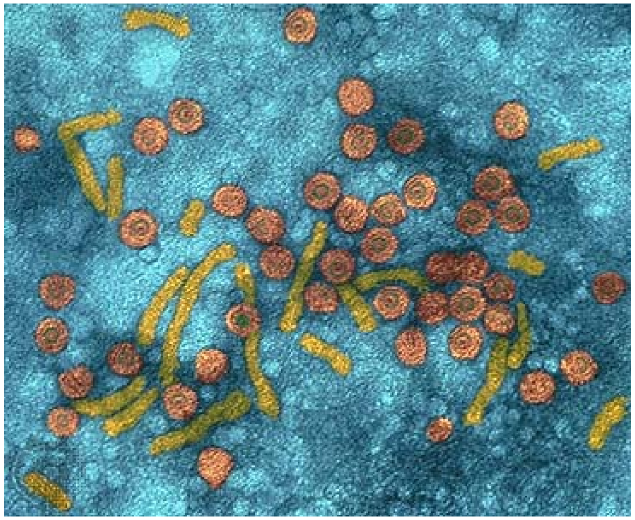


California DTSC Presentation; 8 March 2010

TiO2: Production Methods and Characterization

fred.klaessig@pabionano.com

General Observations

1. Familiar TiO_2 properties, the reasons for product grades, are reported as novel, unique, unsuspected or size-dependent.
2. Those unfamiliar with TiO_2 grades create artifacts (in sample preparation or in interpretation) then ascribed to all forms of TiO_2.
3. The definition of nanoscale has replaced the original concept of nano (size + unique property) with a size-only parameter.

fred.klaessig@pabionano.com

Pigment-Grades & Volumes

"Rule of Thumb" is that maximum scattering occurs at ~0.5 λ

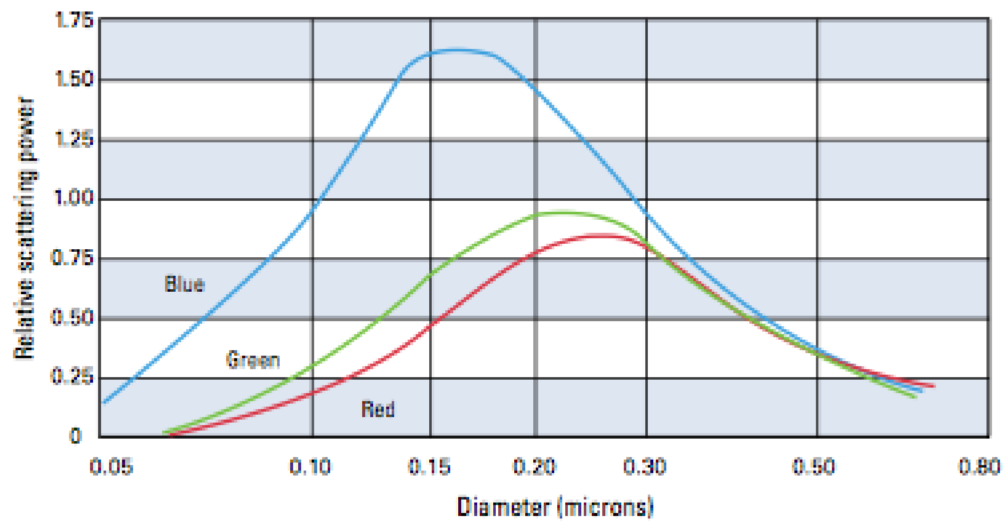
Visible light, λ~ 550 to 600 nm

Particle size of pigment-grade TiO_2 is 260-320 nm

UV, λ ~ 300- 320 nm and particle size should be 140 to 170 nm for UV scattering

<u>Contrary</u> to Wiesner *et alia*, pigment-grades volumes will not migrate to smaller sized particles for performance reasons.

Figure 7. Relative Light Scattering Power versus Rutile Particle Size.



1. Scattering is diameter, not surface area.
2. UV absorption generates primarily heat when electron-hole pairs recombine, and
3. Surface catalytic effects occur when they don't

Taken from DuPont Brochure

fred.klaessig@pabionano.com

Titania Chemistry

Rutile

- Tetragonal
- Acicular Needles and Uneven Fracture
- Sp. Gravity 4.2
- Hardness 6.5-7 mohs
- Band Gap 3.3
- Refractive Index 2.7-2.9

Anatase

- Tetragonal
- Pyramidal and Tabular with Good Cleavage
- Sp. Gravity 3.9
- Hardness 5.5-6 mohs
- Band Gap 3.8
- Refractive Index 2.2-2.5

1. Rutile denser, more abrasive and has higher RI, but is yellower.
2. Anatase preferred in textiles, chalking paints and catalysis.
3. Preference in catalysis may reflect additives in conventional rutile

fred.klaessig@pabionano.com

Large Volume Titania Manufacture

Pyrogenic (chloride)

