Titanium Dioxide and The Importance of Particle Size

Ian Treviranus
ian.treviranus@horiba.com
www.horiba.com/us/particle

What we'll talk about

- **Featured technologies**
- **Applications**
- **Example Particle Size Results**
- **Q&A**

Your interests

- Mill control
- Effect of size on antimicrobial activity and toxicity
- Sizing below 20 nm
- Dispersing TiO_2
- Pigment analysis
- Different technologies
- % Nanoparticles, number concentration
- Advice on choosing TiO_2 grades, etc.

Featured technologies

HORIBA Scientific

- **LA-950 / LA-300**
  Laser Diffraction
- **SZ-100**
  Dynamic Light Scattering & Zeta Potential
- **CAMSIZER & CAMSIZER XT**
  Dynamic Image Analysis
- **PSA300**
  Static Image Analysis
- **SA-9600**
  Flowing Gas BET Surface Area

LA-950: Laser Diffraction

HORIBA Scientific

- Particle size performance leader
- Ninth generation
- Ultra durable
- Lowest total cost of ownership
- Suspension, emulsion, powder, paste, gel
- 10 nanometer – 3 mm

SZ-100: Nanoparticle Analyzer

HORIBA Scientific

- Size: .3 nm - 8 µm
  - 90° and 173°
- Zeta potential: -200 - +200 mV
  - Patented carbon coated electrodes
- Molecular weight: $1x10^3$ - $2x10^7$ g/mol

- Nanoparticles
- Colloids
- Proteins
- Emulsions
- Dispersion stability

CAMSIZER: Image Analysis

HORIBA Scientific

- High resolution size & shape
- Intelligent sieve correlation
- Patented dual capture
- 30 micron – 30 millimeter

What we'll talk about

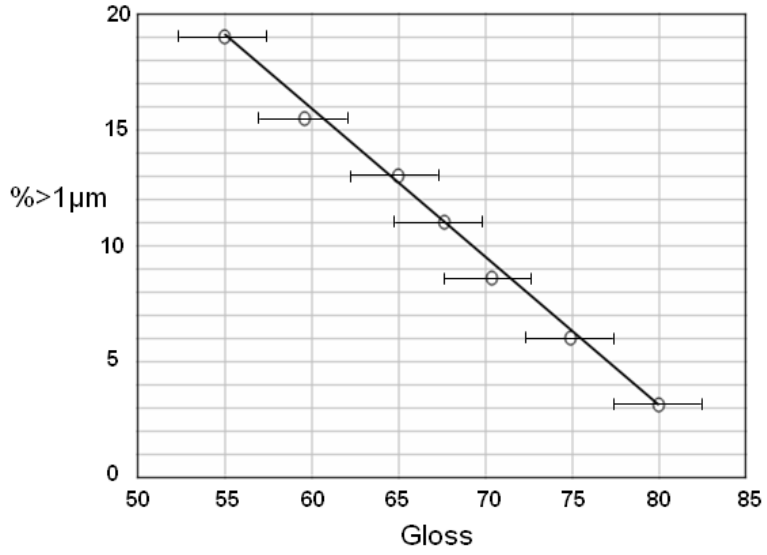
- Featured technologies
- **Applications**
- Example Particle Size Results
- Q&A

The Many Uses of TiO_2

Properties Dependent on Particle Size

- Hue/Tint Strength
- Hiding/Transparency
- Gloss/Flatting and Film Appearance
- Flocculation
- Viscosity
- Stability
- Weather resistance
- Photocatalytic activity
- Air / liquid remediation

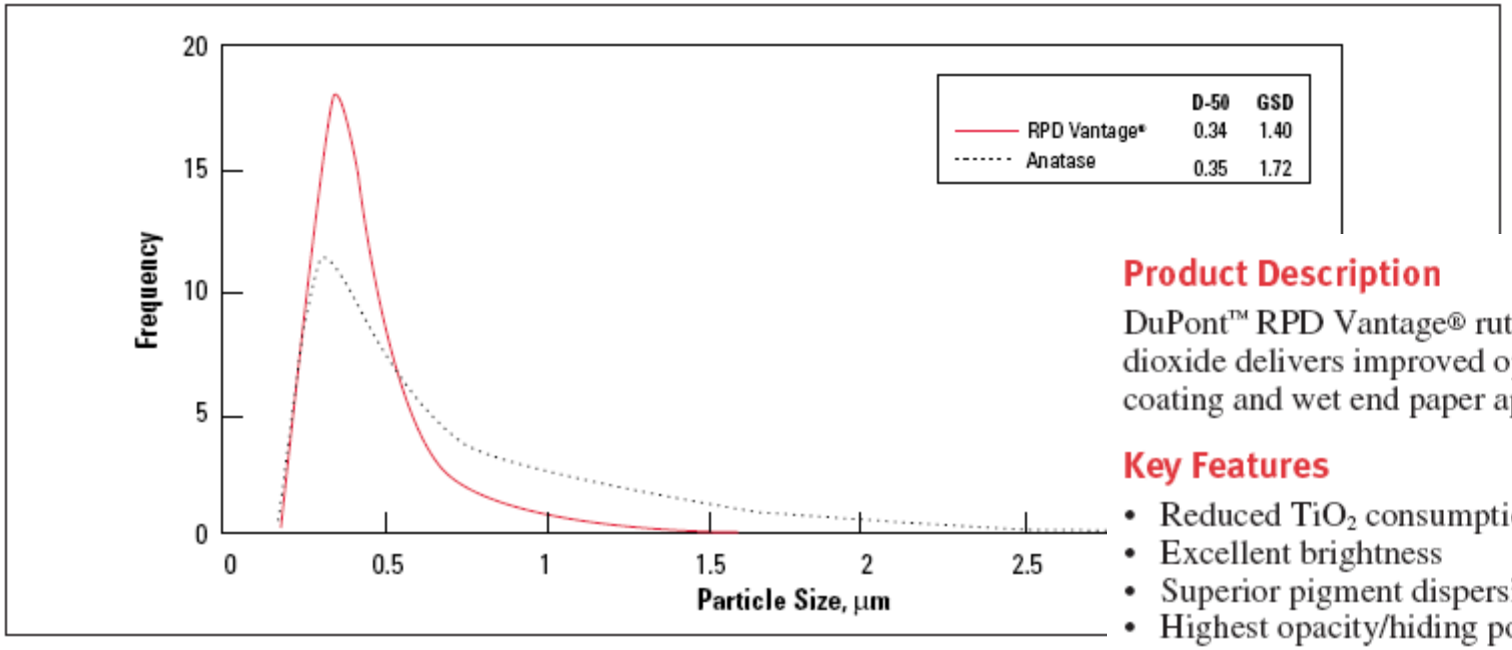
Gloss vs. % > 1 µm

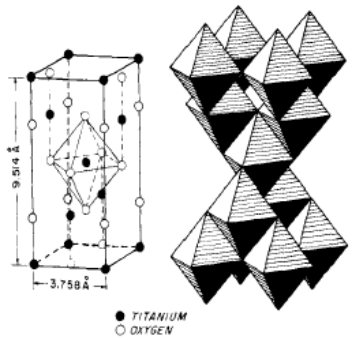


TiO_2 Commercial Data Sheet

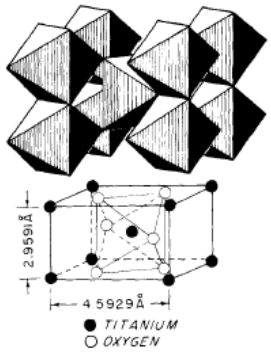
HORIBA Scientific

Figure 1. Particle Size Distribution (Horiba Laser)





Crystal structure of Anatase titanium dioxide



Crystal structure of Rutile titanium dioxide

Product Description

DuPont™ RPD Vantage® rutile paper dry titanium dioxide delivers improved opacifying value for coating and wet end paper applications.

