

# Nanoparticles Improve Coating Performances



presented by

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Manager Nanotechnology

*"The use of Nanoadditives in plastic and coating composites"*  
ICNT, San Francisco 2005

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## Out-line

- Definition of Nanotechnology
- Current applications in coatings and compounds
  - Scratch resistance
    - Influence of surface treatments
    - Nano-Additives for UV curable applications
    - Nano-Additives for solvent-borne coatings
  - UV-stability
- Conclusions

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## Applications / End-Uses of BYK Chemie



Automotive OEM



Printing Inks



Coil Coatings



Wood/Furniture Coatings



Industrial Coatings



Polyurethane Foams



Pigment Concentrates



Powder Coatings



Compounds



Can Coatings



PVC Plastisols



Ambient Curing Resins



Architectural Coatings



Thermoplastics



Automotive Refinish

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## Let's go Nano!



**This is really an innovative approach  
But I'm afraid we can't consider it.  
It's never done before**

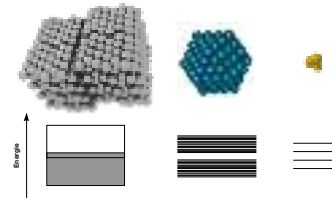
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# Nanotechnology

## • Change in properties due to a change in size

- Conductivity of metals  $\approx 2 \text{ nm}$
- Fluorescence of Q-dots  $\approx 10 \text{ nm}$
- Transparency of ceramics  $\approx 20 \text{ nm}$
- Colour of metals  $\approx 50 \text{ nm}$
- Stiffness of metals  $\approx 250 \text{ nm}$
- Ductility of ceramics  $\approx 500 \text{ nm}$

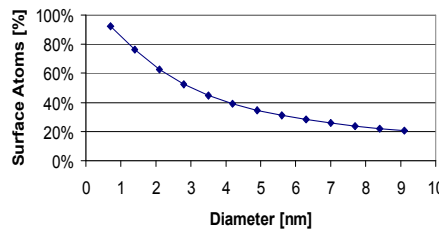


## • Increase in specific surface area

- Reactivity
- Surface energy

## • Shape

- Anisotropy of properties



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# Nanoparticles

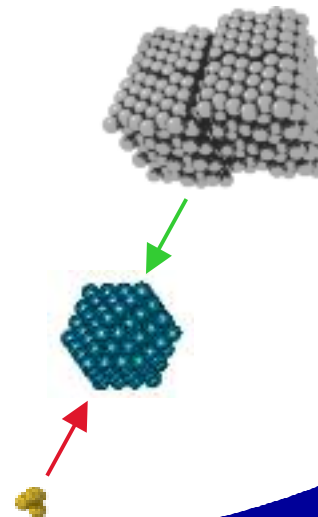
## • Basic Processes

### Top-Down

- Grinding

### Bottom-up

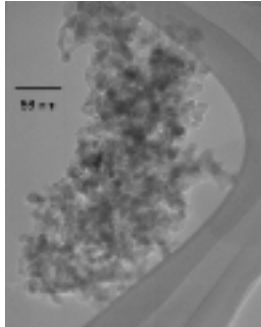
- Gas Phase Synthesis
- Chemical precipitation
- Sol-Gel-Chemistry
- Emulsion techniques
- Plasma-spraying
- Spray drying
- Hydrothermal synthesis
- ...



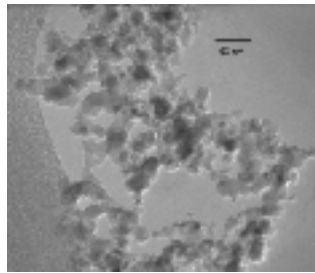
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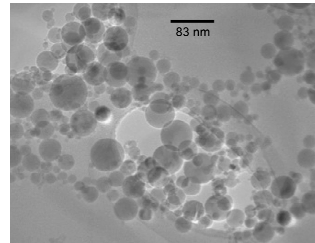
## Nanoparticles



Precipitated Al<sub>2</sub>O<sub>3</sub>



Flame Synthesis Al<sub>2</sub>O<sub>3</sub>



PVS Al<sub>2</sub>O<sub>3</sub>

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## Nanoparticles

### Material

- Silica
- Alumina
- Zirkonia
- Diamond
- Silicone carbide
- Layered Silicates
- Zinc oxide
- Titania
- Ceria
- Iron oxide
- Cupper oxide /Silver oxide
- Metals
- ITO/ATO
- Carbon nanotubes
- Silsesquioxane
- Dendrimers
- Capsules
- .....