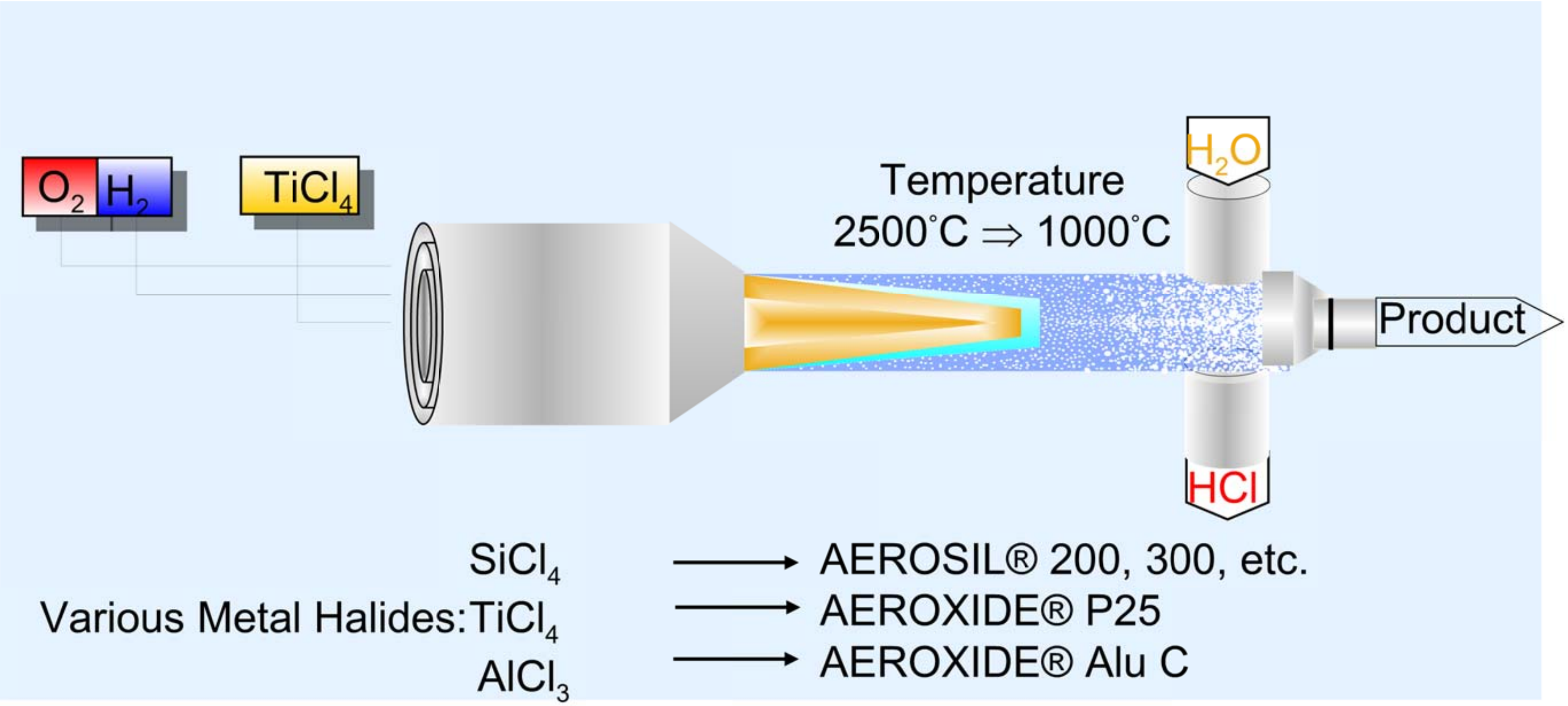
1. Ilmenite ore converted to volatile $TiCl_4$
2. $TiCl_4$ vaporized in an oxygen rich environment
3. TiO_2 particles captured from gas stream
4. Post-treatment by fluidized bed or slurry system

Sulphate (precipitation)

1. Ilmenite ore dissolved in sulphuric acid
2. Precipitated as metatinic acid (TiO_2.0.7 H2)
3. Filtered metatinic acid calcined and milled
4. Post-treatment in slurry sytem

