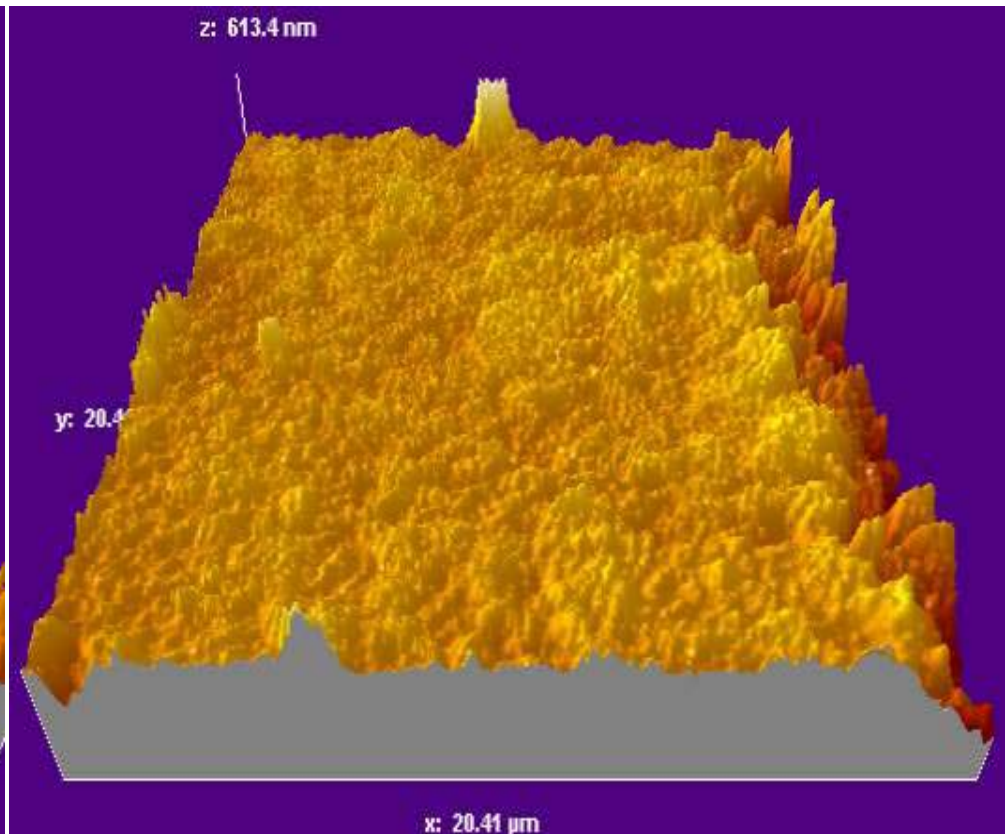
- improves scratch resistance (gloss retention)
- 20nm alumina imparts early resistance properties (24 hrs)
- 40 nm requires longer dry time 96 hours for same properties
- Improves burnish resistance of matted coatings
- Nano-Alumina with wax for best burnish resistance
- Nano-Alumina with wax for best Taber Abrasion resistance
- Improves stress relief resulting in better adhesion