### Property

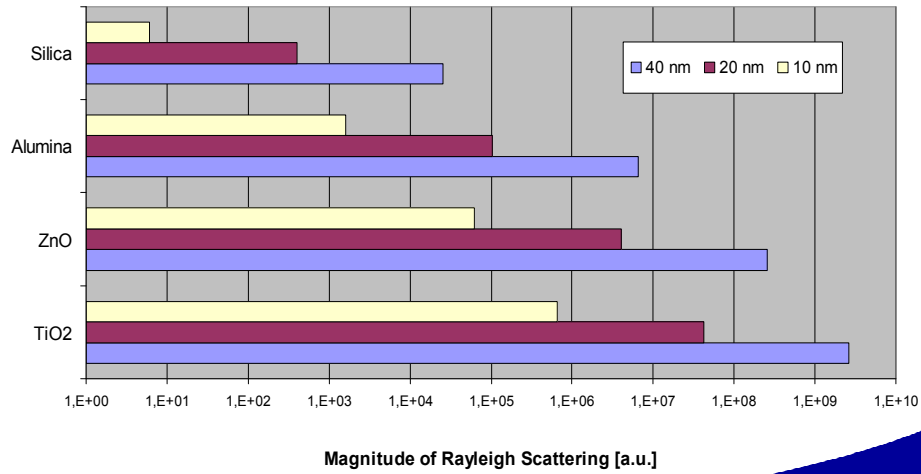
- Hardness
- Hardness
- Hardness
- Hardness
- Hardness
- Barrier / Flame retardant
- UV/bactericide
- UV
- UV
- Magnetism
- Bactericide
- Conductivity
- Conductivity / IR-Absorption
- Conductivity / Mechanical prop.
- Mechanical prop.
- Mechanical prop.
- Carrier

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## Nanoparticles

Effect of Material and Particle Size on Transparency

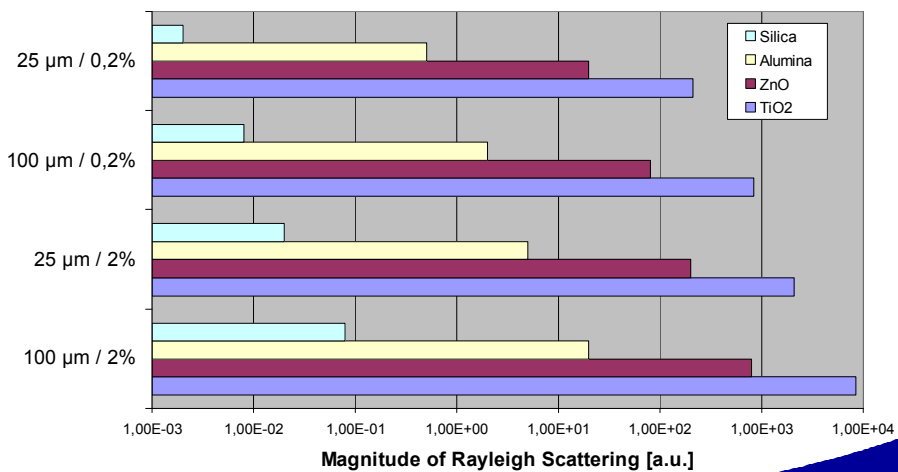


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## Nanoparticles

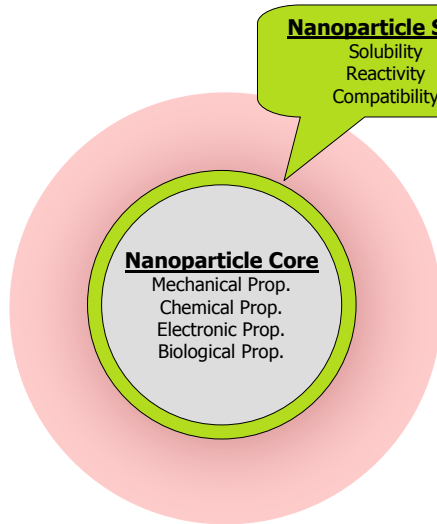
Effect of Material and Film Thickness on Transparency