fred.klaessig@pabionano.com

Pyrogenic Production Process

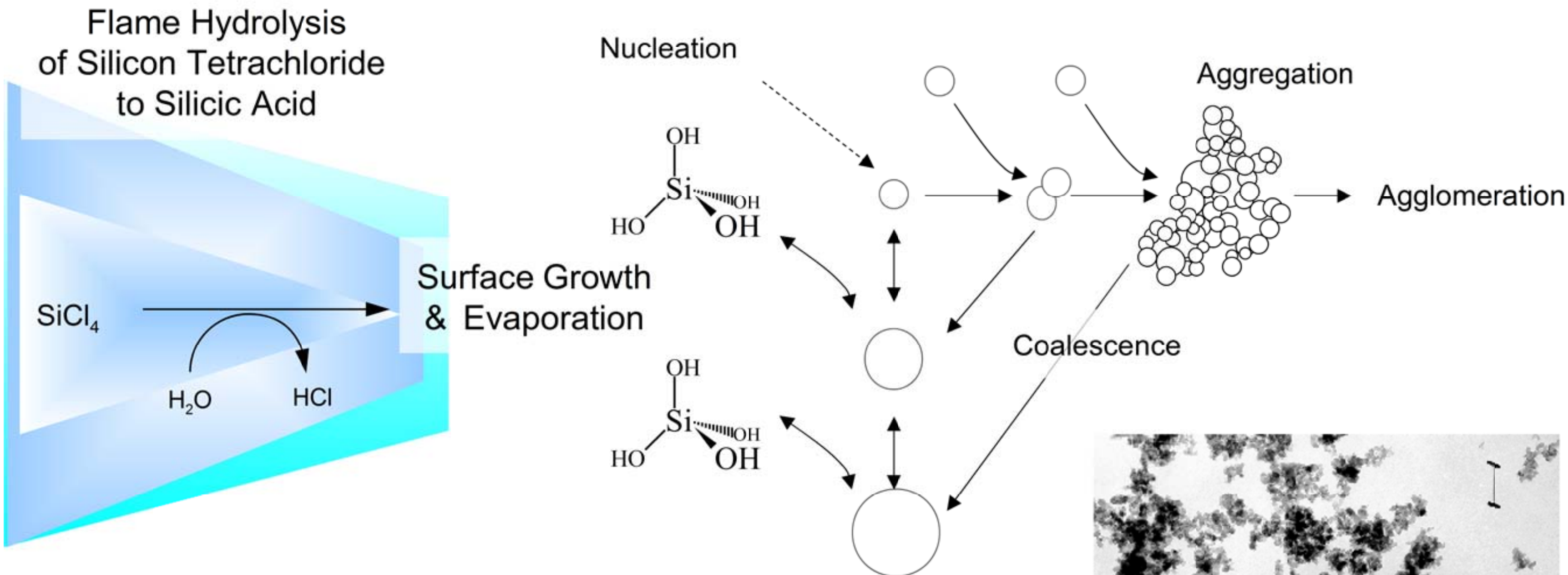


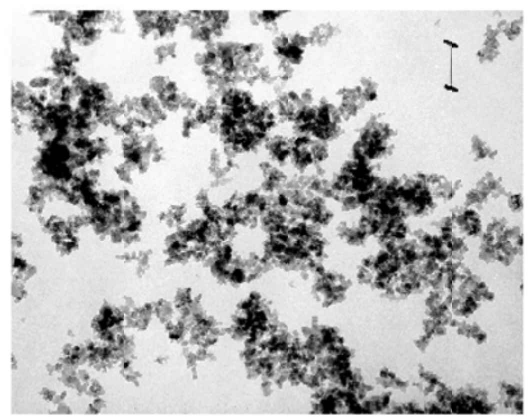
Bagging at manufacturer and “un-bagging” at customer lead to exposure