AFM Control

Gloss 20 ° [%] Haze, modified abrasion scrub tester, ASTM D2486



No Rubs

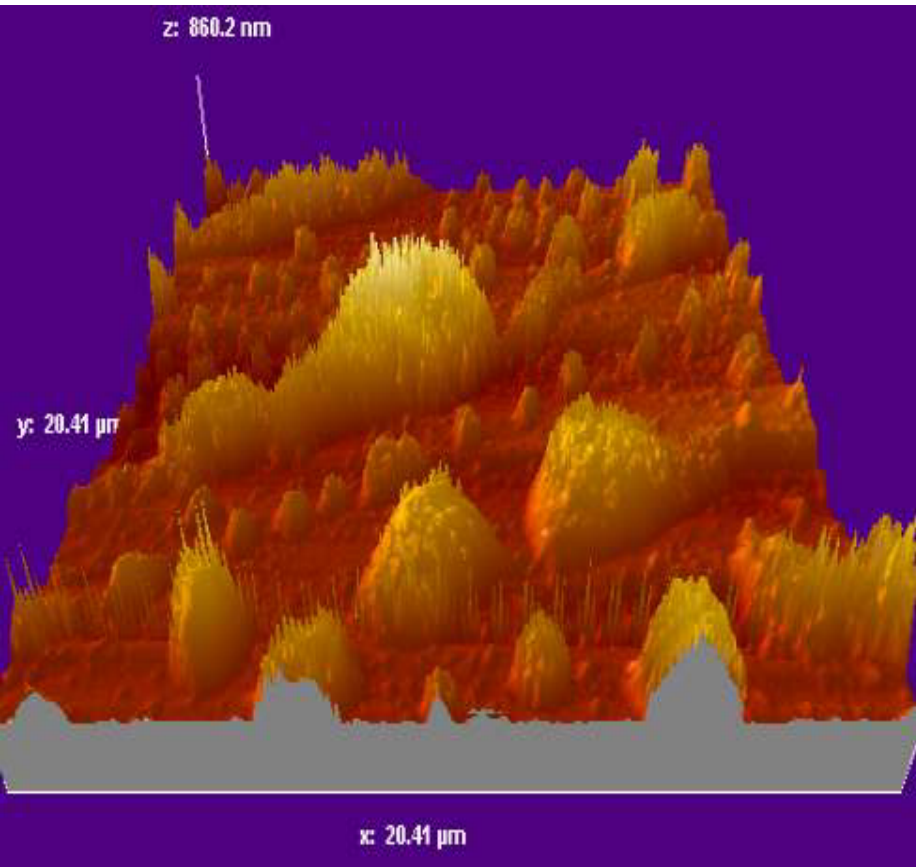


1000 Rubs

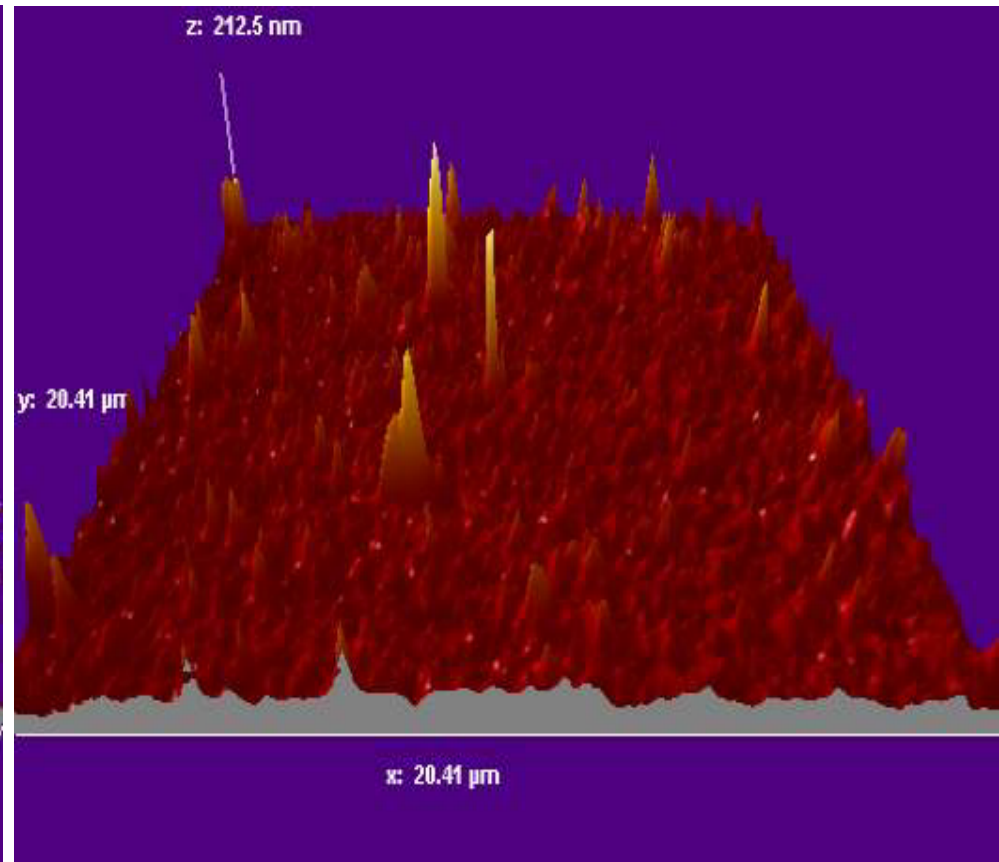
AFM

1.2% (40nm) Nano Alumina

Gloss 20 ° [%] Haze, modified abrasion scrub tester, ASTM D2486



No Rubs

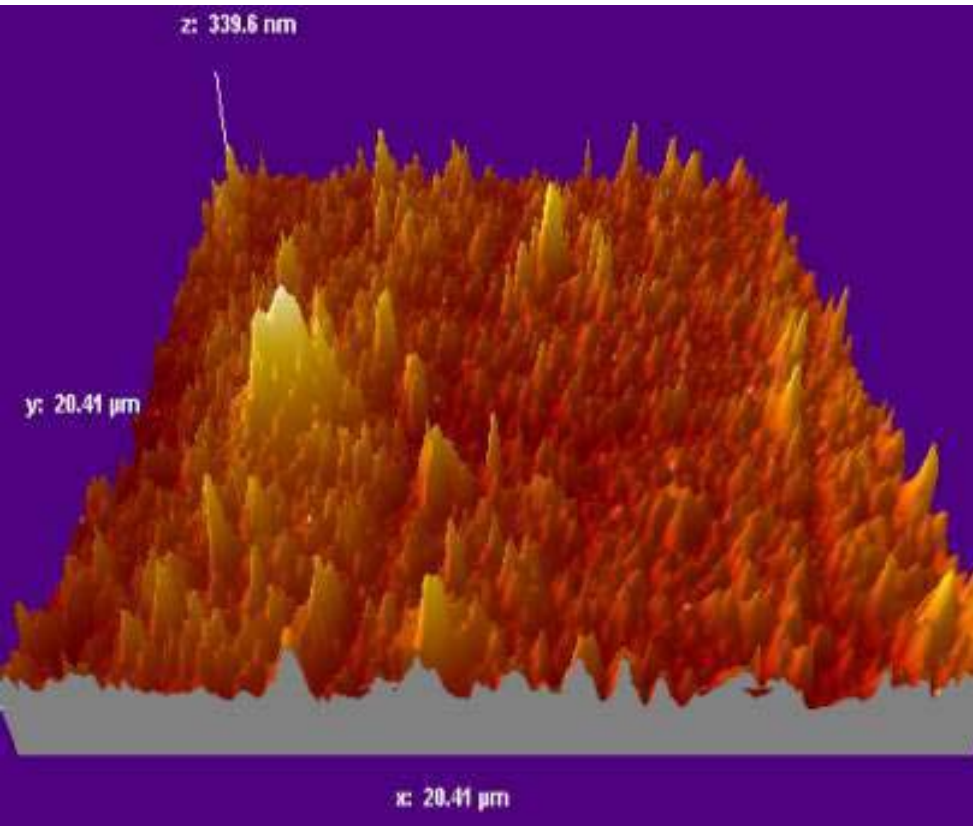


1000 Rubs

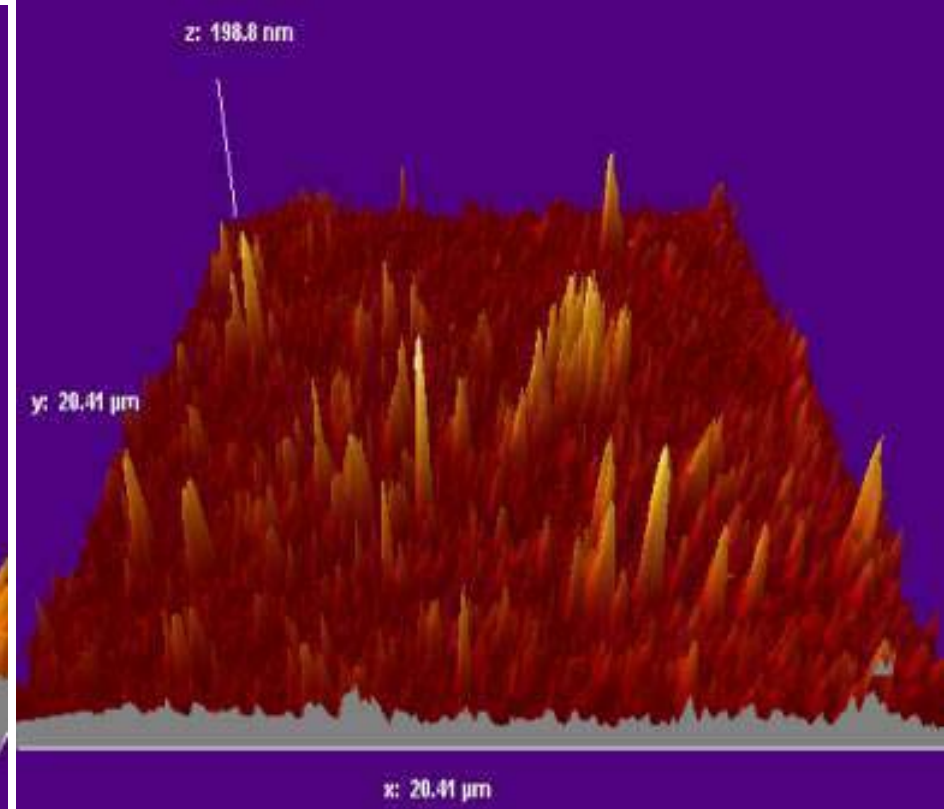
AFM

1.2% Nano Alumina (25 nm)

Gloss 20 ° [%] Haze, modified abrasion scrub tester, ASTM D2486



No Rubs



1000 Rubs

500 rubs

Control



UV Clear

500 rubs

Control



UV Clear w/ 1.2% Nano Alumina

Effect of Nano-Particles on Scratch resistance

- Prevents gloss loss in high gloss systems
- Prevents burnishing in flatted and satin systems
- Smaller nano-particles provide greater scratch resistance



UV light damages surfaces

Surfaces exposed to direct sunlight usually suffer from the solar UV radiation that destroys organic compounds such as