Key Features

- Reduced TiO_2 consumption
- Excellent brightness
- Superior pigment dispersion
- Highest opacity/hiding power

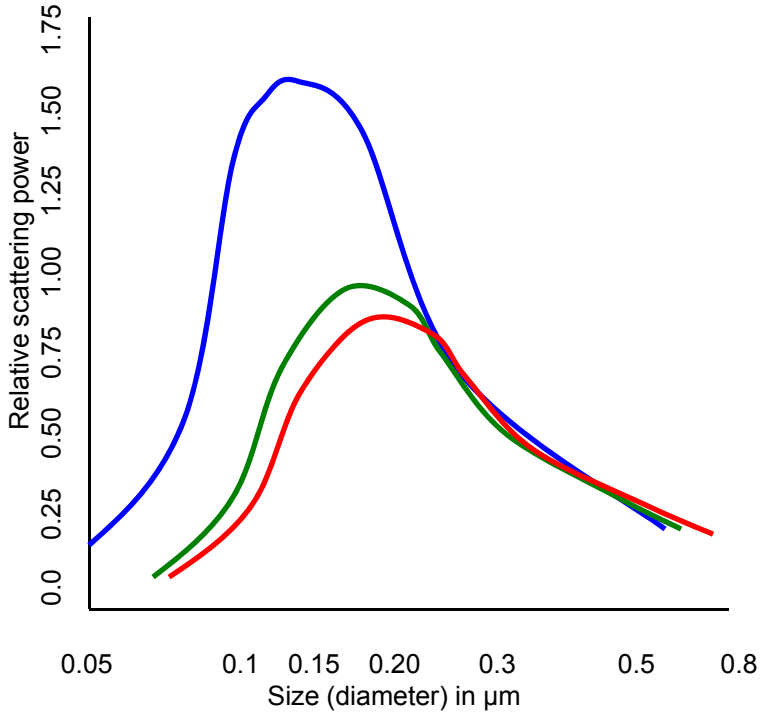
Particle Size

Particle size and distribution are important contributors to light scattering by diffraction. **Figure 1** shows the RPD Vantage® particle size distribution compared against anatase. The lower median particle size (D50) and the narrower geometric standard deviation (GSD) of RPD Vantage® combined with the higher refractive index of rutile result in the highest scattering efficiency.