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# Nanoparticles



## • Nanoparticle Core

- Determines mechanical, chemical, electrical and biological properties

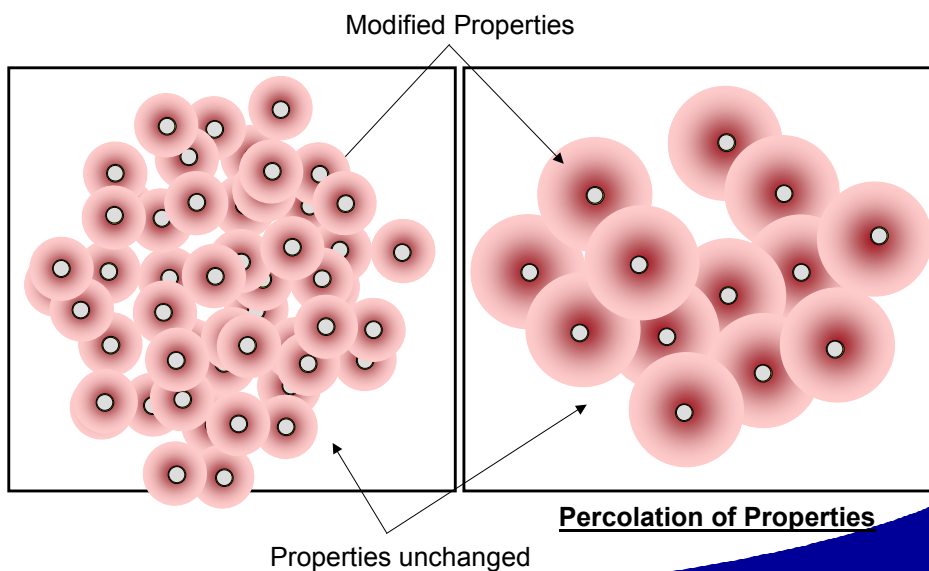
## • Nanoparticle Shell

- Determines solubility, reactivity, and compatibility

## • Interface Region in the Matrix

- Glass Transition Temperature
- Conductivity
- E-Modulus
- Cross-linking density
- ....

# Nanoparticles



NANOBYK's



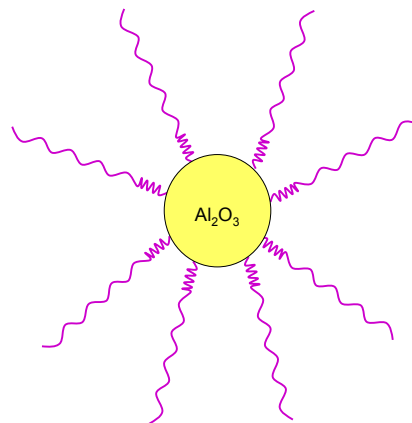
# Paint Application



## Scratch resistance in UV Clear Coatings

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### Nanoadditives for UV-curable coatings



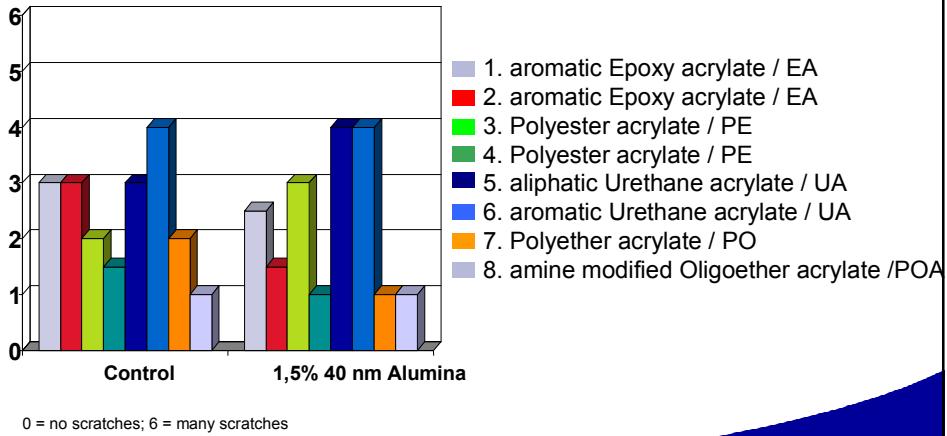
 W&D additive  
 Silicone

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## Nanoadditives for UV-curable coatings