- dyes and pigments
- binders
- polymers
- organic substances in wood



Types of UV-Absorbers for Coatings

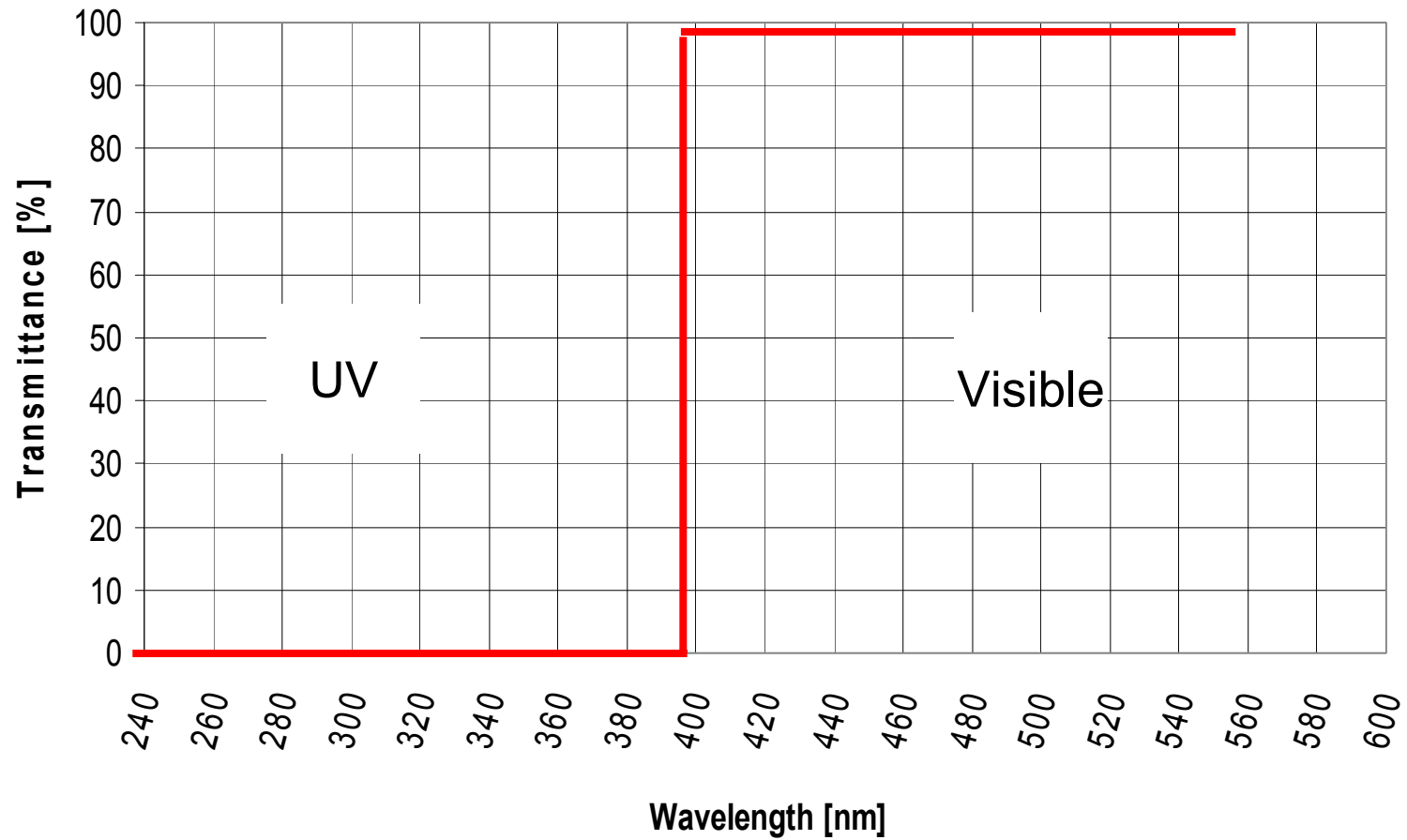
Organic UV absorbers and HALS

- Absorbers
 - Hydroxyphenylbenzotriazoles
 - Hydroxybenzophenones
 - Hydroxyphenyl-S-triazines
 - Oxalic anilides
- HALS (Hindered Amine Light Stabilizers)

Inorganic UV absorbers

- ***Zinc oxide***
- **Cerium oxide**
- Titanium dioxide
- Transparent iron oxide

The Ideal UV Absorber



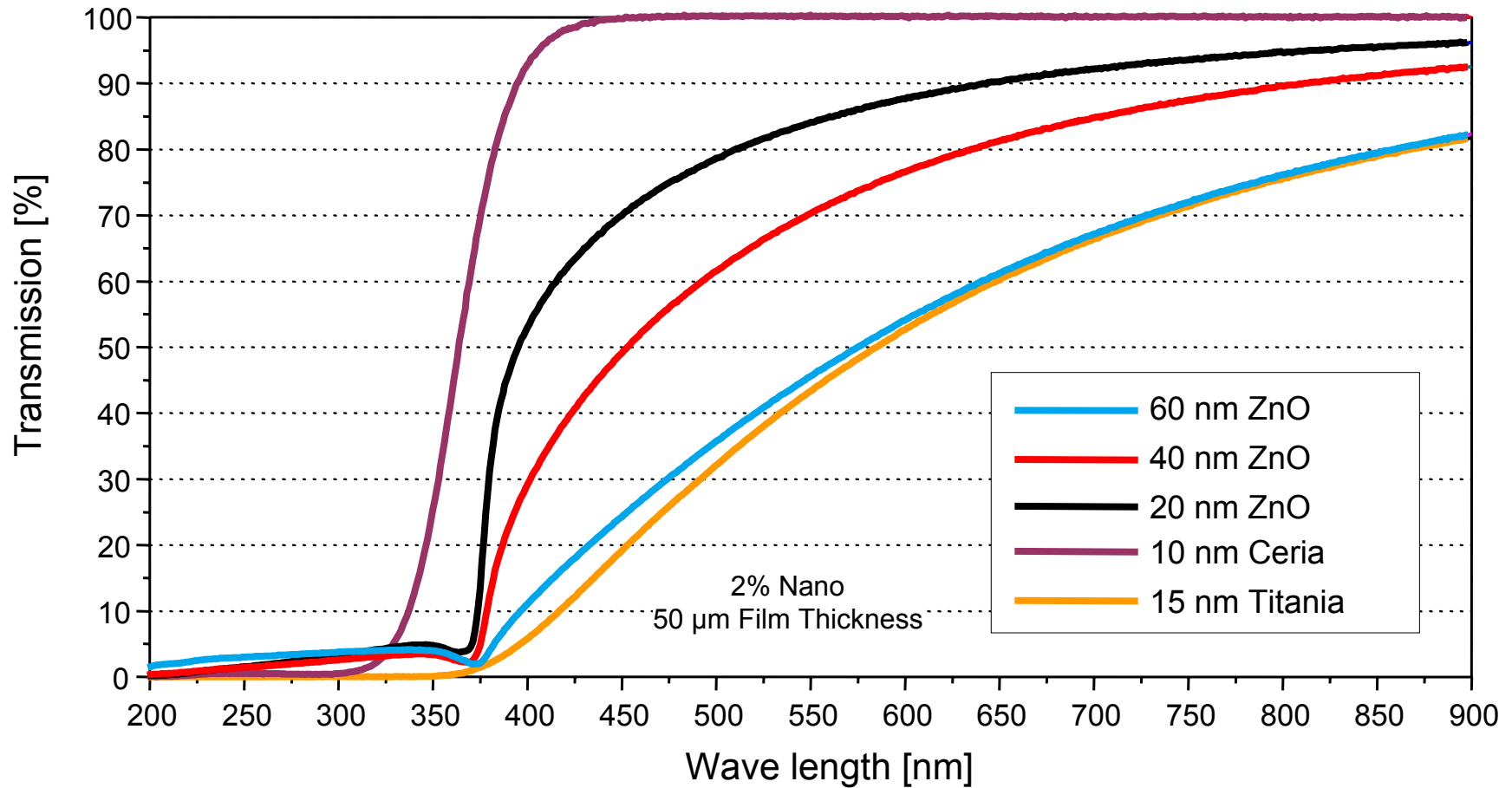
Nanoadditives for UV protection

Property	ZnO*	CeO ₂	TiO ₂	Organic Absorbers
Clarity	o	+	-	+
Long Term Stability	+	+	+	-
No Migration	+	+	+	-
No Photoactivity	+	+	-	+
Chemical Stability	-	+	+	+
UV-Absorption Edge	≈ 375 nm	≈ 350 nm	≈ 375 nm	varies
Absorption Efficiency	o	o	+	+

