Nanomaterial Applications in Coatings

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Outline

- What is Nanotechnology?
- Nanomaterials vs nanoparticles
- What is new and what is old?
- Performance enhancement with Nanoparticles
- Nanotechnology Challenges
- Lotus Leaves and Dolphins

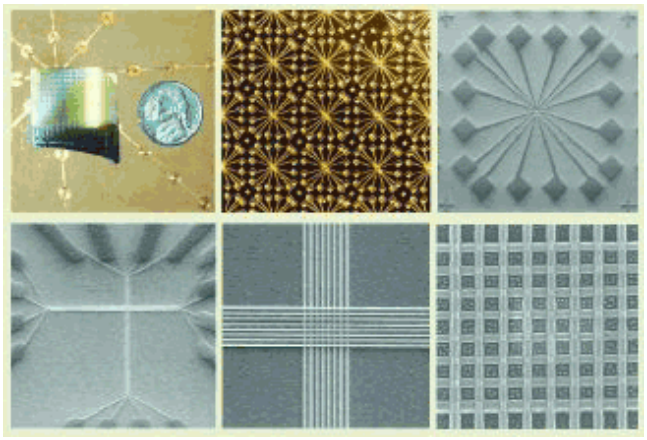
What is Nanotechnology?

- It is a matter of scale (1 – 100 nm)
  - 10 A^o = **1 nm** = 10^{-3} micron = 10^{-9} meter
  - Average human hair is 100,000 nm or… 100 micron or… 0.1 mm in diameter
- 100 – 500 nm: typical polymer latex particle size
- 250 nm: hiding grade TiO_2 particle size

What is Nanotechnology?

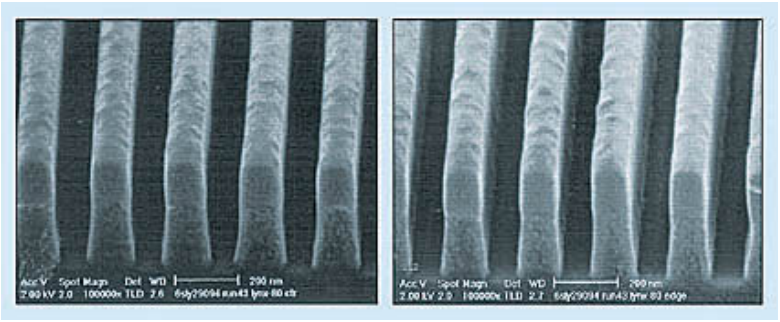
- Nano-Engineering
- Nano-Biotechnology
- Nano-Electronics
- Nano-Materials

Nano-Electronics

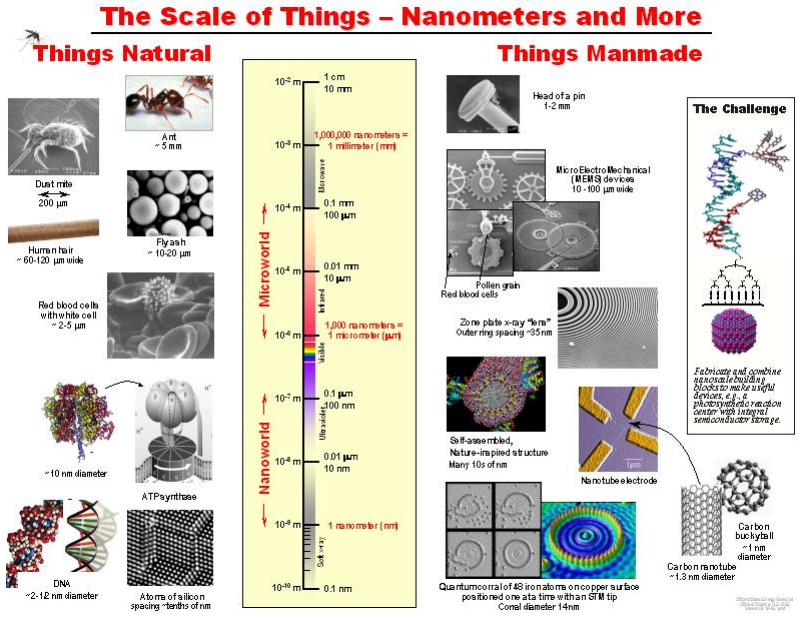


COURTESY OF HEWLETT-PACKARD LABS
http://pubs.acs.org/cen/coverstory/8039/8039nanoelectronics1.html

Nano-Lithography



http://www.reed-electronics.com/semiconductor/index.asp?layout=article&articleId=CA312504&text=low+k



http://www.nano.gov/html/facts/The_scale_of_things.html

Nanomaterial Outlook

- Nanotechnolgy in Coatings: Realizing the Potential (FSCT ACSeries Event, Seattle, WA – June 2005
- Countless Companies and Other Entities
  - 1200 start-ups (50% US)
- US Patent Applications (600 – 1992; 1200 – 1997; 3200 – 2002)
- Market Projections: US Nanomaterials will surpass $1billion in 2007 – *Nanomaterials to 2007, Freedonia*

For more information…..