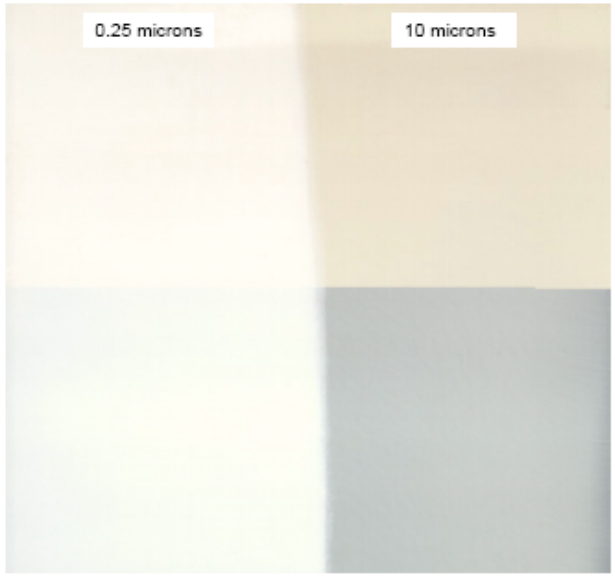
Effect of Size on Hiding Power

HORIBA Scientific

Relative scattering power rutile TiO_2 vs. size



Opacity of TiO_2 mean 0.25 and 10 µm

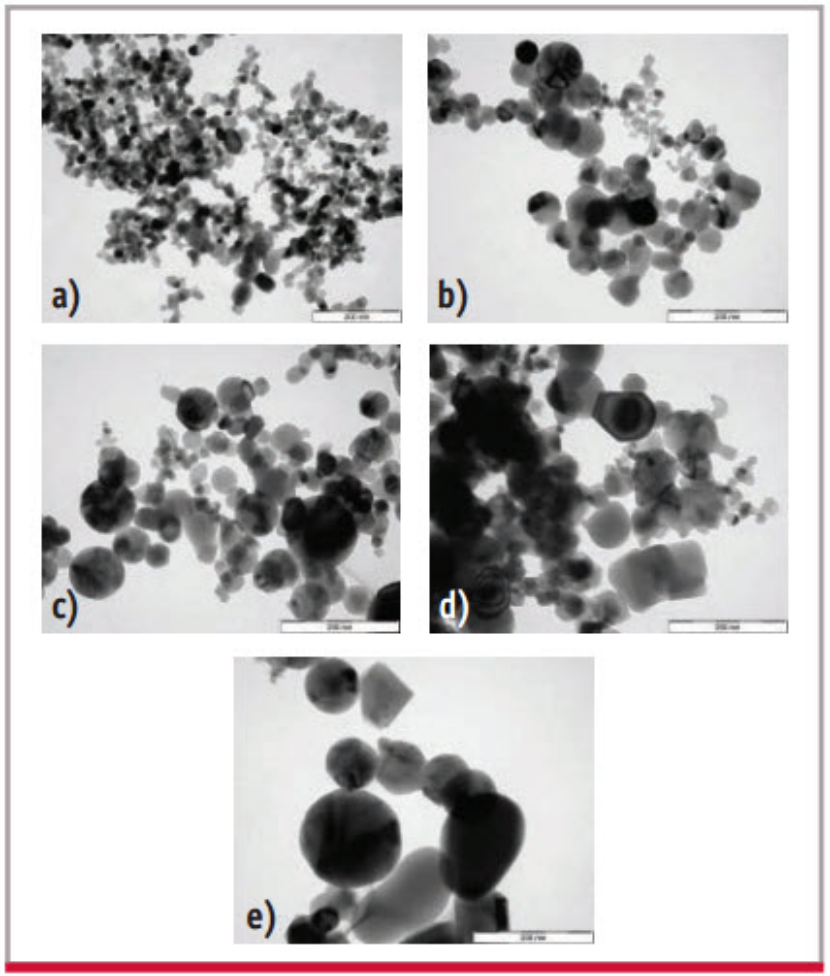


Effect of Size in Sunscreen

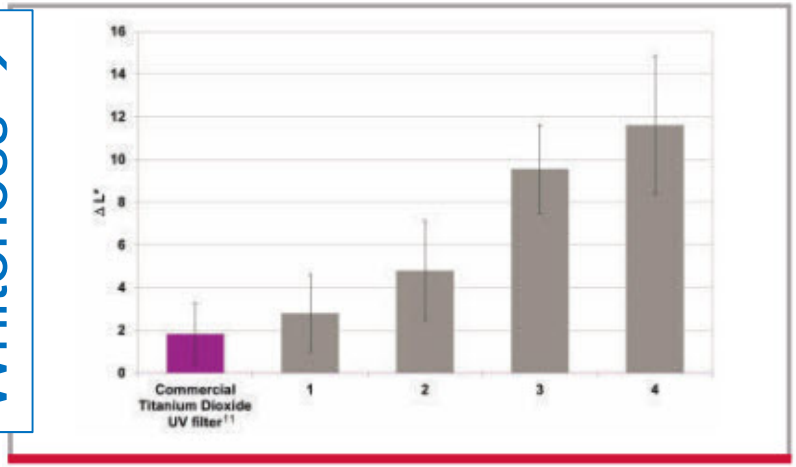
- As median particle size increases…
  - ΔL* decreases, i.e. becomes whiter
  - *in vitro* SPF decreases, i.e. sunburn faster
  - Absorption cross section shrinks, i.e. absorbs less efficiently across multiple wavelengths

Full document available from Evonik's website here: http://personal-care.evonik.com/product/personal-care/en/media-center/downloads/publications/Documents/2013_05_Titanium_dioxide_particle_size_vs_sun_protection_performance_CT.pdf

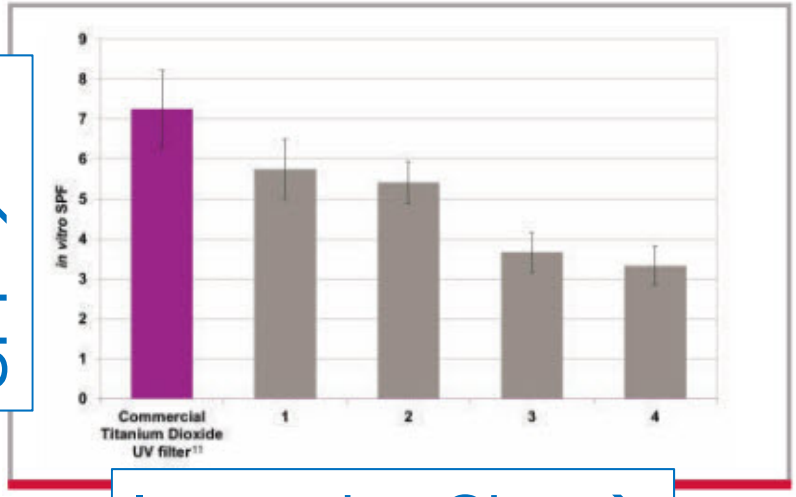
Evonik Sunscreen Study



Increasing Whiteness →



Increasing SPF →



Increasing Size →

Effect of Size in Photocatalysis

- TiO2 photocatalytic activity useful in many applications
  - Antimicrobial coatings
  - Pollution control (noxer blocks, wastewater remediation)
  - Possible explanation for superhydrophilicity (defogging and self-cleaning glass)
- Photocatalysis generally improves as size decreases → surface area and SA / Volume increases

TiO_2 Superhydrophilicity

What we'll talk about

- Featured technologies
- Applications
- **Example Particle Size Results**
- Q&A

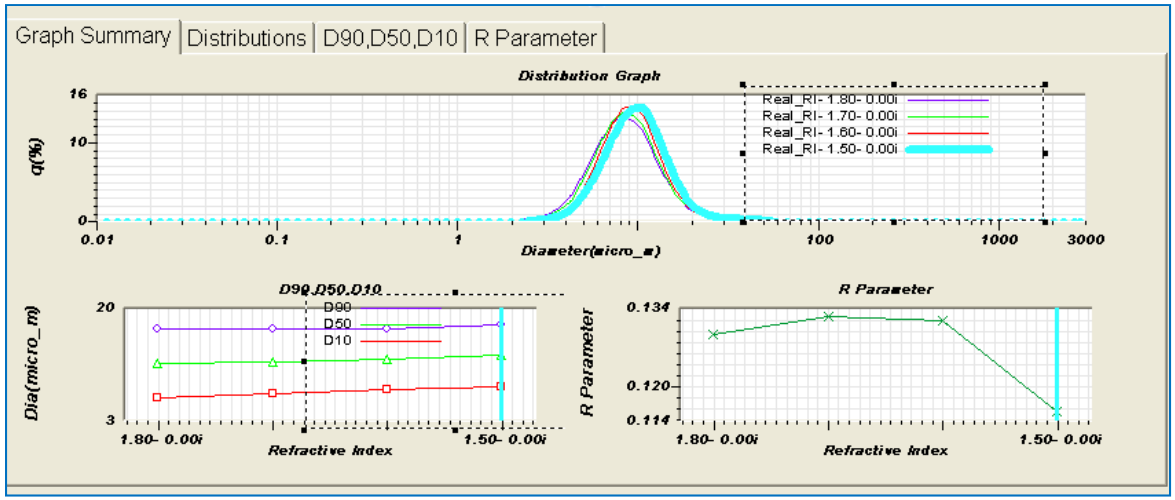
TiO_2 Measurement Procedure

HORIBA Scientific

- Decide wet or dry analysis
- Choose technique: typically laser diffraction, sometimes DLS, others
  - Next HORIBA webinar! Thursday, April 24
- Wet: disperse sample using surfactant and ultrasound
  - Method development using Method Expert
- Dry: Use smallest nozzle, highest air pressure, feedback control

LA-950 Method Expert

- Unique guided method development
- Optimize parameters
- Choose the best refractive index
  - With TiO2 RI well understood, this is useful for coatings, etc.
- Create “one button” SOPs