Grades, abrasion scrub tester, 1000 cycles, eight different resin systems

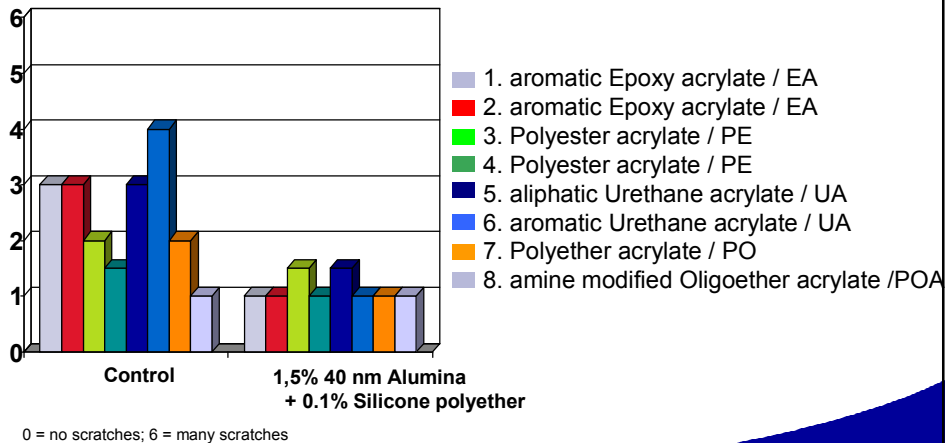


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## Nanoadditives for UV-curable coatings

Grades, abrasion scrub tester, 1000 cycles, eight different resin systems



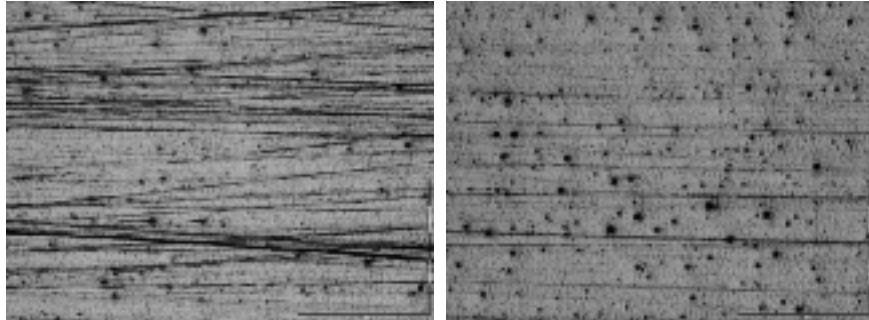
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## Nanoadditives for UV-curable coatings

Microscopic images after 500 cycles of abrasion scrub tester



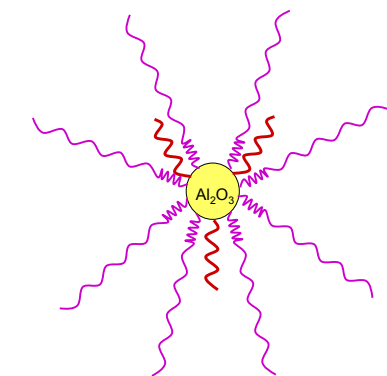
Control

2% 40 nm Alumina  
0,1% silicone polyether

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## Nanoadditives for UV-curable coatings



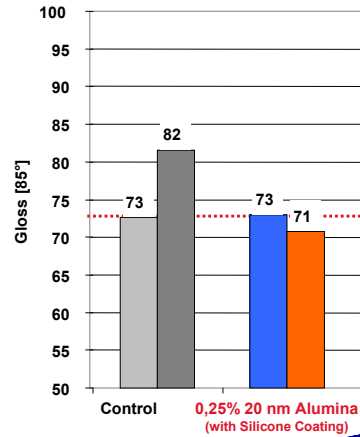
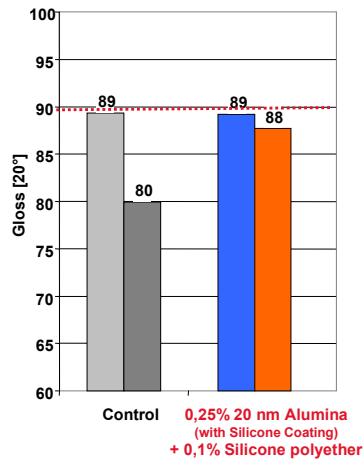
 W&D additive  
 Silicone

