Particle Characterization in the Cosmetics Industry

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Particles in Cosmetics

- Any product containing a powder
- Pigments, talc, mica
- Emulsions (creams, lotions)
- Liposomes; simple, complex
- Types of cosmetics containing particles (emulsion droplets)

<table>
<thead>
<tr>
<th>Lips</th>
<th>Lip gloss • Lip liner • Lip plumper • Lipstick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face</td>
<td>Concealer • Foundation • Face powder • Rouge • Bindi • Thanaka • Tilaka • Cleanser-Toner-Moisturizer</td>
</tr>
<tr>
<td>Eyes</td>
<td>Eye liner • Eye shadow • Kohl • Mascara</td>
</tr>
<tr>
<td>Other</td>
<td>Shampoo-Conditioner-Styling cream • Nail polish • Anti-aging cream • Body powder • Cold cream • Sindoor</td>
</tr>
</tbody>
</table>
Original Foundation: Pan-Cake

- Foundation and powder in one
- Base was talc (particle), not oil or wax
- Applied with wet sponge
- Patent in 1937
- By 1940 1 in 3 N American women owned & wore Pan-Cake
Create our Own Product

- **Base**
  - Talc, rice powder
- **Pigment**
  - Iron oxide
- **Filler**
  - Clay
- **Glitter**
  - Mica
- **SPF**
  - TiO2

They’re all particles!

Can measure size of all using one system: LA-950
Measuring Powders as Powders

- Direct flow of powder to cell
- 0 to 4 bar
- Report P used
- Feedback to control powder flow

LA-950

Add powder to vibrating tray, flows through cell where measurement made. Quick, easy, no glassware to clean.
Base: Rice Powder

- Air Transmittance (R): 0.3 MPa
- Sample Data Acquisition Times (LD): 97.6%
- Sample Data Acquisition Times (LD): 5000
- Refractive Index (R): 1.53-0.0i (1.530 - 0.000i)
- Iteration Number: 15
- Feeder: Auto
- Data Name: Rice Powder Max Dry - 01
- Model Type: LA950DRY

D(ν, 0.1) = 5.50291(μm)
D(ν, 0.5) = 8.54916(μm)
D(ν, 0.9) = 13.30517(μm)
Iron Oxide – 170 Shade

LA-950 wet accessories
Disperse powder into a liquid
Can measure down to 30 nm
Gold Glitter Powder

Measure wet + dry, choose preferred
Verify correct P for dry powder feeder

<table>
<thead>
<tr>
<th>Wet</th>
<th>Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Transmittance (R)</strong></td>
<td>77.4 (%)</td>
</tr>
<tr>
<td><strong>Sample Data Acquisition Times (LD)</strong></td>
<td>5000</td>
</tr>
<tr>
<td><strong>Iteration Number</strong></td>
<td>15</td>
</tr>
<tr>
<td><strong>Refractive Index (R)</strong></td>
<td>1.59 [1.590 - 0.100], Water [1.333]</td>
</tr>
<tr>
<td><strong>Data Name</strong></td>
<td>Gold Glitter Max Wet - 01</td>
</tr>
<tr>
<td><strong>Model Type</strong></td>
<td>LA950WET</td>
</tr>
</tbody>
</table>

- **D(v,0.1)**: 68.01367 (μm)
- **D(v,0.5)**: 99.73002 (μm)
- **D(v,0.9)**: 147.47485 (μm)

- **D(v,0.1)**: 73.44803 (μm)
- **D(v,0.5)**: 106.93343 (μm)
- **D(v,0.9)**: 156.32506 (μm)
Gold Glitter Image Analysis

- Minimum: 3.2 μm
- Maximum: 190.4 μm
- Mean: 103.6 μm
- Std Dev.: 35.0 μm
- Sum: 26.6e+09 μm
- Count: 3068

- D10: 61.2 μm
- D50: 101.2 μm
- D90: 154.8 μm

Chart:
- Sph Vol (μm³)
- Cumulative (%)
Shape Parameters

ISO 9276-6:2008 : Representation of results of particle size analysis –
Part 6: Descriptive and quantitative representation of particle shape and morphology

Meso-shape descriptors

How round?
Circularity: \( C = \frac{4 \pi A}{P^2} \)

Aspect ratio?
\( AR = \frac{x_{F_{\text{min}}}}{x_{F_{\text{max}}}} \)
not for very elongated

Convexity = \( P_c / P \)
\( P_c = \) convex hull perimeter
### Mica

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.3 MPa</td>
</tr>
<tr>
<td>Transmittance (R)</td>
<td>98.2(%)</td>
</tr>
<tr>
<td>Sample Data Acquisition Times (LD)</td>
<td>5000</td>
</tr>
<tr>
<td>Refractive Index (R)</td>
<td>1.59-0.1[1.59-0.1(1.590 - 0.100i)]</td>
</tr>
<tr>
<td>Iteration Number</td>
<td>150</td>
</tr>
<tr>
<td>Feeder</td>
<td>Auto</td>
</tr>
<tr>
<td>Data Name</td>
<td>Mica Max Dry - 01</td>
</tr>
<tr>
<td>Model Type</td>
<td>LA950DRY</td>
</tr>
</tbody>
</table>