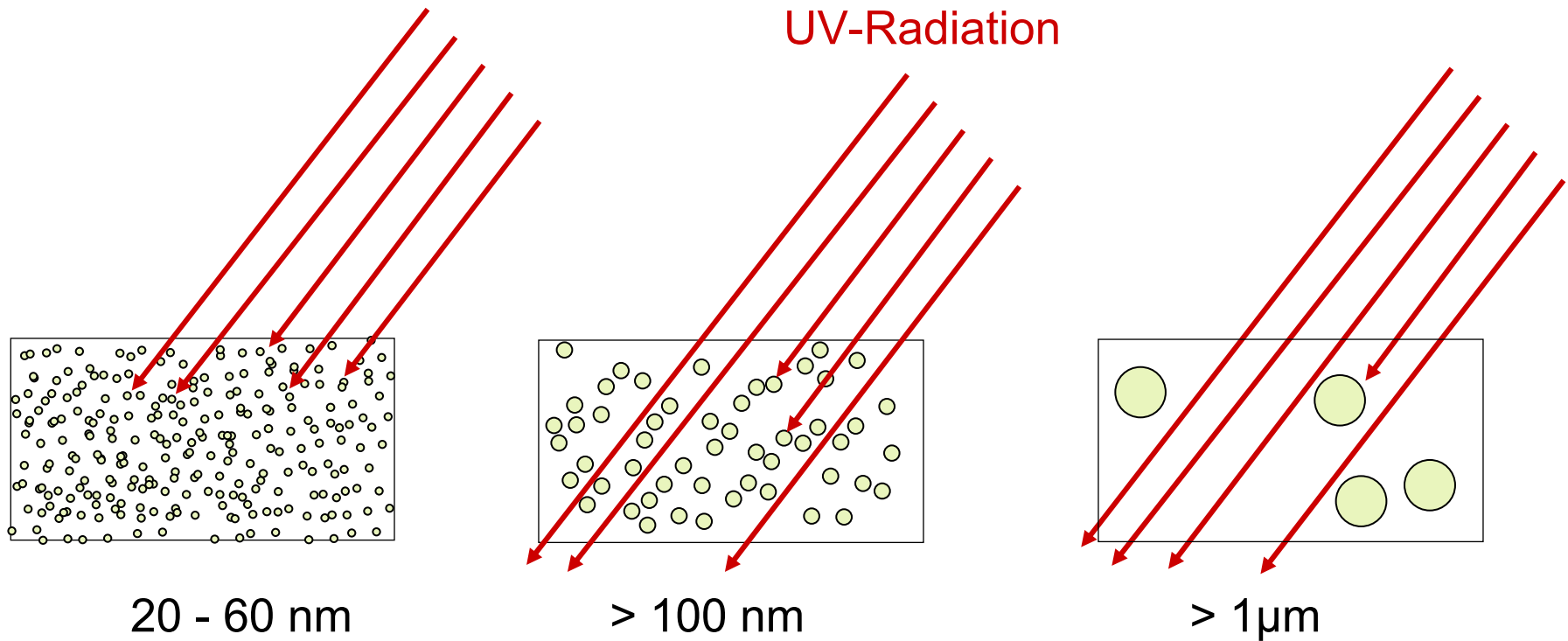
*: ZnO was listed in Europe as Biocide until 2005

Nanoadditives for UV protection

Comparison of ZnO, Ceria and Titania

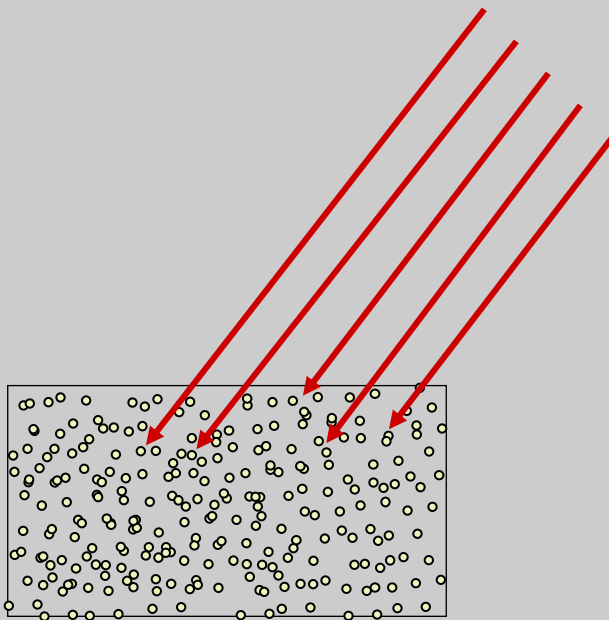


Uniform distribution of the proper particle size ZnO ensures maximum substrate and coating protection



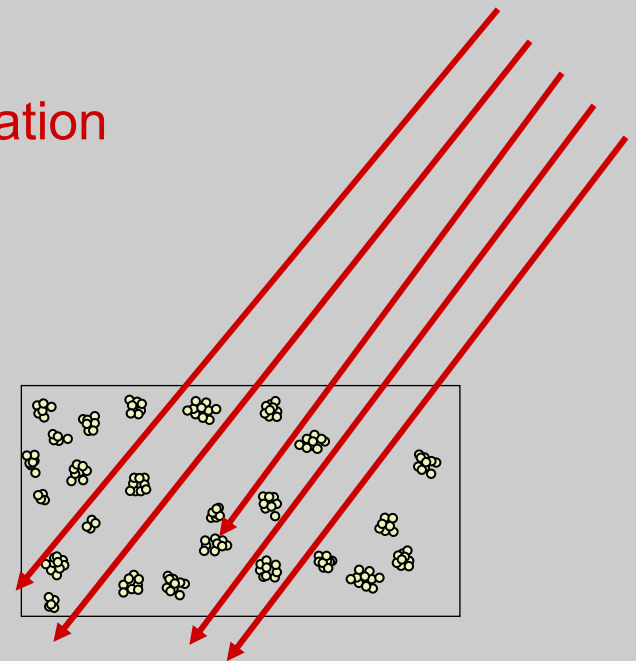
The smaller and finer the ZnO particle distribution the greater the protection!