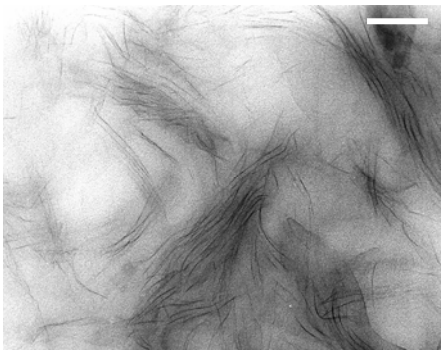
- National Nanotechnology Initiative (www.nano.gov)
- Vision 2020 Nanomaterials Roadmap (www.chemicalvision2020.org)
- Nanocoatings: Intellectual Property Landscape Conference – June, 2003
- "Nanomaterial Technology Applications in Coatings", JCT CoatingsTech – May, 2004
- International Congress of Nanotechnology (ICNT) 2005, Oct. 31- Nov. 4, 2005

For more information…..

- Encyclopedia of Nanoscience and Nanotechnology (American Scientific Publishers)
- Nanotech 2004 (NSTI – Nano Science and Technology Institute)
- Journal of Nanoparticle Research
- www.nanotechweb.org
- Other

“Initial” Interest - Polymer Nano-composites

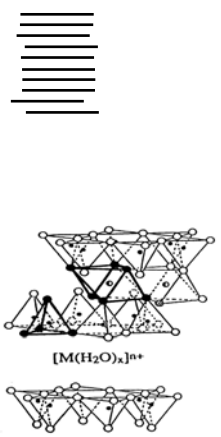
- Nylon/Clay Nanocomposites (Toyota, 1980’s)
  - 70% higher tensile modulus
  - 125% higher flexural modulus
  - Heat distortion temperature increased from 65 ºC to 152 ºC



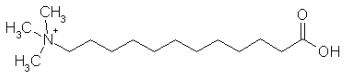
Epoxy / Layered Silicate (Vaia – Nanocomposites 2001 Conf.)

Organo-Clays

Dispersed **Intercalated** **Exfoliated**



Vermiculite Clay



"There's Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics"

by Richard Feynman, 1959

www.zyvex.com/nanotech/feynman.html

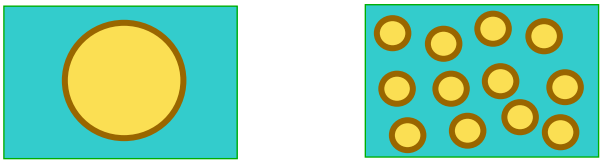
"Why cannot we write the entire 24 volumes of the Encyclopedia Brittanica on the head of a pin?"

"There is nothing that I can see in the physical laws that says the computer elements cannot be made enormously smaller than they are now."

"Atoms on a small scale behave like nothing on a large scale, for they satisfy the laws of quantum mechanics. So, as we go down and fiddle around with the atoms down there, we are working with different laws, and we can expect to do different things."

Key Nano-Attributes - 1

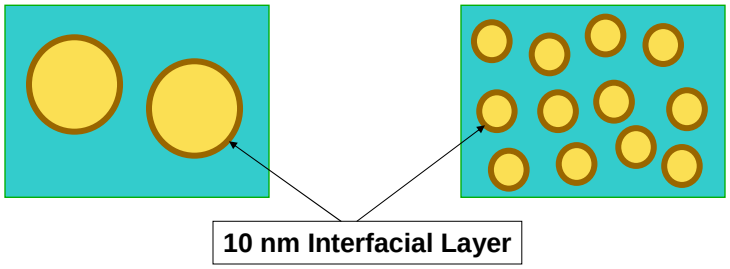
Higher interfacial material content with smaller particles