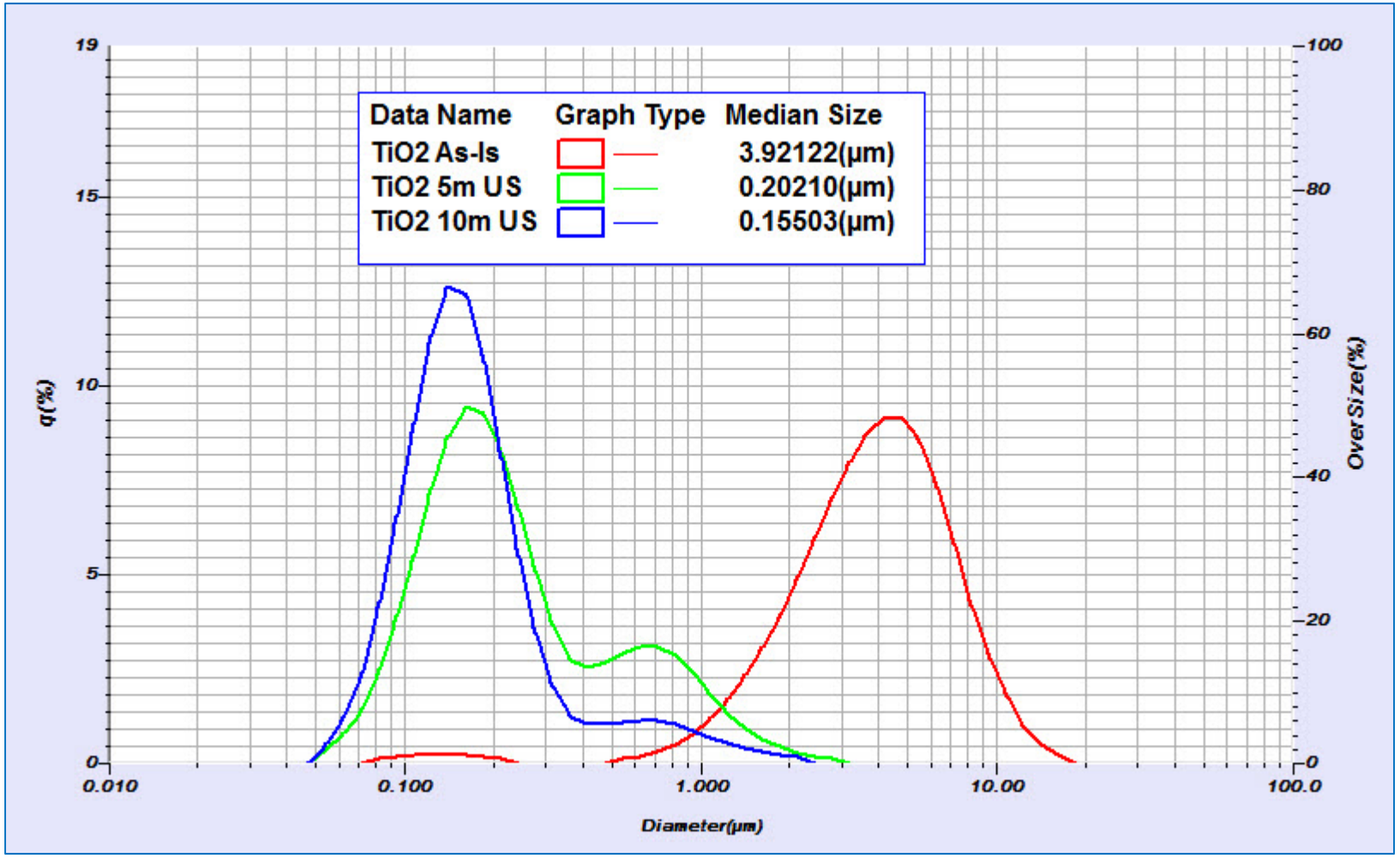


DuPont Ti-Pure Procedure

- Pyrophosphate anion
- Kodak Photo-Flo 200 surfactant
- Significant time (30+ mins.) to disperse
- Designed to use with the HORIBA LA-series particle size analyzers
- Spec'd on D50 and GSD with less than 1% tolerance at 95% CL

Full document available from DuPont's website here:
http://www2.dupont.com/Titanium_Technologies/en_US/tech_info/test_methods/PARTICLE_SIZE_DISTRIBUTION_OF_RPS.pdf

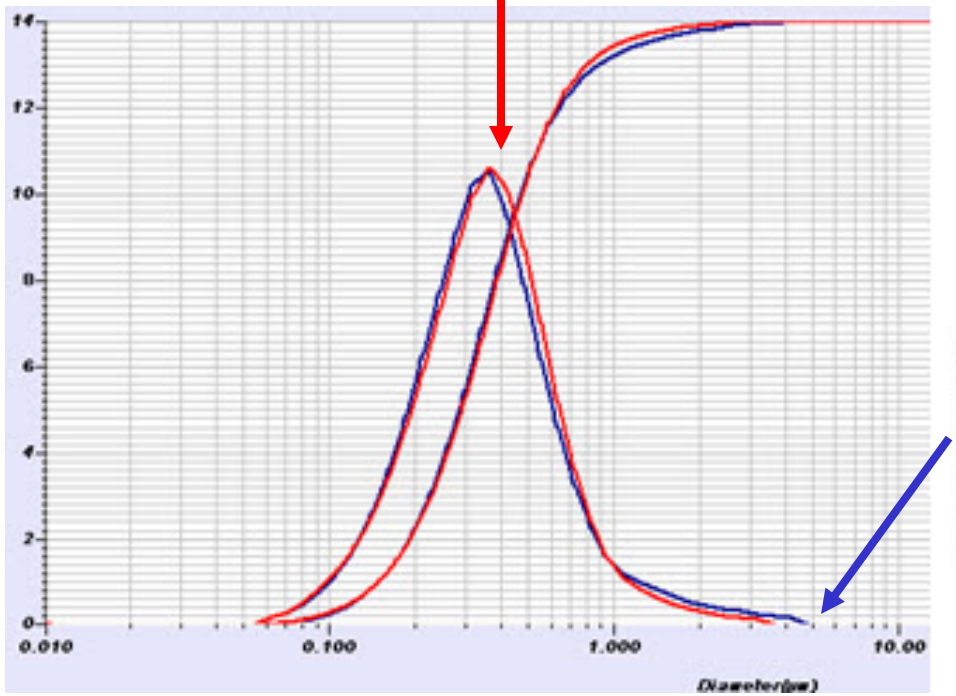
Importance of Sample Prep



Dry Analysis of Two Samples

Mean Size	:	0.44614(µm)
Mode Size	:	0.3615(µm)
Geo.Std.Dev.	:	1.8683(µm)
R Parameter	:	1.3147E-1
D(v,0.1)	:	0.16820(µm)
D(v,0.5)	:	0.34653(µm)
D(v,0.9)	:	0.74838(µm)

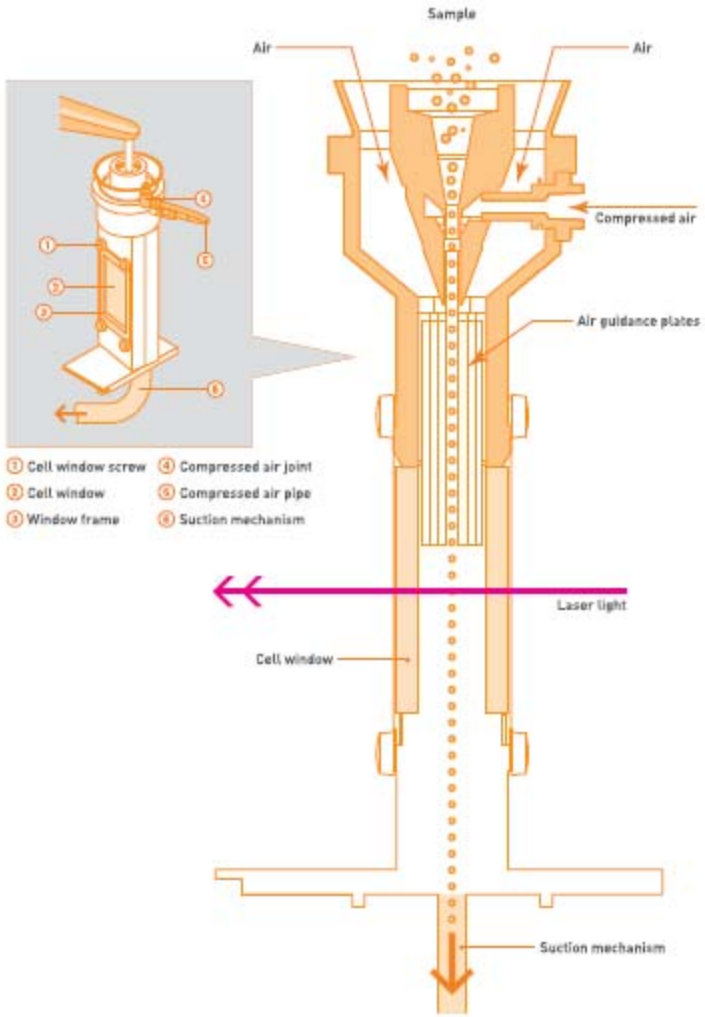
Able to reproducibly distinguish 2 samples with 12 nm difference @ D(v,0.5)