Optimum Stabilization of Nanoparticles is necessary to see benefits of Nanotechnology



no agglomerates

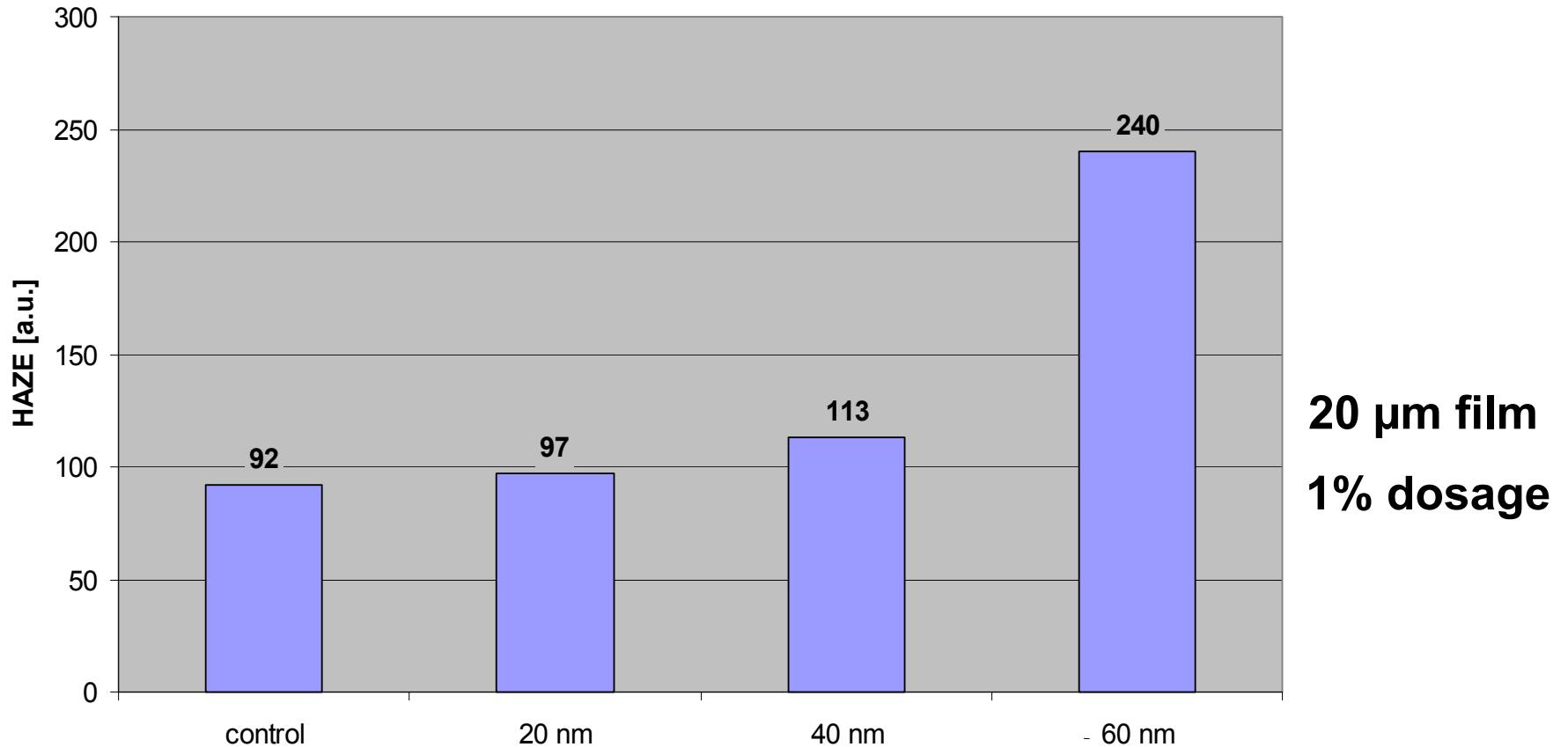
UV-radiation



agglomerates

Transparency of NANOBYK-3800 series

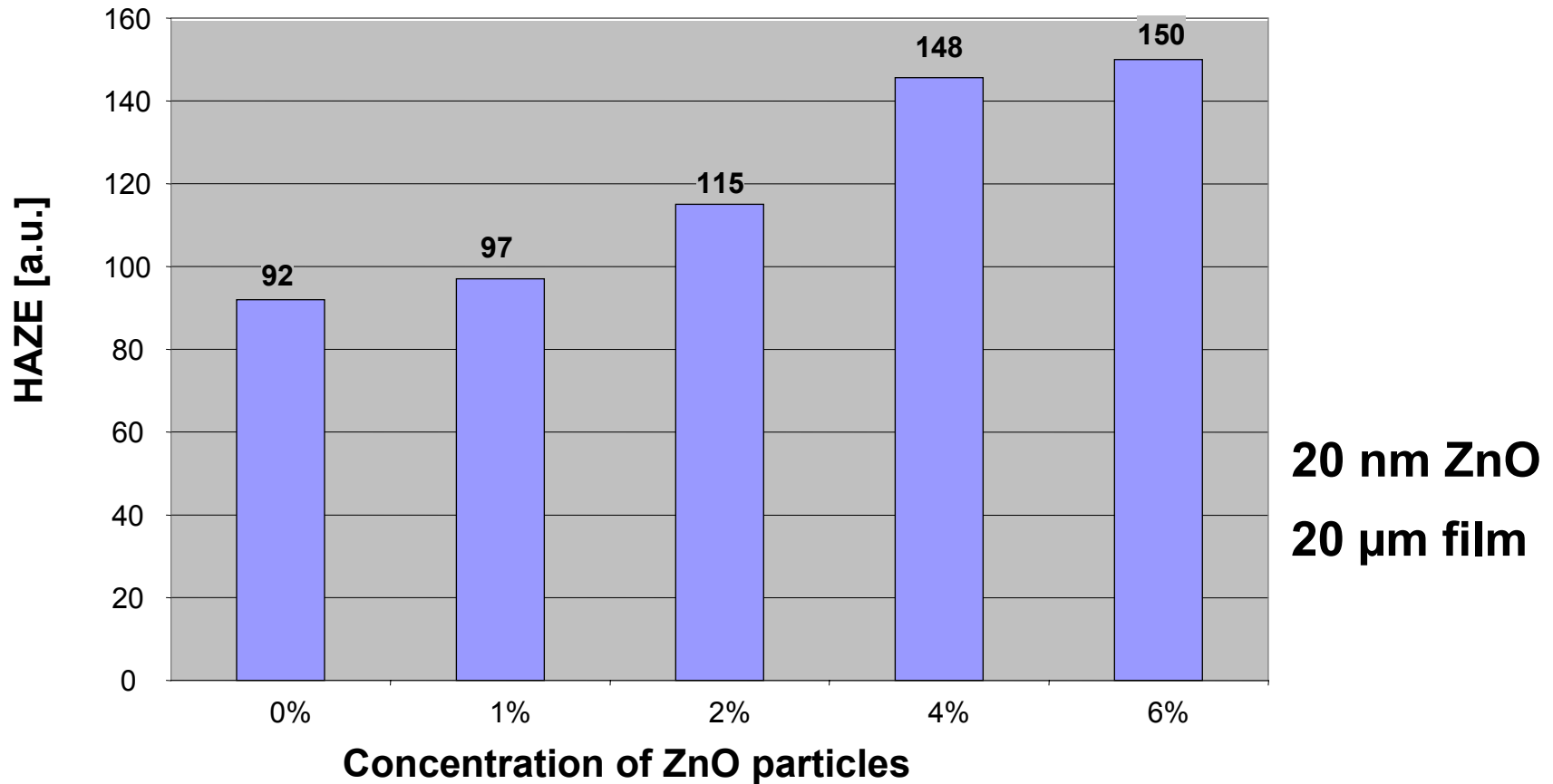
Influence of particle sizes



The smaller the particles the lower the haze!

Transparency of NANOBYK-3800 series

Influence of particle concentration

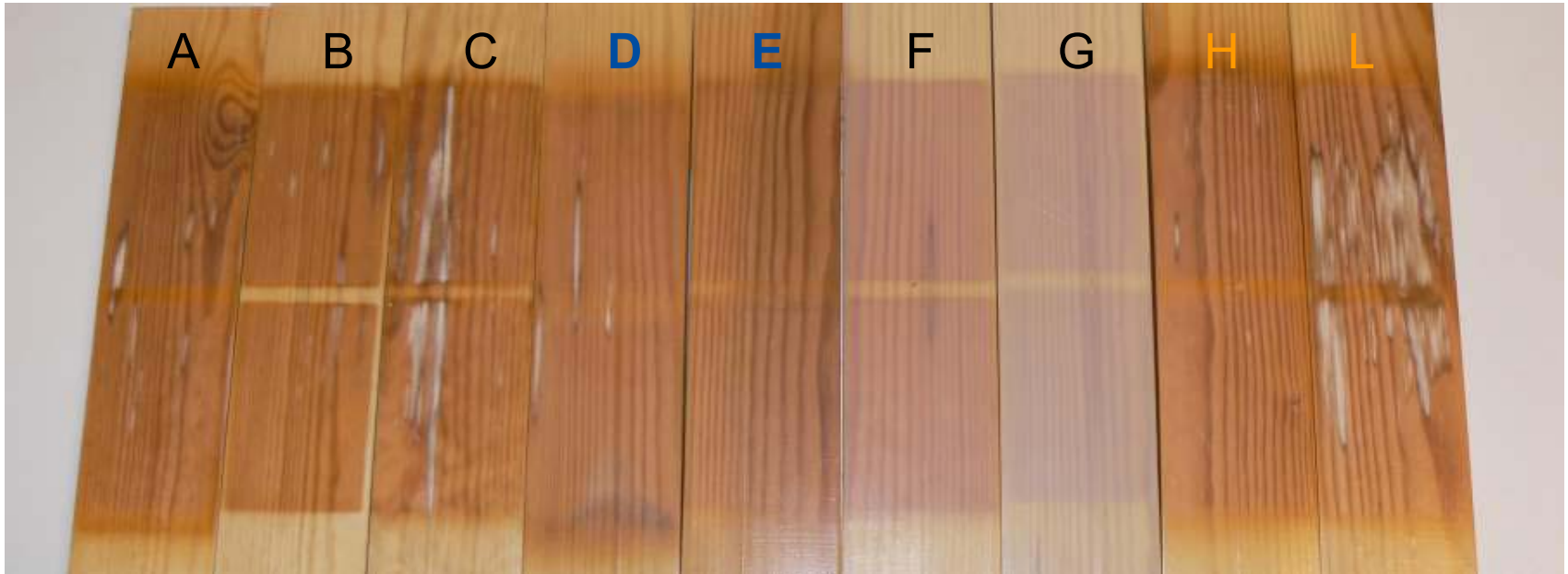


The lower the particle concentration the lower the haze!

Nanoscale ZnO for UV protection

Thin Film (30 μm) Coating – 2000 h QUV-A Testing

Furniture & Parquet Coating



A: Control

B: 0,5% Organic Absorber

D: 0,5% 40 nm ZnO

F: 0,5% 15 nm TiO₂

H/L: Competitive ZnO Samples

C: 1,0% Organic Absorber

E: 1,0% 40 nm ZnO

G: 1,0% 15 nm TiO₂

Results in Water Borne Coatings

Thin Film Glazing (Bayhydrol 2342 Aqueous Aliphatic)

750h QUV-B Dry Testing

Control

2.5% 40nm ZnO

2.5% 20nm ZnO



Latest's Results from Water Based Coatings

Thick Film (120 μm) Coating – 1000 hrs QUV-A Dry Testing

Furniture & Parquet Coating

Control

2% 20nm ZnO

2% 40nm ZnO

2% 60nm ZnO



Nanoadditives for UV protection

Aqueous-based Acrylic PUD Formula – Natural Exposure: 15 months – 10 nm Ceria*

Douglas fir (1% on active matter)