Behavior of Interfacial material is different from behavior of bulk material

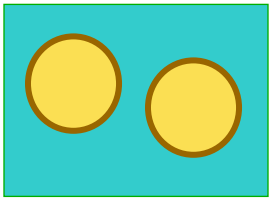
Interfacial Material Volume

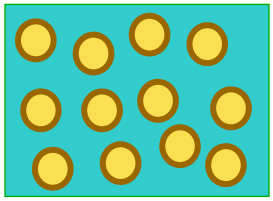
Particle Diameter (nm)	**300**	**250**	**200**	**150**	**100**	**50**
Interfacial Volume Fraction	0.03	0.04	0.05	0.06	0.10	0.22



Dispersed particle volume fraction is 0.3 in all cases

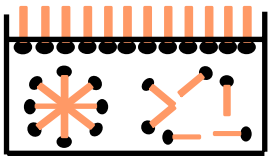
Key Nano-Attributes - 1





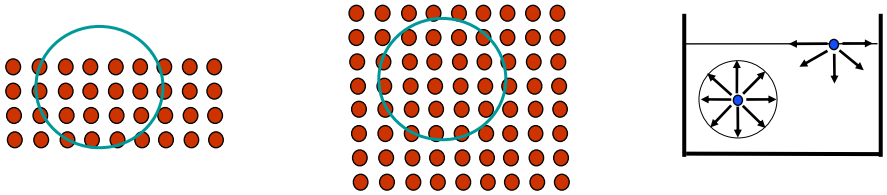
Polymer molecules at interface

Surfactants at water/air interface



Key Nano-Atributes - 2

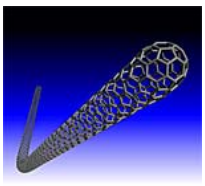
Bulk atom/molecule principles may not apply



"Non-Scalable Region"

Size Dependence of Surface Atom Content

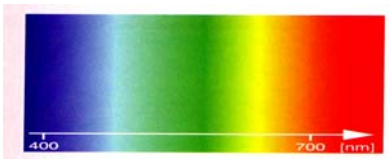
- A particle of 10nm diameter has 20% surface atoms
- A particle of 2nm diameter has 80% surface atoms
- A particle of 1nm diameter has 100% surface atoms
  - Single wall Carbon nanotube

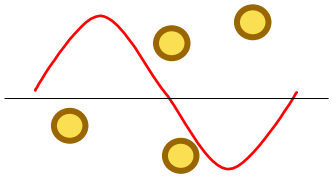


A capped single-wall carbon nanotube with a slight bend.
http://www.thomas-swan.co.uk/pages/nano_images.html

Key Nano-Attributes - 3

Size smaller than wavelength of visible light

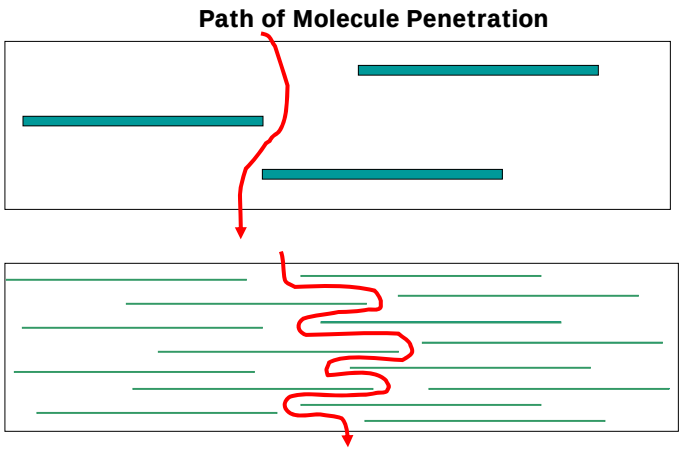




Nano-Composites: Potential Advantages

- Optical Clarity
- Mechanical Properties
  - Reinforcing effect
  - Scratch, Mar Resistance
- Barrier Properties
- Other

Barrier Property Improvements



Microcomposite
Aspect Ratio
25:1

Nanocomposite
Aspect Ratio
250:1

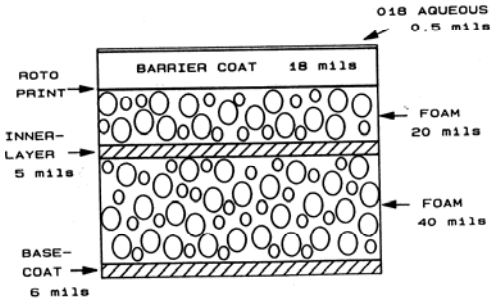
At the same loading level nanocomposites can display much better barrier properties