Mean Size	:	0.45286(µm)
Mode Size	:	0.3183(µm)
Geo.Std.Dev.	:	1.9285(µm)
R Parameter	:	8.0177E-2
D(v,0.1)	:	0.16169(µm)
D(v,0.5)	:	0.33394(µm)
D(v,0.9)	:	0.77890(µm)

Measure Powders as Powders

HORIBA Scientific



- Simplify dispersing
- Quick, easy, clean
- Measure in natural state for more actionable results
- Lower costs

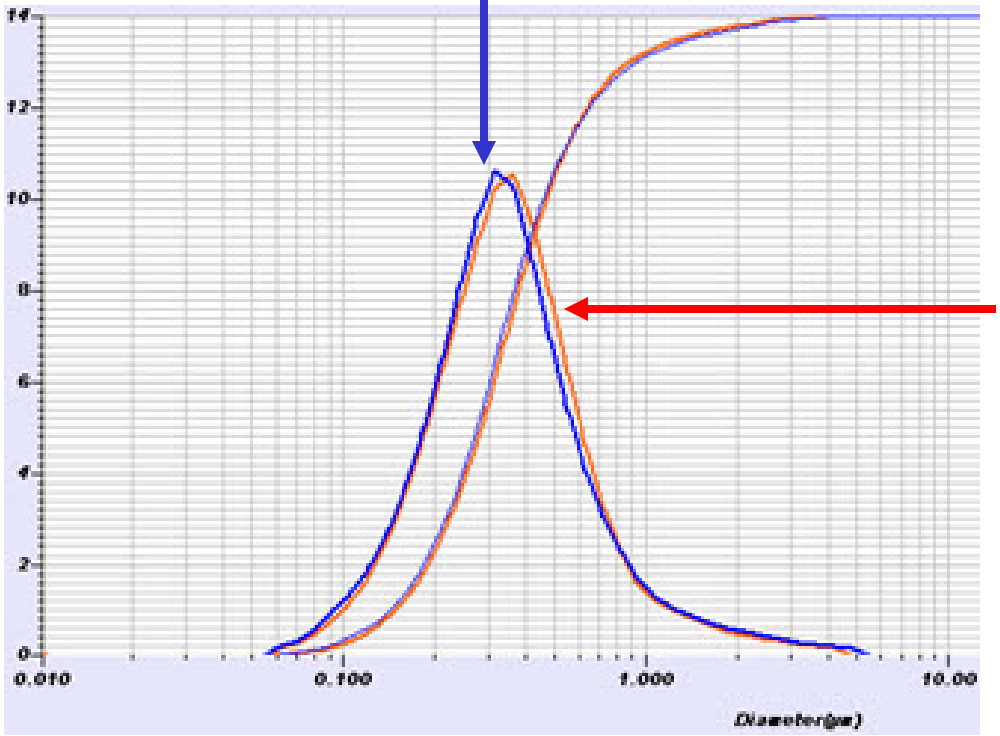
Webinar TE016: Optimizing Dry Powder Measurements

Wet vs. Dry

Only 8 nm difference!
Dry dispersion below 350 nm median

Mean Size	:	0.42307(µm)
Mode Size	:	0.3635(µm)
Geo.Std.Dev.	:	1.7940(µm)
R Parameter	:	6.8993E-2
D(v,0.1)	:	0.16831(µm)
D(v,0.5)	:	0.35496(µm)
D(v,0.9)	:	0.71036(µm)

Wet



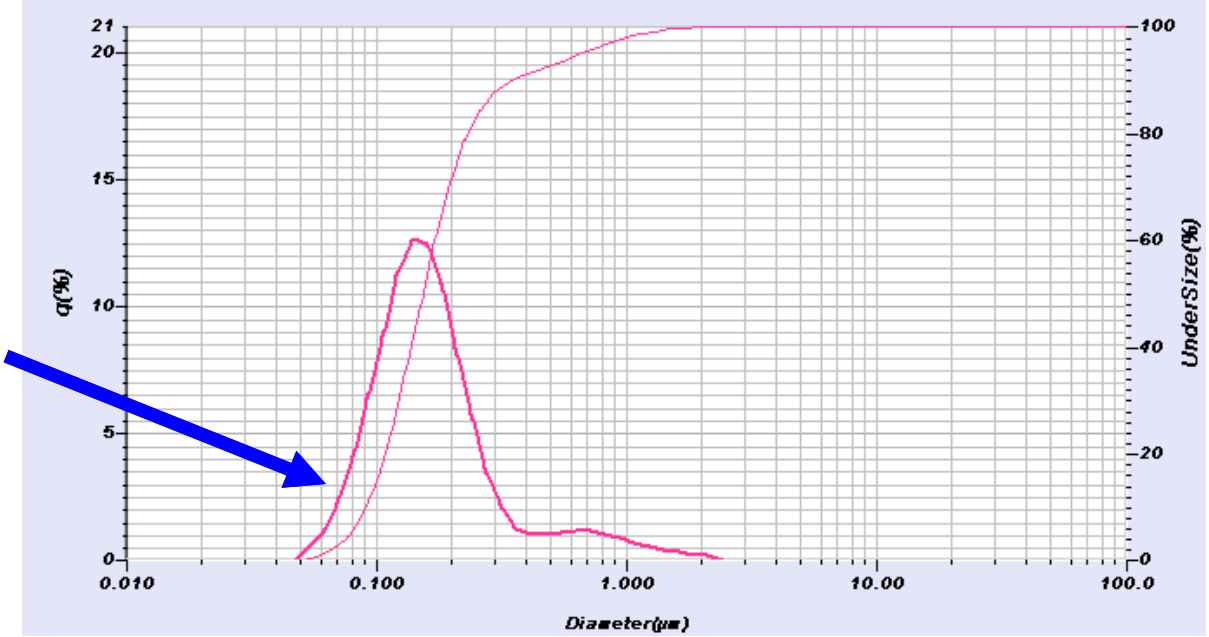
Mean Size	:	0.44614(µm)
Mode Size	:	0.3615(µm)
Geo.Std.Dev.	:	1.8683(µm)
R Parameter	:	1.3147E-1
D(v,0.1)	:	0.16820(µm)
D(v,0.5)	:	0.34653(µm)
D(v,0.9)	:	0.74838(µm)