- \( D(v,0.1) = 3.94080(\mu m) \)
- \( D(v,0.5) = 4.96686(\mu m) \)
- \( D(v,0.9) = 6.28450(\mu m) \)
**Kaolin Clay**

Note: small % below 100 nm, making this a “nanoparticle. Safety concerns?
Sunscreen: TiO2

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

Note: %< 100nm depends on sample treatment (ultrasound)
“Preliminary scientific research has shown that many types of nanoparticles can be toxic to human tissue and cell cultures…”

- Suggests banning all cosmetics with particles <100nm
- Many sunscreens contain ZnO or TiO2 particles <100 nm
Nanoparticle Safety

- NGO Friends of the Earth issue report requesting ban on all skin care products w/particles <100nm
- Claim: some nano-articles are dangerous, so ban all
- Industry claims some nano-particles are safe, so don’t worry
- FDA says we only believe data in peer reviewed journals, but form task force to investigate
- In 2012 Cosmetics manufactures must notify European Commission of any “nanoscale materials” in products
Nanoparticle or Not?

SSA = \( \frac{6}{\rho D} \)

D from SEM ~50 nm
D from SSA ~60-70 nm
D from DLS ~250 nm
(light scattering due to Brownian motion)

So: is this a nanoparticle?

Used ultrasound to disperse to primary particles or use weak acid to break bonds
D from DLS ~50 nm
### Acoustics: ZnO Study

<table>
<thead>
<tr>
<th>POWDER Name, Manufacturer</th>
<th>Median size, microns</th>
<th>Cum % of nanoparticles &lt;100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide, 99.5+% by Acros Organics</td>
<td>0.273±0.01</td>
<td>11.0±1.4</td>
</tr>
<tr>
<td>Zinc oxide, reagent ACS by Acros Organics</td>
<td>0.430±0.02</td>
<td>7.0±0.5</td>
</tr>
<tr>
<td>Z50-500 USP powder packaged by Fisher Scientific</td>
<td>0.561±0.017</td>
<td>2.7±0.39</td>
</tr>
<tr>
<td>Z52-500 USP powder packaged by Fisher Scientific</td>
<td>0.660±0.037</td>
<td>1.9±0.4</td>
</tr>
<tr>
<td>S80249 by Fisher Scientific</td>
<td>0.398 ± 0.001</td>
<td>6.1±0.2</td>
</tr>
<tr>
<td>Zinc oxide ACS reagent grade by MO Biomedicals, LLC</td>
<td>0.349±0.017</td>
<td>8.2±2.1</td>
</tr>
<tr>
<td>Zinc oxide Polystormor by Mallinckrodt Chemicals</td>
<td>0.223±0.009</td>
<td>19.6±1.8</td>
</tr>
<tr>
<td>Zinc oxide Nanopowder by American Elements</td>
<td>0.631±0.1</td>
<td>4.7±2.5</td>
</tr>
</tbody>
</table>
Acoustics: ZnO Study

- Zinc oxide, reagent ACS by Acros Organics
- Zinc oxide, 99.5+% Acros Organics
- Z50-500 USP
- Z52-500 USP
- S80249 by Fisher Scientific
- Zinc oxide 99.99% by Alfa Aesar
- Zinc oxide ACS MO Biomedicals, LLC
- PolystormorTM by Mallinckrodt Chemicals
- Nanopowder America Elements

Zinc oxide, reagent ACS by Acros Organics
Zinc oxide, 99.5+% Acros Organics
Z50-500 USP
Z52-500 USP
S80249 by Fisher Scientific
Zinc oxide 99.99% by Alfa Aesar
Zinc oxide ACS MO Biomedicals, LLC
PolystormorTM by Mallinckrodt Chemicals
Nanopowder America Elements
Percentage of nano particles in Z52-500 sample after incremental additions of the Mallinckrodt Chemicals sample. The X-axis is a percentage calculated from the known amount of the added Mallinckrodt sample, assuming that it contains 20% on nano-particles, according to the Table 1. The Y-axis is a percentage calculated from the attenuation spectra, which is measured for the mixture.
DT-1201 Hardware

- Sample
- Servomotor with transducer
- Dispersion chamber
- Detector
- Frequency: 1-100 MHz
- Variable gap: 0.15-20 mm
Piezo crystal

Electrodes

Zeta Potential Probe

Colloid Vibration Current

\[ CVI = C \frac{\rho_p - \rho_m}{\rho_m} \phi \mu_d \nabla P \]

Dynamic Mobility

\[ \mu_d = \frac{\varepsilon_m \varepsilon_0 \zeta (\rho_p - \rho_s) \rho_m K_s}{\eta (\rho_p - \rho_m) \rho_s K_m} \]
Zeta Potential