Approaches to Making Nano-Composites (Inorganic/Organic)

- Dispersion of layered inorganics in polymer
- In-situ generation of nano-phases
- Incorporation of nano-particles

Nanocomposite coating applications include floor wear-layers

- Waterborne Clear Coats Containing Nano-Layered Silicate (US 5124202–Armstrong, 1992)
- Sol-Gel Hybrid Coatings (US 50203140 – Armstrong, 1991)
- Alumina / Epoxy Coatings (Nanophase, 2001)



Nanoparticles

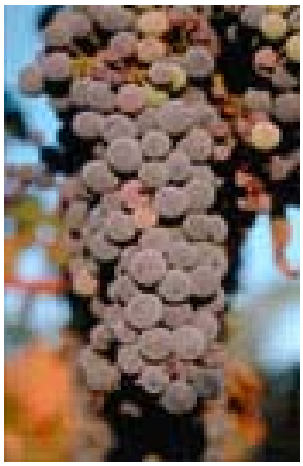
- Wide range of applications
  - Coatings
  - Plastics
  - Data storage
  - Cancer and tumor treatment
  - Drug delivery

Nano-Particles for Coatings

- Inorganics
  - Colloidal Silica
  - Fumed Silica
  - Silicates
  - Titania
  - Alumina
  - Zinc Oxide
  - POSS
- Organics
  - Acrylics
  - Urethanes
- Carbon Black
- Organo-Clay
- Other

Fumed Silica

- Fused nano-particles
- Surface area comparable to nano-particles
- Aqueous and non-aqueous (e.g. UV) grades
- Scratch, mar resistance



Available Nanomaterials and Their Properties in Coatings

- **Aluminum Oxide**
  - Mechanical properties
- **Zinc Oxide**
  - UV / light –stability
  - Anti-microbial
- **Indium / Antimony Tin Oxide**
  - Antistatic
  - IR-absorption
- **Titanium Dioxide**
  - UV / light –stability
  - Anti-microbial
- **Copper Oxide**
  - Anti-microbial
- **Silicon Dioxide**
  - Mechanical properties
- **Cerium Oxide**
  - UV / light –stability
  - Mechanical properties
- **Iron Oxide**
  - UV / light –stability
  - Magnetism
- **…**

Photocatalytic TiO_2 Nanoparticles

- Self-cleaning surface
- Antibacterial Activity
- Super hydrophilicity
  - Anti-fogging activity

Radical Reactions

$$TiO_2 + \text{UV light} \longrightarrow e^- + hole^+$$
$$e^- + hole^+ \longrightarrow TiO_2 + \text{heat}$$

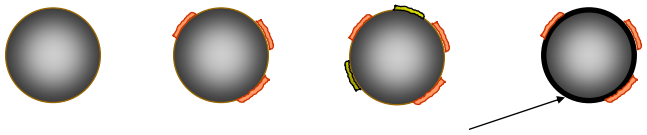
$$hole^+ + OH^- \longrightarrow OH^\bullet$$
$$e^- + O_2 \longrightarrow O_2^{-\bullet}$$
$$O_2^{-\bullet} + OH^\bullet + (\text{-}CH_2\text{-}) \longrightarrow \text{intermediates}$$
$$O_2^{-\bullet} + OH^\bullet + \text{intermediates} \longrightarrow CO_2 + H_2O$$

$$\text{UV light} + O_2 + (\text{-}CH_2\text{-}) \longrightarrow \text{intermediates}$$
$$\text{UV light} + \text{intermediates} \longrightarrow CO_2 + H_2O$$

Titanium Dioxide Pigments

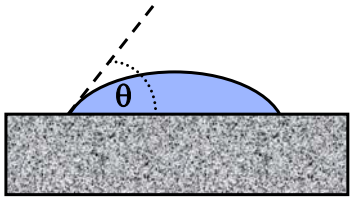
Chalking: loose pigment particles form on the surface from the erosion of the binder as a result of photodegradation.