Taken from Evonik Degussa Sources

fred.klaessig@pabionano.com

Fundamentals of Particle Formation in Flame Pyrolysis





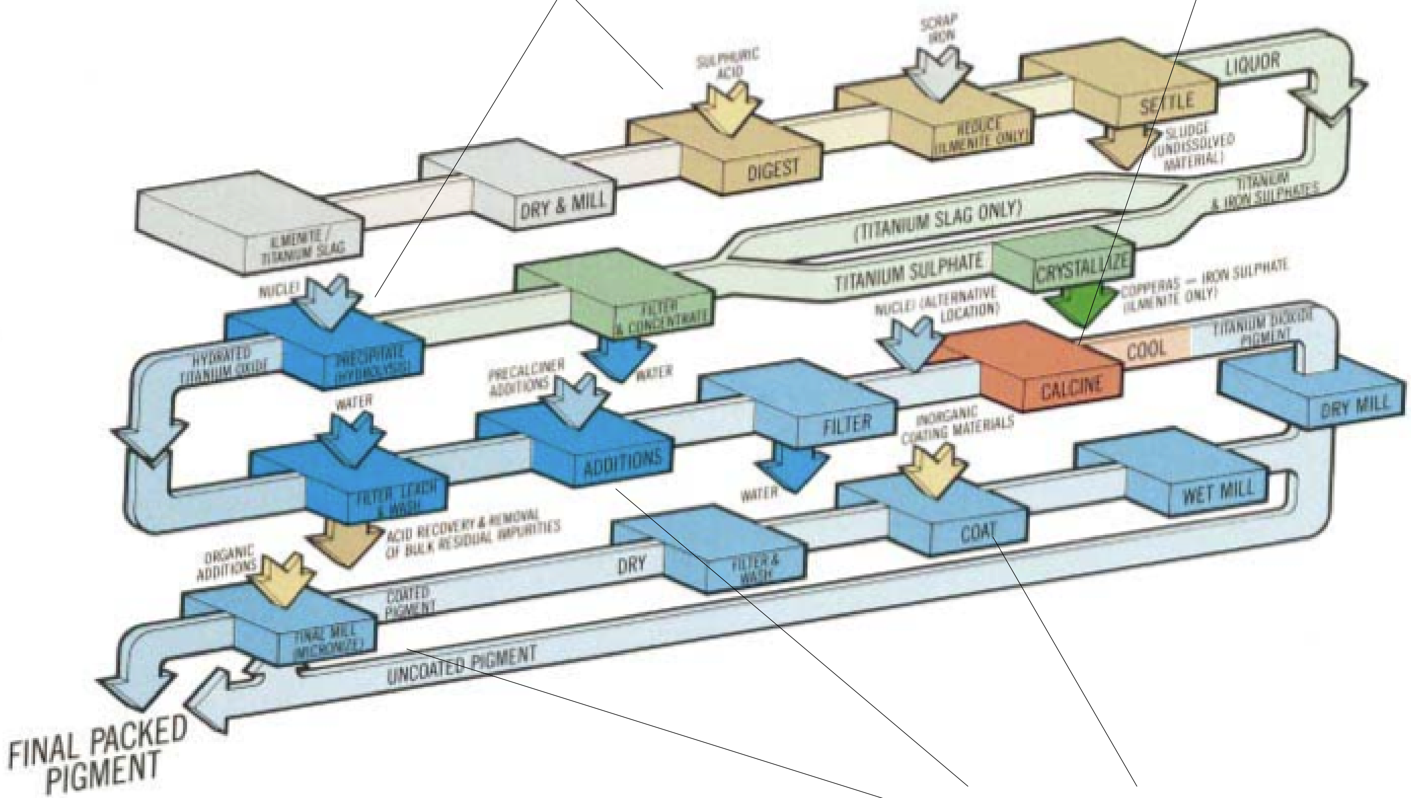
Aggregation represents fusing or sintering including coalescence into a larger particle

Taken from Evonik Degussa and Zachariah Sources

fred.klaessig@pabionano.com

Sulphate Process –
Dissolve, Precipitate and Calcine

Figure 1 The sulphate process



Additives

fred.klaessig@pabionano.com

Rutile Additives

<u>Rutile Promoters</u>

•$AlCl_3$ to flame

•Al- and PO_4 Salts to mother liquor

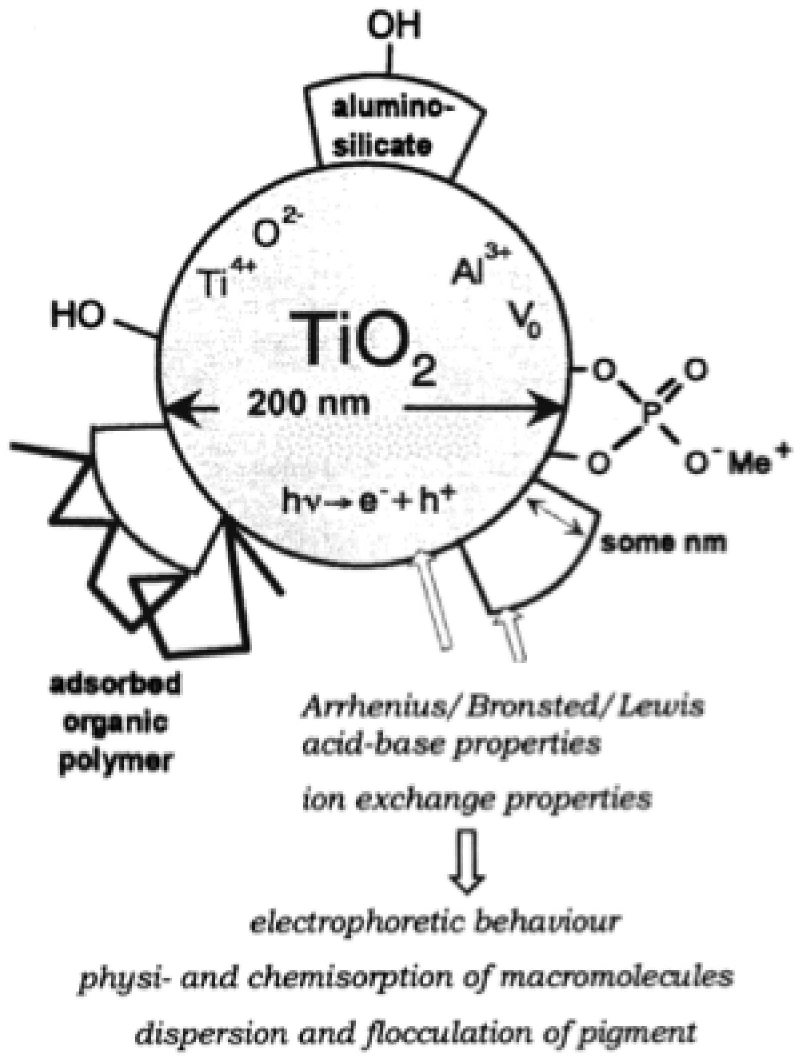
<u>Coatings</u>

•Silica, alumina and alumino silicate coatings as slurries

•TMP (trimethylolpropane) and AMP (aminomethylpropanol) for wettability in dispersing