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## Nanoadditives for UV-curable coatings

Gloss 20 ° [%], dry abrasion scrub tester, 1000 cycles



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## Nanoadditives for UV-curable coatings

Observation: Synergistic effects with Organosiloxanes

Hypothesis:


different kinds of particle-additive-matrix interactions


- (1) surface interaction between nanoparticle surface and polar modified polysiloxane unit (formation of core-shell-particle)
- (2) surface interaction between polar modified polysiloxane unit and coating matrix
- (3) long-distance interaction between the core shell nanoparticles in the coating matrix

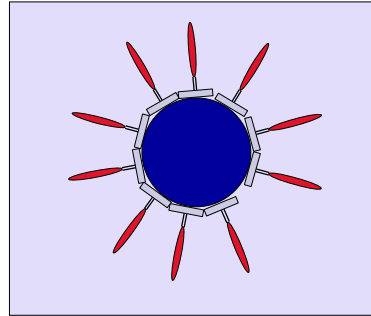
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## Nanoadditives for UV-curable coatings

 matrix

 nanoparticle

 polar modified polysiloxane



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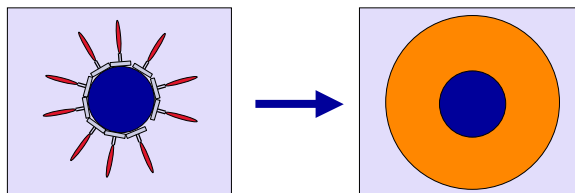


## Nanoadditives for UV-curable coatings

 polar modified polysiloxane

functions:

- (1) compatibility between matrix and nanoparticle
- (2) stabilization of nanoparticles against agglomeration
- (3) effect on phase boundary properties



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NANOBYK's



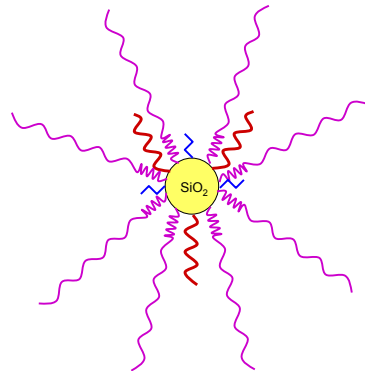
# Paint Application




## Scratch Resistance in Solvent Based Clear Coats

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### Nanoadditives for Solvent-Born clear coatings



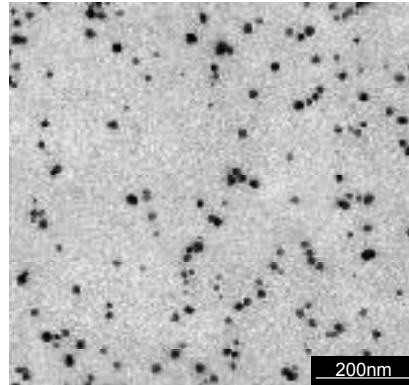
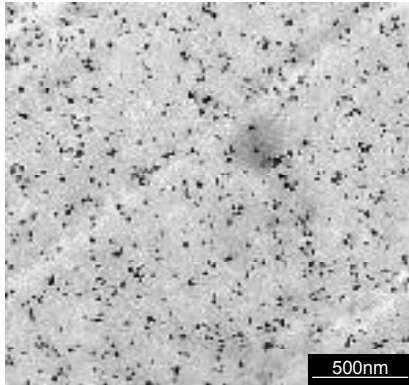
-  W&D additive
-  Compatibilizer
-  Silicone

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## Nanoadditives for Solvent-Born clear coatings

TEM-pictures (50 000 times enlargement)



System: 2 Pack Acrylate / NCO

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## Nanoadditives for Solvent-Born clear coatings

Difference of silicone addition versus silicone modification

System: 2 Pack Acrylate / NCO



Control



2% Nanosilica + silicone



2% silicone-modified Nanosilica

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## Nanoadditives for Solvent-Born clear coatings



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## Nanoadditives for Solvent-Born clear coatings