	Type I Anatase	Type II Rutile	Type III Rutile	Type IV Rutile
Product Name	LW	R-900	R-900, R-901	R-960
TiO_2 min.%	94	92	80	80
Chalking	free	medium resistant	medium resistant	medium resistant
Surface treatment	none	Al_2O_3	$SiO_2 + Al_2O_3$	$SiO_2 + Al_2O_3$



Complete encapsulation to protect TiO2 from UV free radical reaction

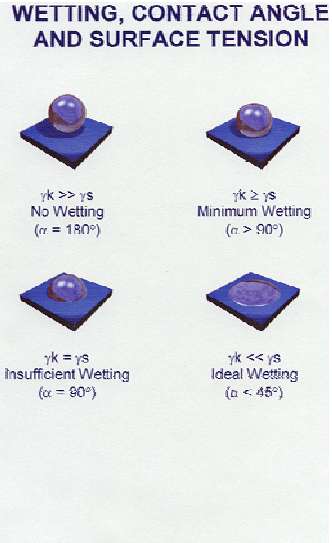
Contact Angle – Wetting



θ - Contact Angle

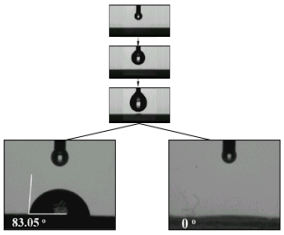
Zero Contact Angle

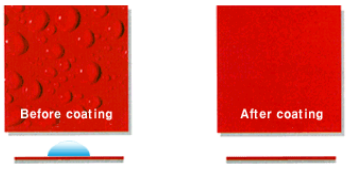
Spontaneous Wetting & Spreading



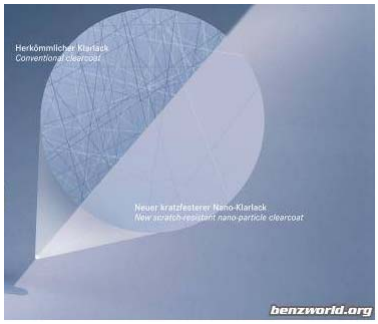
Photocatalytic TiO_2 Nanoparticles

- Super hydrophilicity
  - Anti-fogging activity
- Self-cleaning surface





http://www.nano-pac.com/en/jj/na02.htm

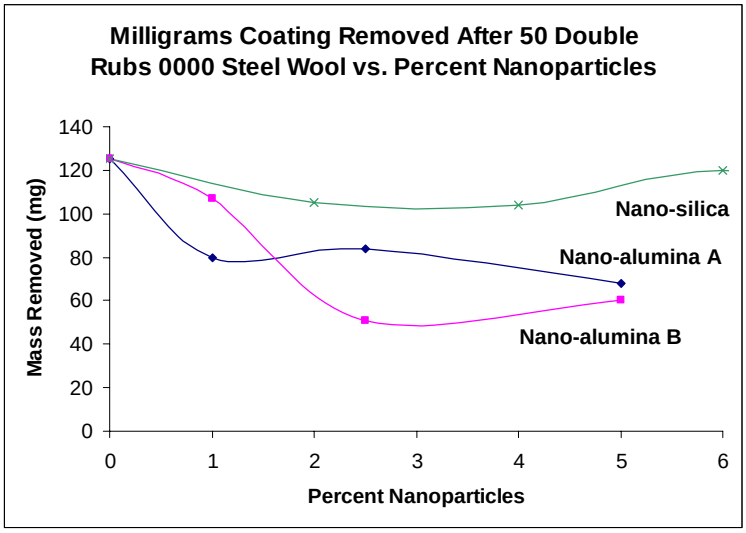


Our Studies

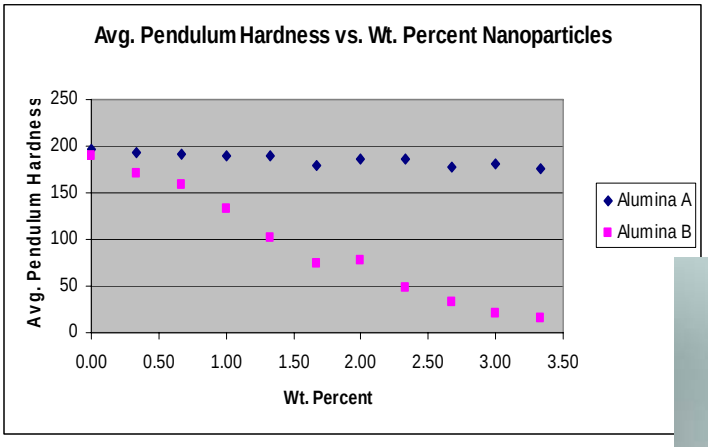
- Coating System
  - 2K Polyurethane automotive refinish formulation