Dry

Sunscreen with TiO_2

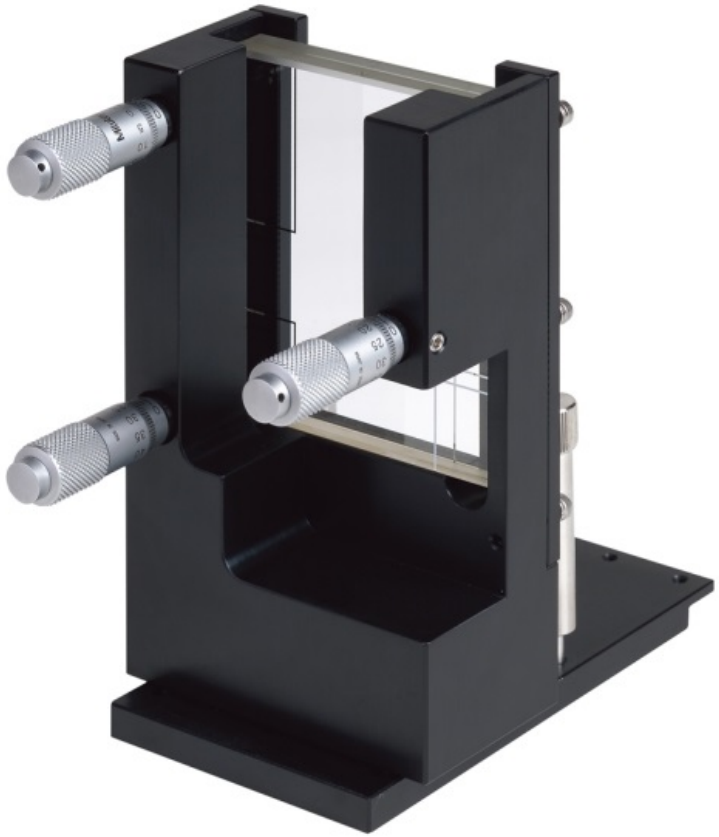
Mean Size	: 0.21941(µm)	
Median Size	: 0.15503(µm)	
R Parameter	: 0.2560	
D(v,0.1)	: 0.09093(µm)	
D(v,0.5)	: 0.15503(µm)	
D(v,0.9)	: 0.36061(µm)	
Cumulative % on Diameter	: (1)0.100 (µm)-	14.473(%)

Powder dispersed in water using surfactant and ultrasound.
Note: 14.5% < 100nm
Safety concerns?

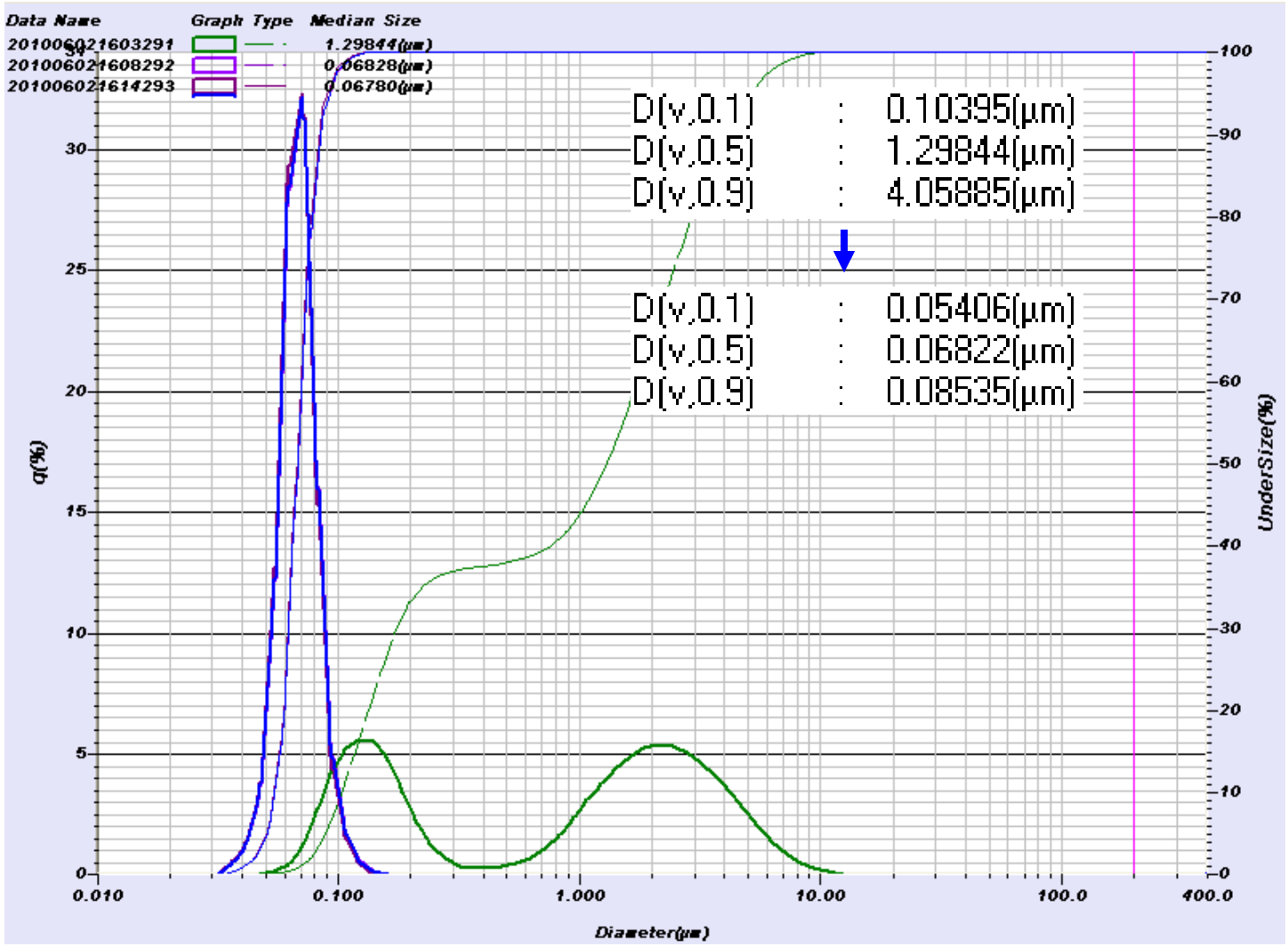


Measure Without Dilution

- Concern that dilution in anything but perfect background will change PSD
- Possible solution with Paste Cell accessory
- Small amount of paste/gel/cream between two glass plates