Dosage*	Crockmeter gloss retention (10 cycles)		
	Acrylic / NCO	Polyester / NCO	Acrylate / Melamine
Control	33	19	28
0.5%	82	60	79
1.0%	86	72	86
1.5%	<b>91</b>	69	<b>90</b>
2.0%	90	<b>81</b>	91
5.0%	94	84	

\* % Nanoparticles on solid resin

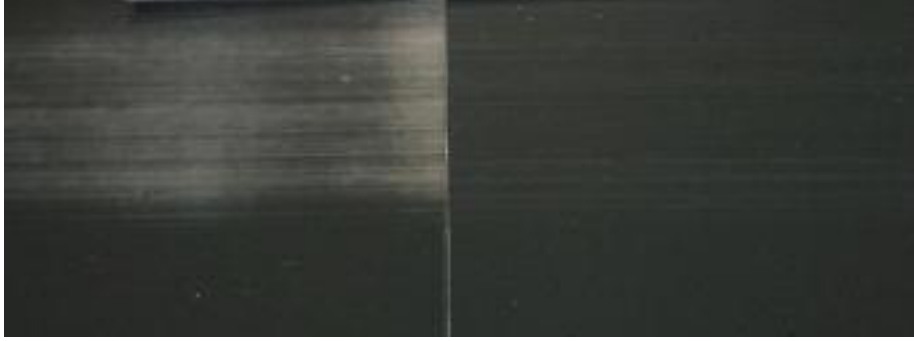
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## Nanoadditives for Solvent-Born clear coatings

Mineraloil-based air drying PU-wood coating  
(Reichhold UROTUF-F77M60)

Microscopic images after 100 cycles of abrasion scrub tester



Reference with 0,1% Silicone  
Gloss retention: 25%

0,60% 20 nm Alumina with 0,1% Silicone  
Gloss retention: 82%

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NANOBYK's



## Paint Application Dielectric Properties

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## Nanoparticles to improve Dielectric Strength

	<u>Standard</u>	<u>Standard with 30% Filler</u>	<u>Standard with 1% Nanomaterial</u>	<u>Standard with 3% Nanomaterial</u>
Bond Strength, 25°C, lbs.	21	23	18	20
Bond Strength, 150°C, lbs.	6	4	4	4
Dielectric Strength, vpm	3300	4200	3500	<b>4300</b>
Pulse Endurance, minutes	4	> 6000	4	<b>&gt; 6000</b>



The P.D. George Company

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ALTANA  
Electrical Insulation

NANOBYK's



## Paint/Plastic Application UV Protection

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Chemie



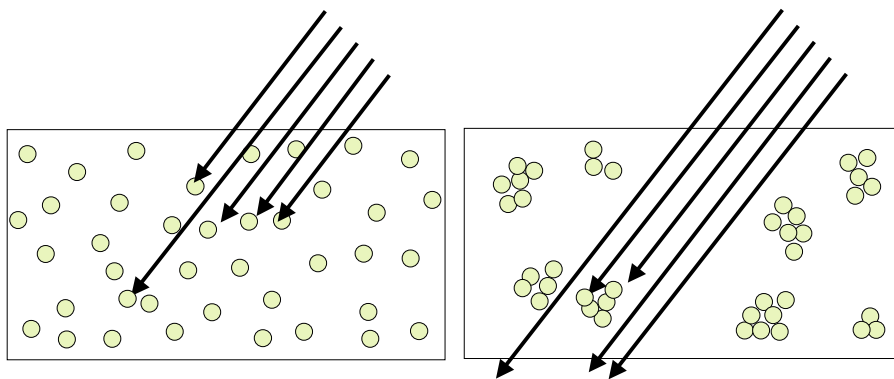
## Nanoparticles for UV protection

Active ingredient	Chemistry	Activity	Cost of goods	Refractive Index
Zn	Oxide	moderate	low	2,0
Zn	Doped oxide	moderate	low	2,0
Ti	Coated Oxide	high	moderate	2,4
Ce	Oxide	moderate	moderate	2,2

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## Nanoparticles for UV protection



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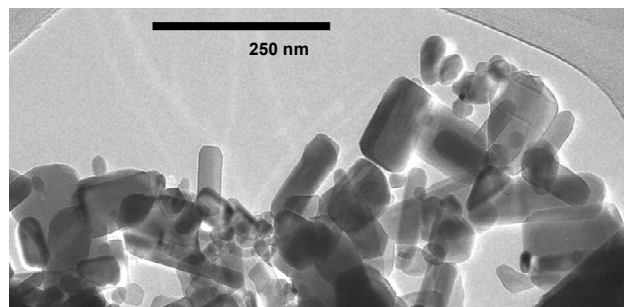
## Nanoparticles for UV protection