Nanoparticles	Solvent	% Solids	Avg. Particle Size(nm)
Alumina-A	Dowanol DPnB	38	32
Alumina-B	Tripropylene glycol diacrylate	40.9	32
Alumina-C	Methoxypropyl acetate	32	32
Silica-A	Methoxypropyl acetate / methoxypropanol	32	unknown

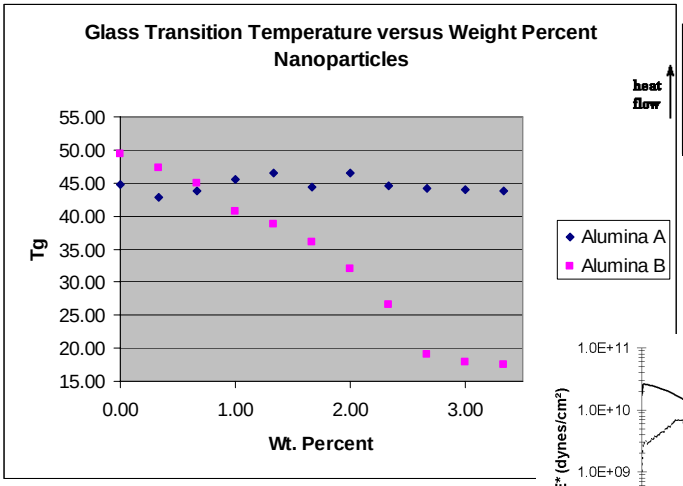
Scratch Resistance of Auto Refinish Coatings

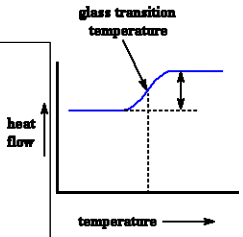


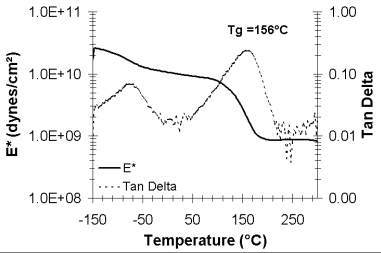
Pendulum Hardness



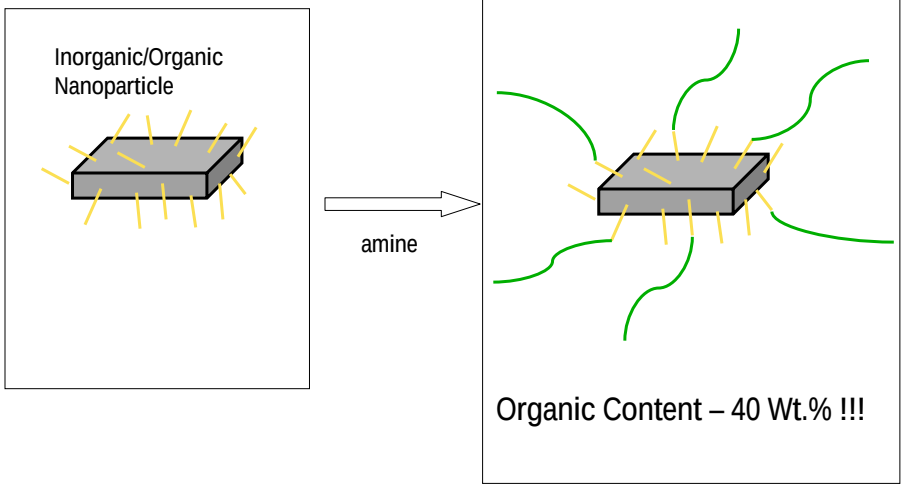
Glass Transition Temperature (Tg) of Coatings







Functionalized Nanoparticles for Epoxy Coatings



Scratch Mechanisms

- Nano-Indentation
  - Jeff Comer, Dr. Lipiin Sung (NIST)
- AFM

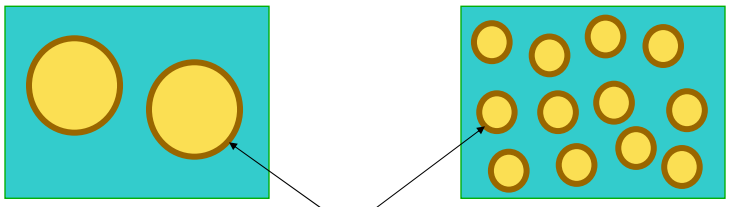



Nano-Particles in Coatings: Challenges

- Dispersion and Dispersant Demand
- Rheology
- Functionalization
  - Application Specific?
- Characterization
- Cost/Performance Balance
- Health Effects
  - Nanosafe2.org
  - "Nanoparticles: health impacts?", David Warheit (DuPont), *Materials Today*, Feb. 2004, p32
  - "Nanoscience and nanotechnologies: opportunities and uncertainties", http://www.nanotec.org.uk/finalReport.htm, July 2004