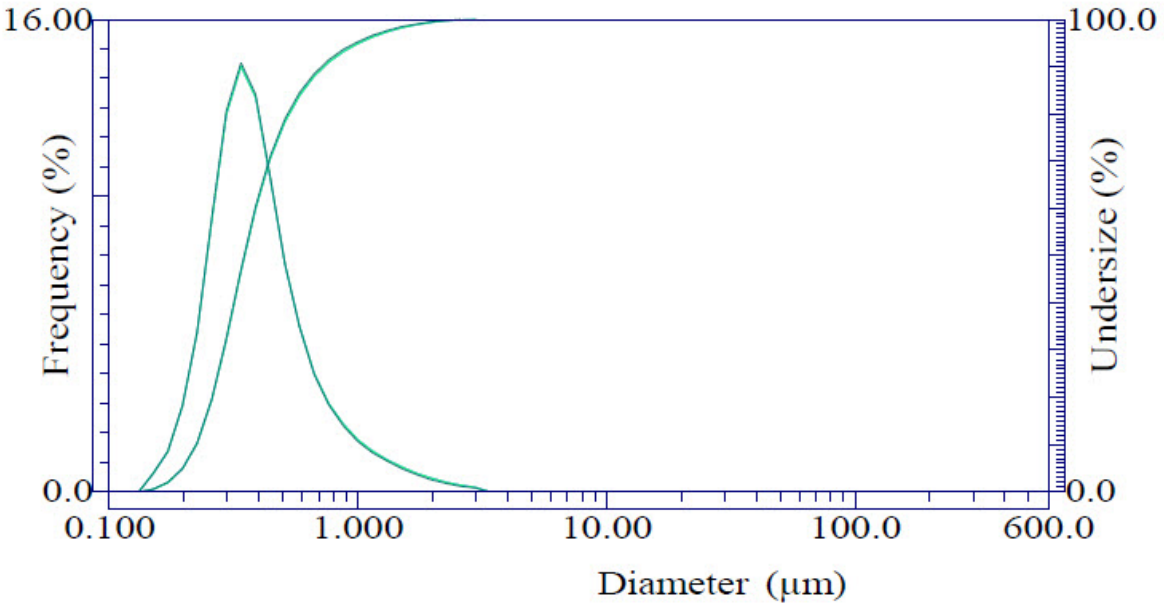


LA-950 Monitors Milling

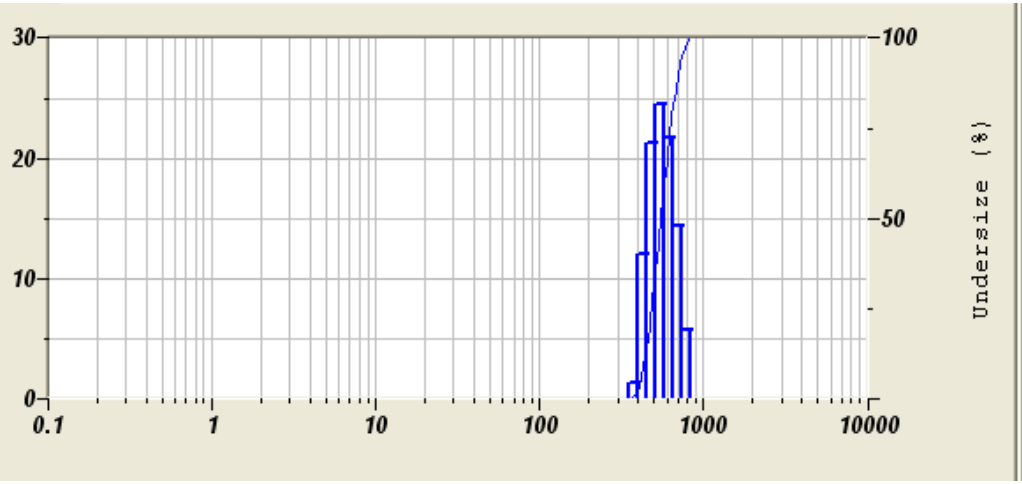


LA-300 Result

- 0.1 – 600 microns
- Portable, rugged
- Suitable for micron-range dispersions



TiO_2 Size & Zeta Potential on SZ-100



Date	:	mardi 13 mars 2012 13:40:23
Measurement Type	:	Particle Size
Sample Name	:	TiO2 P2
Scattering Angle	:	173
Temperature of the holder	:	24.8 °C
Run duration	:	60 Seconds
Representation of result	:	Scattering Light Intensity
Count rate	:	1766 kCPS

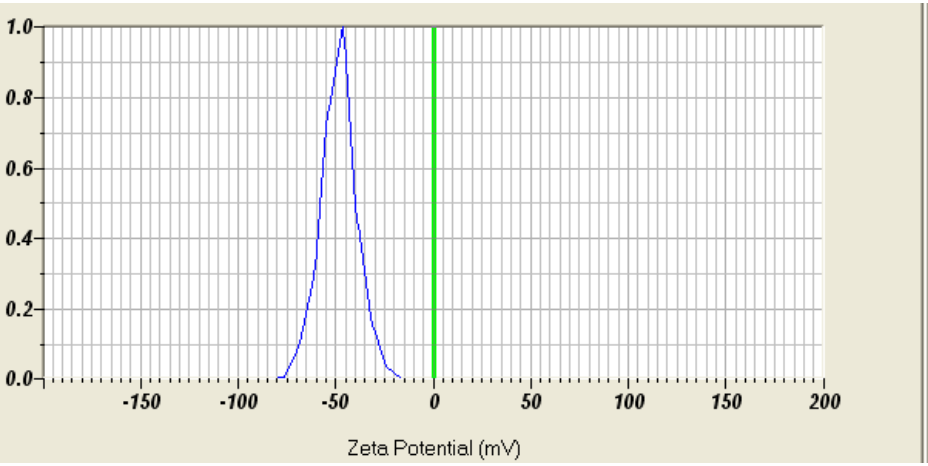
Calculation Results

Peak No.	S.P.Area Ratio	Mean	S. D.	Mode
1	1.00	567.1 nm	99.9 nm	546.6 nm
2	---	--- nm	--- nm	--- nm
3	---	--- nm	--- nm	--- nm
Total	1.00	567.1 nm	99.9 nm	546.6 nm

Cumulant Operations

Z-Average	:	566.7 nm
PI	:	0.047

Size, note: Intensity distribution



Measurement Results

Date	:	jeudi 23 février 2012 10:50:08
Measurement Type	:	Zeta Potential
Sample Name	:	TiO2 pH 7
Temperature of the holder	:	25.0 °C
Viscosity of the dispersion medium	:	0.895 mPa·s
Conductivity	:	0.105 mS/cm
Electrode Voltage	:	3.4 V