Ceria



**Conventional
organic UV
absorber**



**Organic UV
absorber +
Huls**



Reference

***: Patent Protected Technology**

Nanoadditives for UV protection

Aqueous-based Acrylic PUD Formula – 1600 h Xenon Test – 10 nm Ceria*

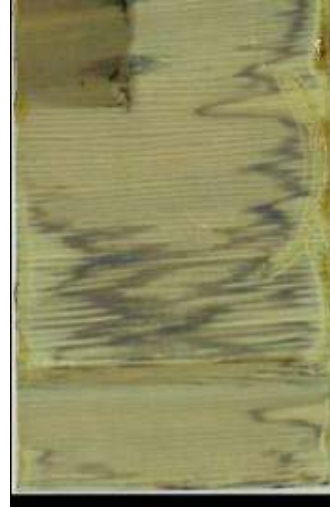
Red Cedar (1% on active matter)



Ceria



**Conventional
organic UV
absorber**



**Conventional
mineral UV
absorber**



Reference

*: Patent Protected Technology

Conclusion

The Difference Dispersion Brings



Transparency and functionality is the key driver for nanotechnology in paint application

- **Synthesis, Material, Particle size, and Boundry Phase** determine nanomaterials performance benefits
- **Low refractive index** and **high efficiency** are key in nanotechnology for paint application.

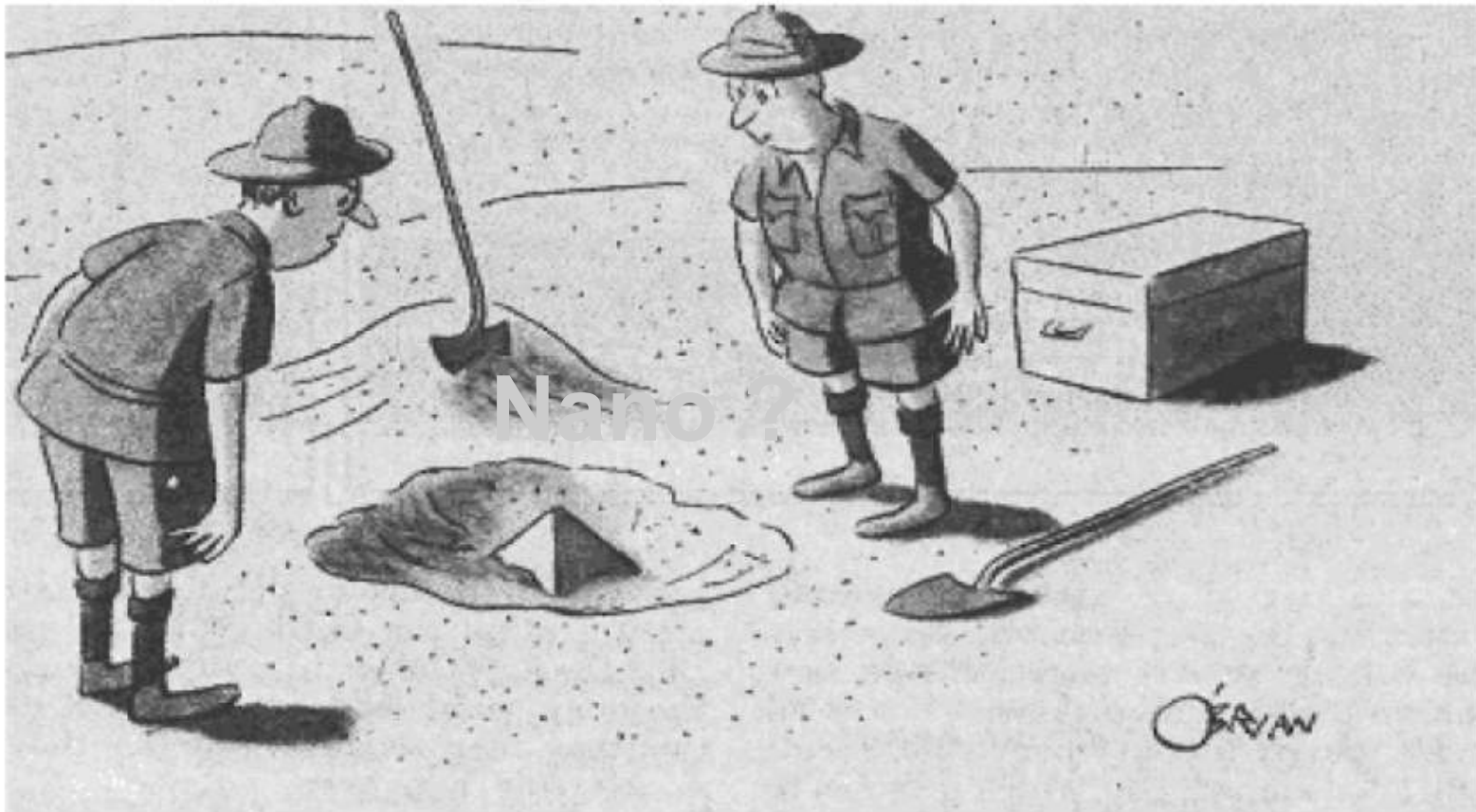
Nanoparticles improve

- **Scratch resistance of high gloss high transparent coatings to low gloss transparent coatings**
 - UV Coatings: 0,3 – 2,0% Nanoparticles
 - 2K Coatings: 1,0 – 2,0% Nanoparticles
 - Air-Drying solvent based coatings: 0,3 – 2,0% Nanoparticles
 - Air-Drying water based coatings: 0,3 – 3,0% Nanoparticles
 - Forced-Dried solvent based coatings: 1,0 – 4,0% Nanoparticles

UV-Protection in transparent and pigmented coatings **1,0 – 6,0% NP**

NANOBYK-3650: Handling Ease





“This could be the discovery of the century. Depending, of course, on how far down it goes.”