Dispersant Demand

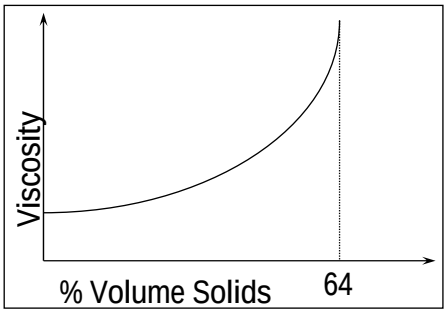
Particle Diameter (nm)	300	250	200	150	100	50
Interfacial Volume Fraction	0.03	0.04	0.05	0.06	0.10	0.22

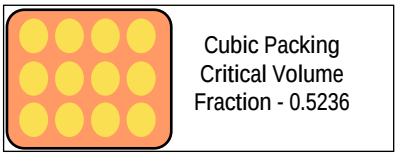


10 nm Interfacial Layer

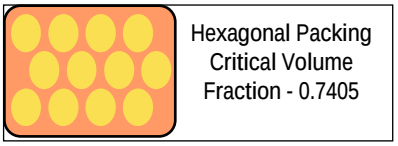
Dispersed particle volume fraction is 0.3 in all cases

Effect of Dispersed Phase on Viscosity





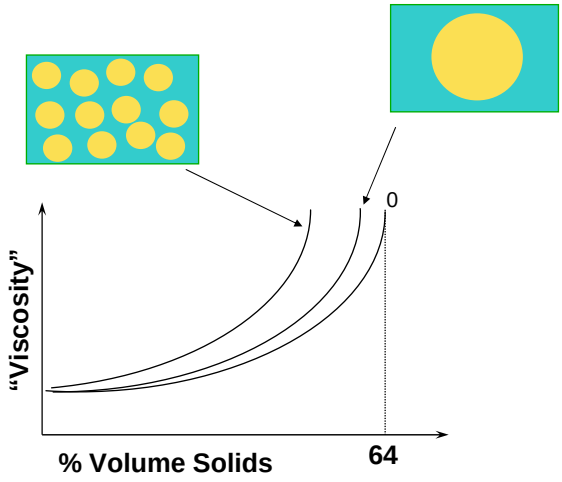
Cubic Packing
Critical Volume
Fraction - 0.5236



Hexagonal Packing
Critical Volume
Fraction - 0.7405

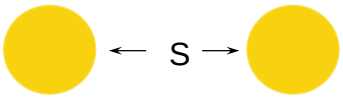
For Random Packing, Critical Volume Fraction - 0.64

Particle Size Effect on Viscosity



Flocculation & Aggregation of Particles

DLVO Theory
(Two Particles)



Inter-Particle Forces

a - Van der Waals, Long-range *(Attractive)*
b - Electrostatic, Long-range *(Attractive or Repulsive)*
c - Steric, Short-range *(Repulsive)*
d - Solvation, Short-range *(Attractive or Repulsive)*
e - Born, Atomic-range *(Repulsive)*

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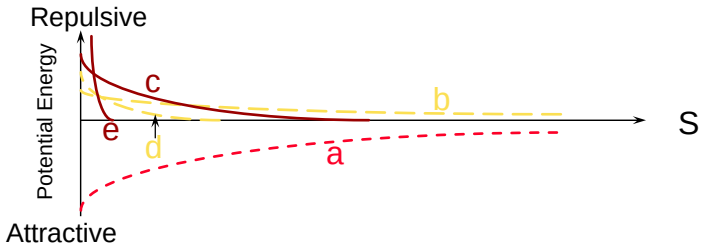
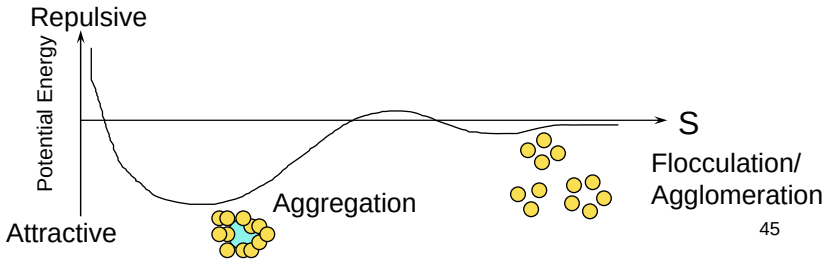
Flocculation & Aggregation of Particles