- If surface has + charge, then - ions attracted to surface
- + ions attracted to – ions, builds electric double layer
- Slipping plane: distance from particle surface where ions move with particle
- ZP = potential (mV) at slipping plane
Stability

- Want stable dispersion
- Either suspensions or emulsions
- Suspensions sediment & flocculate
- Emulsions phase separate, creaming or coalescence
Stabilization

- Steric stabilization: coat surface with polymers
  - Particles can’t touch so they don’t interact
- Electrostatic stabilization: alter surface chemistry to put charge on particle surface
  - Repel like magnets
pH Titration of Rutile 7%vl & Alumina 4%vl

PSD unstable @ IEP
aggregates form
Skin Cream

Emulsion w/SPF 15

- Oil phase
- Water phase

**Graphical Data**

- Mean Size: 0.41213 (μm)
- Median Size: 0.18935 (μm)
- Chi Square: 5.313640
- R Parameter: 1.6798E-1
- D(v,0.1): 0.10214 (μm)
- D(v,0.5): 0.18935 (μm)
- D(v,0.9): 0.38762 (μm)
- Cumulative % on Diameter: (1)0.100 (μm) - 9.155 (%)
Emulsion Stability

Greater zeta potential

Add surfactant to Stabilize emulsion
Test zeta potential Vs. surfactant conc.
Emulsions

- **Creams**: semi-solid emulsions, mixtures of oil & water
- **Ointment**: viscous semisolid preparation used topically
  - Vehicle of an ointment is known as ointment base
  - Hydrocarbon bases e.g. hard paraffin, soft paraffin
  - Absorption bases e.g. wool fat, beeswax
  - Water soluble bases e.g. macrogols 200, 300, 400
  - Emulsifying bases e.g. emulsifying wax, cetrimide
  - Vegetable oils e.g. olive oil, arachis oil, coconut oil
Liniment, (or embrocation) is a medicated topical preparation for application to the skin. Preparations of this type are also called balm.

- Liniments are of a similar viscosity to lotions (being significantly less viscous than an ointment or cream) but unlike a lotion a liniment is applied *with friction*; always rubbed in.

- Liniments are typically sold to relieve pain and stiffness

**Paste**: substance that behaves as a solid until a sufficiently large load or stress is applied, at which point it flows like a fluid.
Microemulsions are Transparent & thermodynamically stable, <150 nm

Collected with HORIBA LB-500
Liposomes

Penetration of Tritiated Atropine into Skin

<table>
<thead>
<tr>
<th>Skin Location</th>
<th>40 nm Liposome</th>
<th>Aqueous Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratum Corneum</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>Epidermis</td>
<td>6000</td>
<td>2000</td>
</tr>
<tr>
<td>Dermis</td>
<td>4000</td>
<td>1000</td>
</tr>
<tr>
<td>Subcutaneous</td>
<td>2000</td>
<td>500</td>
</tr>
<tr>
<td>Plasma</td>
<td>1000</td>
<td>100</td>
</tr>
</tbody>
</table>

Discussion
A Horiba LA 900 particle size analyzer was used to determine the average particle size for the following evaluations.

Brookosome® ACE
The Brookosome® ACE liposome alone shows a very tight, nearly symmetrical distribution around 0.25 microns. This distribution indicates the presence of a well defined, stable unilamellar vesicle.

Gel Test Vehicle
The Brookosome® ACE liposome was then dispersed into a carbomer gel, under low shear mixing. As with the undispersed test liposome, the particle size remains well defined, with the average particle size at 0.26 microns. This evaluation indicates that unilamellar liposomes can withstand manufacturing processes using low shear; these processes include not only mixing but also the pumping stress associated with the transfer and filling of a finished product.
Liposome Delivery

**Liposome approaches skin barrier layer**

- Active ingredient
- Polar ends
- Non-polar bilayer
- Hydrophilic pocket

**Liposome fuses with skin barrier layer**

**Liposome dissolves & releases actives (retinol?)**

**Penetrates into skin**
Liposomes by DLS

Liposome size after 5 passes through 100 mm membrane, mean size ~ 250 nm

Liposome size after 20 passes through 100 mm membrane, mean size ~ 150 nm

Retinol Formulation - Delivery

“Retinal contained in the core space of the vesicle which has a mean diameter of 10~50nm”…

Ingtradians: Retinol (liposome)
Summary

- Many cosmetic products either powder (particle) based, or contain powders
- Wide range measured by laser diffraction (LA-950)
- Image analysis provides additional shape information
- Acoustics measures size & zeta potential with no dilution
- DLS for sub-micron size + dilute zeta potential
For More Details

- Visit horiba.com

- Application Notes:
  - AN152 Measuring Emulsions using Acoustics
  - AN161 Particle Size Analysis of Cosmetics
  - AN171 Measuring Nanoparticles using Acoustics
  - AN174 Measuring Liposomes using DLS

- Webinars:
  - State of the Art Laser Diffraction Performance
  - The DT Series Acoustic Spectrometers
  - Size and Stability for Biotech and Nanotech

Thank-you