•Cerium and Zirconium Oxides and Silanes for special grades

Coatings may be encapsulating (dense) or discontinuous (fluffy)



From Gesenhues

Sol Gel Manufacture

Chemistry:

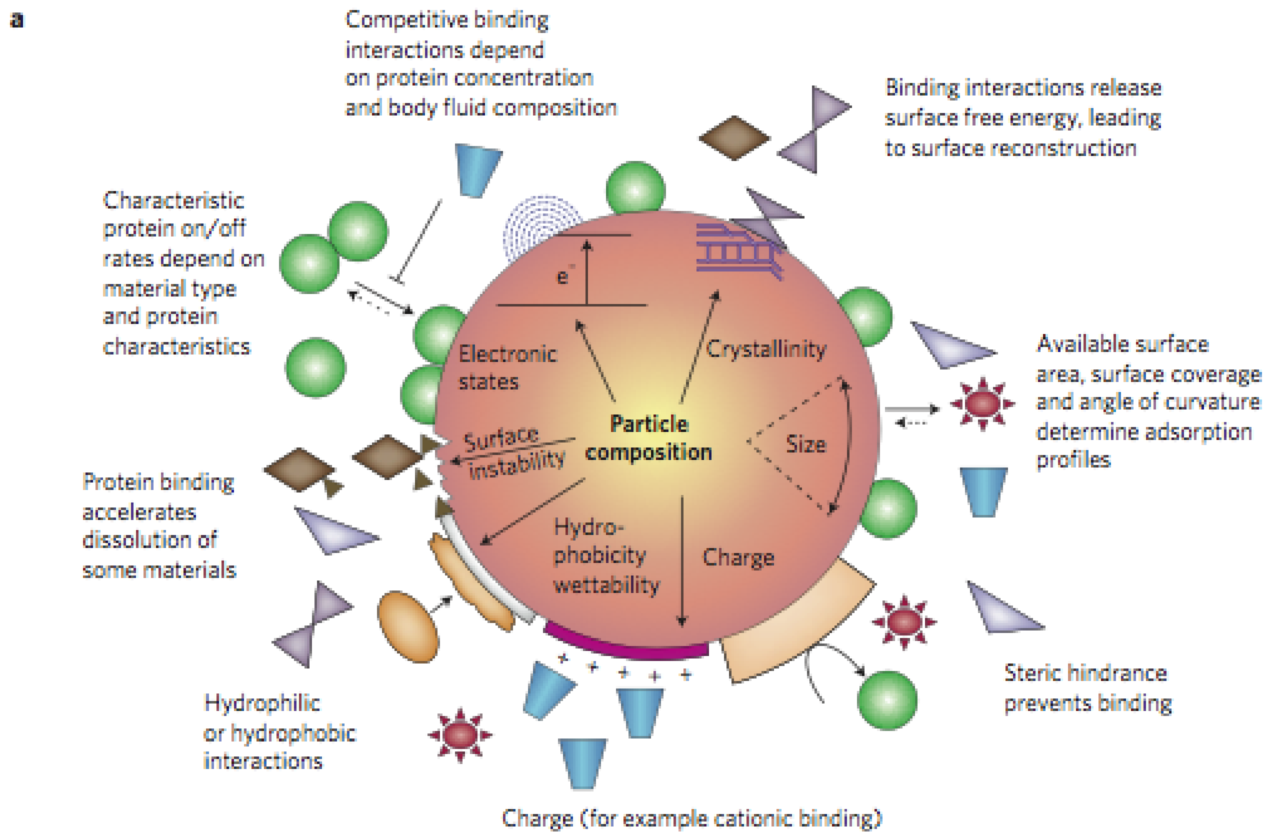
1. TiX + $H_2O \rightarrow TiO_2$ + reaction products
2. X may be Cl_4, OCl_2 and OR (alkoxide)
3. pH, heating, seeding, used to control morphology & gelling
4. Additional processing to add dopants, remove water & soluble salts, particle size
5. Polycondensation, entrapped reactants, large amorphous fraction are quality issues

Uses:

- Specialty Applications with smaller volumes
- Precipitation favors acicular morphology
- "Hard to reach" surfaces or container shapes
- Ease of Doping
- Dip Coating followed by calcination

fred.klaessig@pabionano.com

Applied to Biological Interactions ?