Property	ZnO	TiO <sub>2</sub>
Refractive Index	2,0	2,4
No Photoactivity	+	-
Chemical Stability	o	+
Bio-activity	+	-
UV-Absorption	< 400 nm	< 370 nm
Absorption Efficiency	o	+

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## Nanoparticles for UV protection



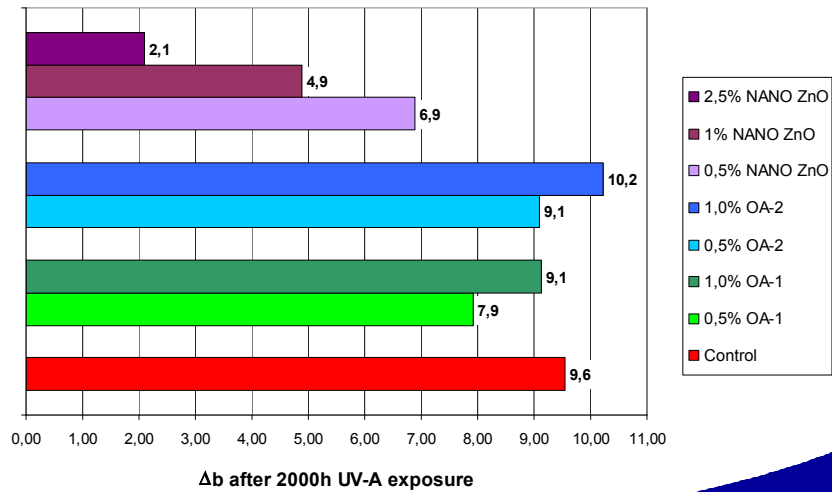
Grade	Particle Size $d_{50}$ , nm	Surface Area $m^2/g$
NanoArc	30	35
NanoTek	60	17

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## Nanoparticles for UV protection

QUV Test – Plastic Application



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## Currently available nanomaterials and their properties

Property \ Material	Aluminum-oxide	Zinc Oxide	Indium Tin Oxide	Antimony Tin Oxide	Silica
Scratch resistance	X				X
Mechanical properties	X	X			X
UV-stability		X			
Conductivity			(x)	(x)	
Anti-static			X	X	
IR-absorption			X	X	
Barrier Coating					X

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## Nanoadditives overview

Trade name	Material	Particle Size	Active content	Medium	Property
NANOBYK-3600	Alumina	40 nm	50%	Water	<u>Scratch resistance</u> in aqueous UV coatings
NANOBYK-3601	Alumina	40 nm	30%	TPGDA	<u>Scratch resistance</u> in non-aqueous UV coatings
NANOBYK-3602	Alumina	40 nm	30%	HDDA	<u>Scratch resistance</u> in non-aqueous UV coatings
NANOBYK-3610	Alumina	20 nm	30%	PMA	<u>Scratch resistance</u> in non-aqueous coatings
NANOBYK-3650	Silica	20 nm	25%	PMA	<u>Scratch resistance</u> in non-aqueous coatings
LP-Products	Zinc Oxide	30 nm / 60 nm	30-50%	Various	<u>UV-Protection</u>

## Conclusions

- **Transparency is the key driver for nanotechnology in paint application**
  - Synthesis, material and particle size determine Nanomaterials performance
  - Low refractive index and high efficiency are key in nanotechnology for paint application.
- **Nanoparticles improve**
  - Scratch resistance of high gloss high transparent coatings
    - UV Coatings: **0,3 – 1,0% Nanoparticles**
    - 2K Coatings: **1,0 – 2,0% Nanoparticles**
    - Air-Drying solvent based coatings: **0,3 – 1,0% Nanoparticles**
  - Long-term UV stability of polymer composites
    - All coatings **1,0 – 4,0% Nanoparticles**
  - Dielectric Properties
    - Unsaturated Polyesters **1,0 – 3,0% Nanoparticles**
  - Impact resistance of thermoplastics
    - PP **1,0 - 2,0% Nanoparticles**

## Summary



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