Calculation Results

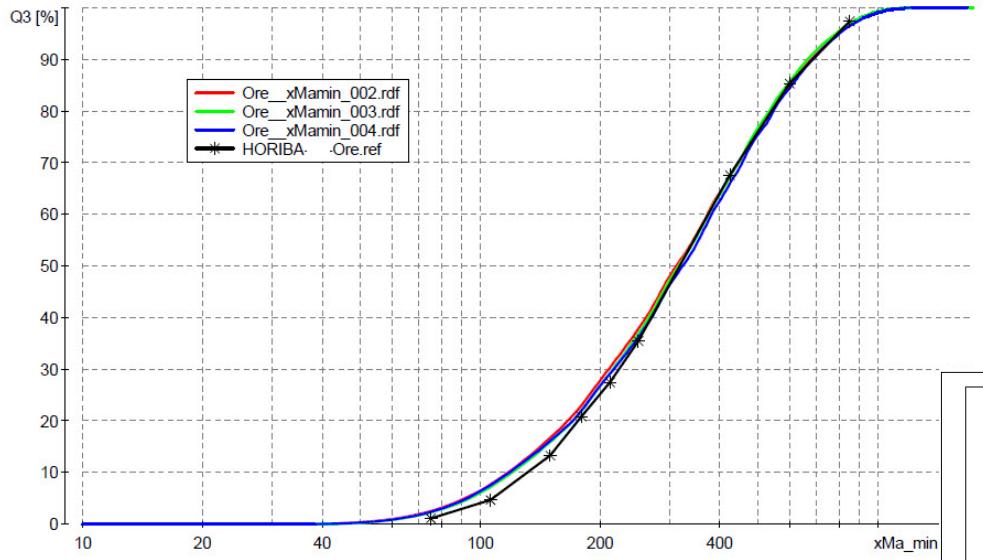
Peak No.	Zeta Potential	Electrophoretic Mobility
1	-48.4 mV	-0.000375 cm2/Vs
2	--- mV	--- cm2/Vs
3	--- mV	--- cm2/Vs

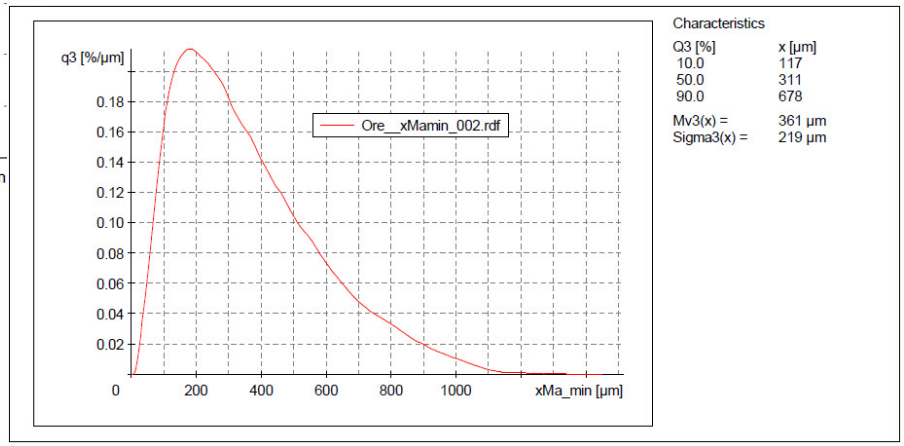
Zeta Potential (Mean)	:	-48.4 mV
Electrophoretic Mobility mean	:	-0.000375 cm^2/Vs

Zeta potential @ pH = 7

Upstream TiO2 Processing

- CAMSIZER Dynamic Image Analyzer can measure ilmenite ore and coke with excellent sieve matching





Mean value SPHT3 = 0.854
Mean value Symm3 = 0.883
Mean value b/l3 = 0.689

Summary

- Particle size plays critical role in the performance of many TiO_2 applications
  - Hiding strength – pigment
  - Whiteness & SPF – sunscreen
  - Antimicrobial efficacy – coatings
  - Photocatalytic efficiency – pollution control
- TiO_2 (and related) applications extend from nanometers to millimeters
- HORIBA has the expertise and technology for every TiO_2 application

HORIBA Scientific

Thank you

ありがとうございました

ขอบคุณครับ

谢谢

اشكُرْ

Gracias

Grazie

Σας ευχαριστούμε

धन्यवाद

நன்றி

Tacka dig

Danke

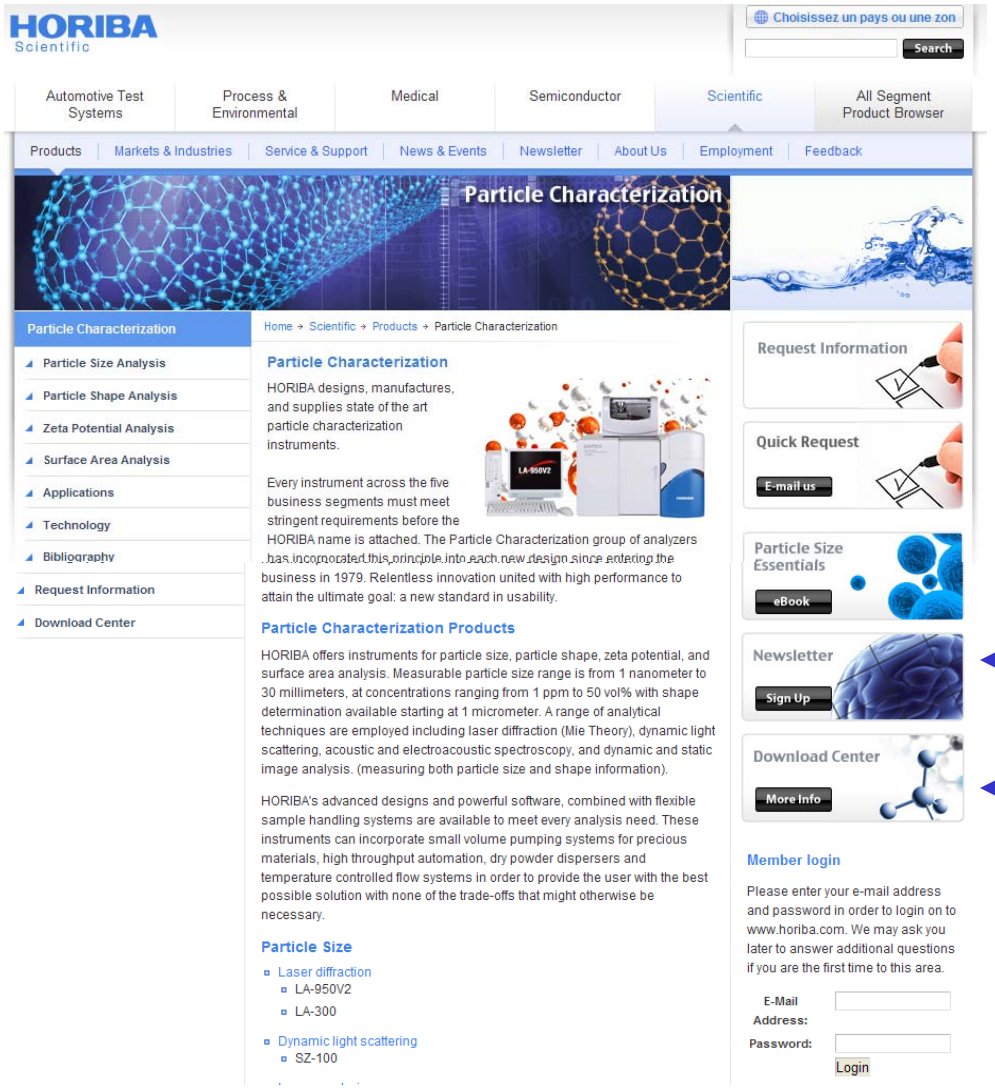
Merci

Obrigado

감사합니다

Большое спасибо

www.horiba.com/particle



Ian Treviranus
Product Line Manager
ian.treviranus@horiba.com

Talk to us, ask questions
labinfo@horiba.com

Receive news of updates

View application & technical notes (170+), webinars (70+), white papers.