From Nel *et alia*

fred.klaessig@pabionano.com

Parameters for EF&E Models

- Standard Concepts in Models:
  - Composition (molecular structure)
  - Melting Point
  - Boiling Point
  - Vapor Pressure
  - pH
  - Solubility
  - Octanol/Water Partition
  - Soil/Organic Partition
- ISO/OECD Parameters:
  - Composition *
  - Surface Chemistry *
  - Surface Charge (Zeta Pot.)*
  - Solubility/Dispersibility*
  - Particle Size Distribution
  - Agglomeration/aggregation
  - Shape
  - Surface Area*

Asterisked Parameters will differ among TiO_2 Grades

Wettability & Photocatalytic Parameters not addressed

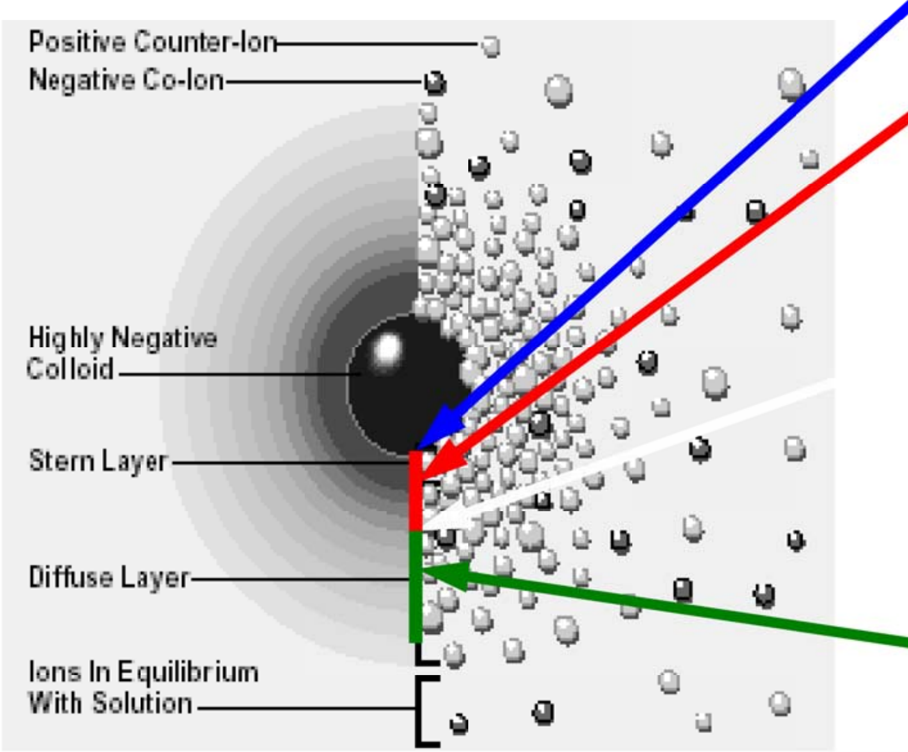
fred.klaessig@pabionano.com

Need for Surface Nomenclature

Substrate	Surface Coating	Projecting Species	Product or Example
TiO_2.0.7 H20	None	Ti-OH; H_20	Metatinic Acid
TiO_2	None	Ti-OH	P-25
Al: TiO_2	Alumina	Al-OH	R-100 & Uf-1
Al:TiO_2	Alumina/ alumina silicate	Al-OH Si-OH	Uf-2
TiO_2	PBS-present	Ti-OH Ti-PO_4	Uf-3 (P25)
TiO_2	Reacted with As	Ti-OH Ti-O-AsO_4	EPA Case Study
TiO_2	Silane treated	Ti-O-Si-C8	T805
TiO_2 (??)	Alumina	Simethicone	Eusalex T-2000

fred.klaessig@pabionano.com

Characteristics of Surface Charge: Definitions



Particle surface

Stern Layer: Rigid layer of ions bound to particle surface and ions travel with the particle

Plane of hydrodynamic shear: Also called **Slipping Plane:** Boundary of the Stern layer:
ions beyond the shear plane do not travel with the particle

Diffuse Layer:
Also called **Electrical Double Layer:** Ionic concentration not the same as in bulk; there is a gradient in concentration of ions outward from the particle until it matches the bulk

From PV Moghe Lecture Notes

Effect of Coatings on pH of i.e.p.