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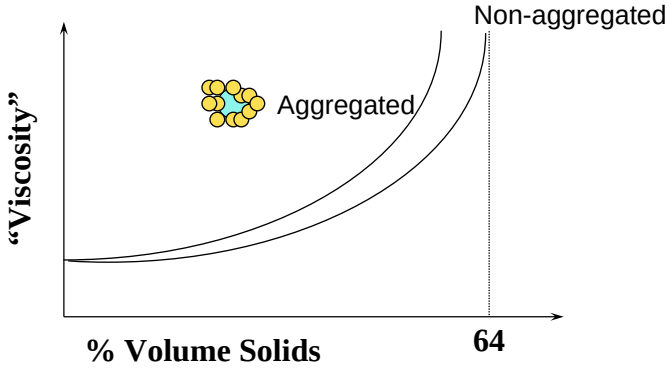
Effect of Particle Flocculation / Aggregation on Viscosity



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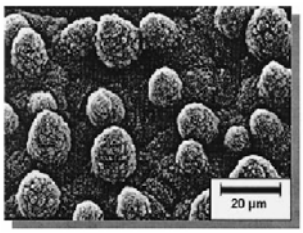
Lotus Effect

Rainwater cleans lotus leaves because of their bumpy surface.



Abramzon, et al., Chemistry & Life (1982)
Barthlott et al., Annals of Botany (1997)

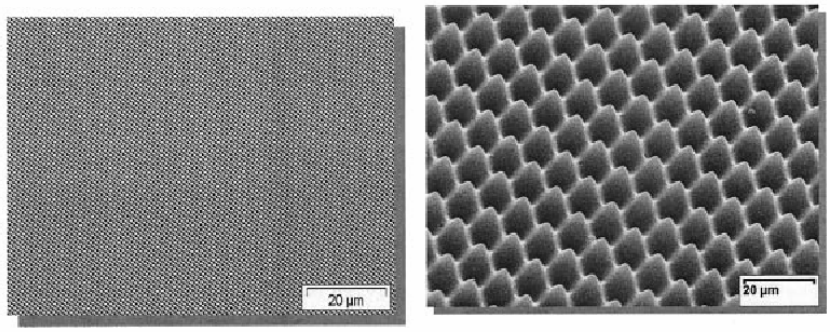
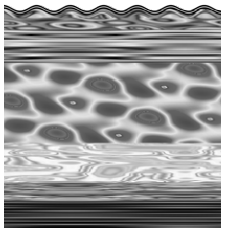


Figure 2. SEM image of self-cleaning surfaces with different structure size

Nun, Oles, & Schleich, Macromol. Symp., **187**, 677-682 (2002)

Nanostructuring Methods

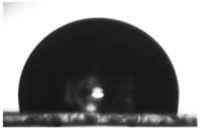


Nano-Structuring Methods

Transformation of a Simple Plastic into a Superhydrophobic Surface

Erbil, Demirel, Avci, and Mert, *Science*, Vol 299, Issue 5611, 1377-1380 , 28 February 2003

A



B

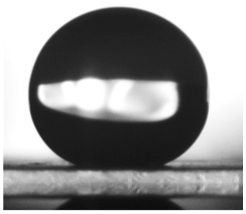
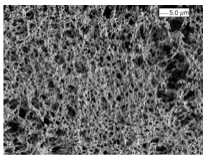
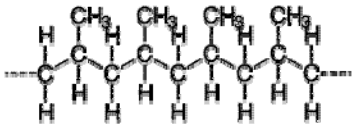


Figure 1. (**A**) The profile of a water drop on a smooth i-PP surface that has a contact angle of 104° ± 2°. The i-PP film was prepared by melting at 200°C between two glass slides and crystallizing at 100°C. (**B**) The profile of a water drop on a superhydrophobic i-PP coating on a glass slide that has a contact angle of 160°. The i-PP was dissolved in a 60% p-xylene/40% MEK mixture by volume at an initial concentration of 20 mg/ml at 100°C. The solvent mixture was evaporated at 70°C in a vacuum oven. The morphology of the i-PP coating is shown in Fig. 4.

Fig. 4. SEM picture of an i-PP coating obtained using the nonsolvent MEK as described in Fig. 1B





Questions?