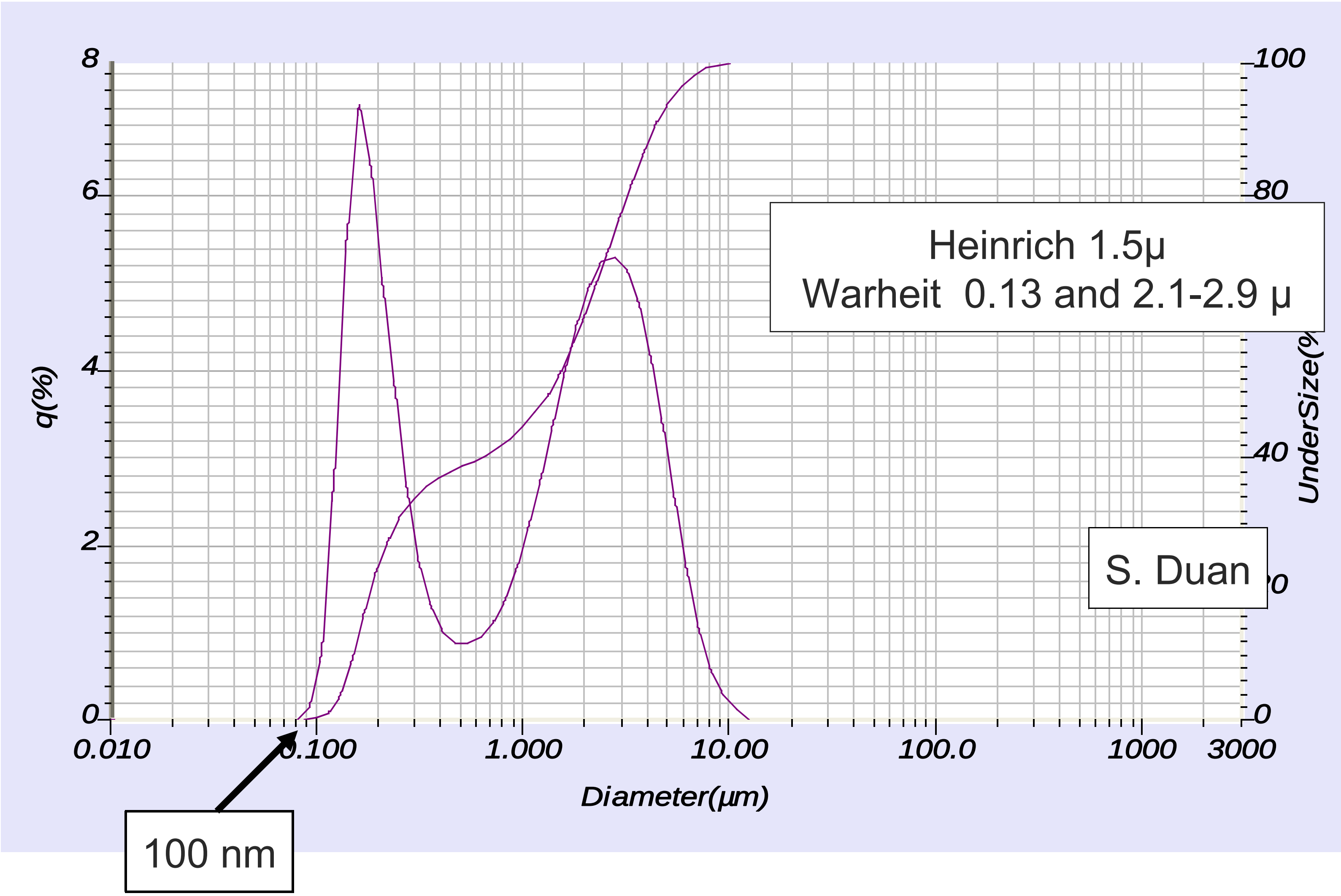
Sample	pH of i.e.p.	pH at Yield	% Ti
Uncoated Al:TiO_2	7.9	7.8	60%
2% Alumina-coated Al:TiO_2	8.1	8	34%
4% Alumina + Silica coated Al:TiO_2	6.6	6.3	23%
1% Silica-Coated Al:TiO_2	1.5	3	33%
TiO2 (literature)	~ 6.5	N/A	100%

Adsorbed species from sample preparation affected size

Sample	Size with PBS	Size w/o PBS
F-1 (pigment)	2667 nm	382 nm
uf-1 (alumina)	2144 nm	136 nm
uf-2 (silica/alumina)	2891 nm	150 nm
uf-3 (P-25)	2691 nm	129 nm

fred.klaessig@pabionano.com

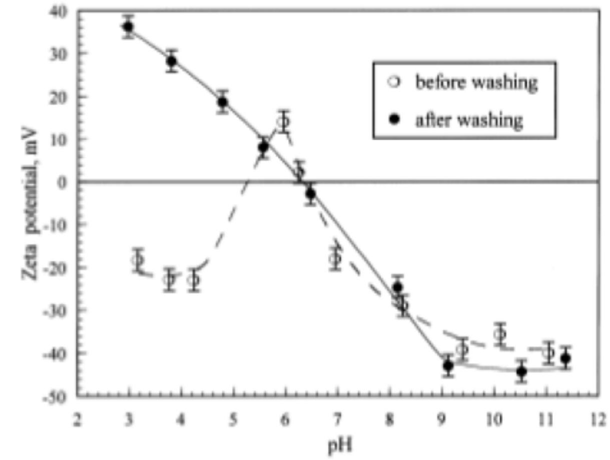
PSD in DI sonicated 600 s; median particle 1.5μ; peaks at 0.17 and 2.8 μ



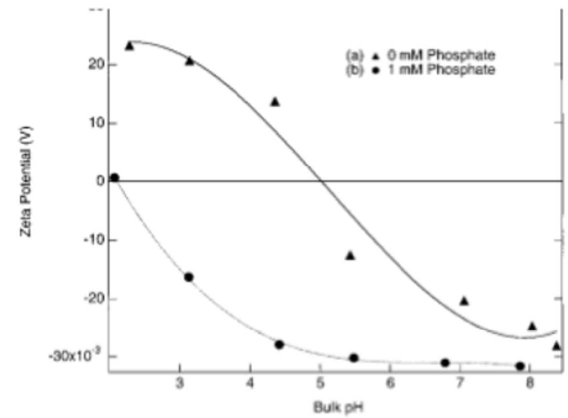
fred.klaessig@pabionano.com

Sources of Artifacts

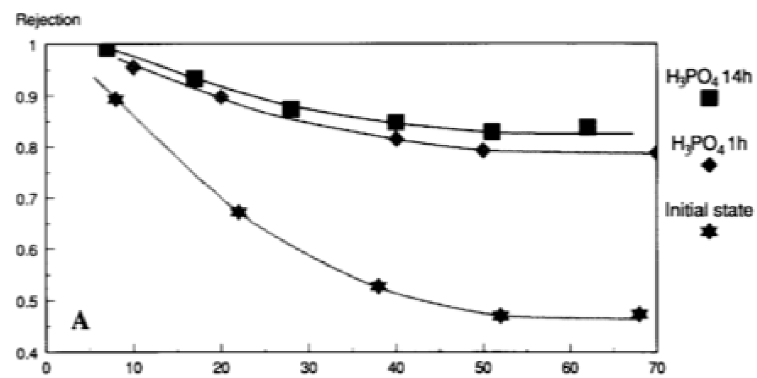
“Store bought” titania had silica and organic nitrogen that was washed off in simple caustic; probably a pigment grade with silica and AMP coating.



Use of PO_4 anion in buffers changes zeta potential



PO_4 pre-treatment of titania membrane alters rejection rate of BSA indicative of competitive adsorption phenomena



Suggestions

- Retain product identity (grade and manufacturing process) in EF&E analyses to match “chemistry of particle surface” to the local “chemistry of environment” for protocol development
- Nomenclature, even an interim one, is needed to communicate surface chemistry and substrate.

fred.klaessig@pabionano.com

Citations 1

Slide	Reference(s)
3	a) Robichaud, Uyar, Darby, Zucker, Wiesner, "Estimates of upper bounds and trends in nano-TiO2 production as a basis for exposure assessment." Environ Sci Technol. 2009 Jun 15;43(12):4227-33 b) http://zodiaq.fr/Titanium_Technologies/en_US/tech_info/literature/Coatings/CO_B_H_65969_Coatings_Brochure.pdf
7	Zachariah and Carrier, J. Aerosol. Sci., 1999, 30(9): 1131- 1151
8	www.huntsman.com/pigments/Media/Manufacture_and_Generals_Properties.pdf
9	Ulrich Gesenhues," Chem. Eng. Technol., 2001, 24: 7
11	Nel, Mädler, Velegol, Xia, Hoek, Somasundaran, Klaessig, Castranova, Thompson; Nature Materials 8, 543-557, 2009
13	a) Warheit, Webb, Reed, Frerichs, Sayes , Toxicology. 2007 Jan 25;230(1):90-104 b) External Review Draft Nanomaterial Case Studies: Nanoscale Titanium Dioxide in Water Treatment and in Topical Sunscreen
14	http://www.rci.rutgers.edu/%7Emoghe/583homework.html
15	a) Morris, Skinner, Self, Smart; Colloids and Surfaces A: Phys. & Eng. Aspects, 1999, 155(1): 27-41; b) See Warheit above.

fred.klaessig@pabionano.com

Citations 2

Slide	Reference(s)
16	a) Heinrich, Fuhst, Rittinghausen, Creutzenberg, Bellmann, Koch, Levsen, Inhalation Toxicology 1995, 7(4): 533-556; and b) See Warheit above
17	a) Somasundaran *et alia*; Colloids and Surfaces B: Biointerfaces, 1998, 11(3): 131-139 b) Randon *et alia*; Journal of Membrane Science, 1995, 98:119-129. c) Nelson *et alia*; Langmuir, 2000, 16: 6094-6101.

fred.klaessig@pabionano.com

Thank You

The presentation was reviewed by colleagues from :

- BASF (Ray David, Pat Aikens)
- DuPont (Gary Whiting, Michael Kletter)
- Evonik (Shaun Clancy)

Fred Klaessig, Pennsylvania Bio Nano Systems (215) 858- 7555

fred.klaessig@pabionano.com