NANOTECHNOLOGY FOR WATER-BASED PAINT IMPROVEMENT

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BiPHOR™
The New White Pigment

Definitions of nanoscience and nanotechnology

- *Nanoscience* is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.

- *Nanotechnology* is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.

Source: http://www.royalsoc.ac.uk

Nanotechnology tools

- Chemical synthesis
  - Well established for over a century
- Self-assembly
  - Widely used by Mother Nature
  - Increasingly used since the 80’s
- Nanomanipulation
  - At some point in the future
  - Problem: Avogadro’s number is very large

Aluminum phosphates are versatile materials

- Crystalline or amorphous
- A broad range of synthetic methods
- A **broad range of product properties**
  - Depending on the synthetic method
- Particles, fibers, crystals, films
- Particles are used as
  - Catalyst support
  - Adjuvants in fabrication of vaccines
  - Anti-acid medicines
  - Anti-corrosive paint additives

Can we make a white pigment out of aluminum phosphate?

- **YES, WHITE PIGMENT BASED ON HOLLOW PARTICLE FORMATION**
  - **ORTOPHOSPHATE**
  - **POLYPHOSPHATES**
- **PARTICLE VOIDS ARE**
  - **PREFORMED**
  - **FORMED DURING PAINT DRYING**
  - **AN EMERGING PROPERTY**
  - **THE OUTCOME OF A RARE NANOSTRUCTURE FORMATION PROCESS**

Characteristics of BiPHOR™ aluminum phosphate

- Non-crystalline solid
- Controllable stoichiometry and hydration
- Nano-structured particles with core-and-shell structure
- Nanosized particles are easily dispersed
  - stable towards settling
- Nanoparticles are strongly compatible with latex particles and other particulate solids
- Non-corrosive

Free of environmental and toxicological problems

- Green chemistry process
- Wet-chemistry under mild conditions
- Zero-effluents
- Residues can be safely discarded
  - composting

Biological Tests

The tests were conducted in compliance with U.S. Environmental Protection Agency's by ABC Laboratories, USA.

Title: Aluminum Polyphosphate: Acute Toxicity to the Fathead Minnow, *Pimephales promelas*, Determined Under Static Test Condition.

Nominal concentrations of BiPHOR™ in water: 0 (control), 0.01, 0.10, 1.0, 10, 100, and 1,000 mg/L.

Results: Mortality and sub-lethal responses were not observed in any of the control or test substance treatments after 96 hours of exposure.

Source: ABC Laboratories, Inc. 7200 E. ABC Lane, Columbia, Missouri.

A deep scientific basis

- Beppu MM, Lima ECDO, Galembeck F.; Aluminum phosphate particles containing closed pores. Preparation, characterization, and use as a White pigment; JOURNAL OF COLLOID AND INTERFACE SCIENCE, 1996, 178 (1): 93-103.

- Lima ECD, Beppu MM, Galembeck F, Valente JF, Soares DM.; Non-crystalline aluminum polyphosphates: Preparation and properties; JOURNAL OF BRAZILIAN CHEMICAL SOCIETY, 1996, 7 (3): 209-215.

- Lima ECD, Beppu MM, Galembeck F.; Nanosized particles of aluminum polyphosphate; LANGMUIR, 1996, 12 (7): 1701-1703.

- Beppu MM, Lima ECD, Sassaki RM, Galembeck F.; Self-opacifying aluminum phosphate particles for paint film pigmentation; JOURNAL OF COATINGS TECHNOLOGY, 1997, 69 (867): 81-88.

- De Souza EF, Bezerra CC, Galembeck F.; Bicontinuous networks made of polyphosphates and of thermoplastic polymers; POLYMER, 1997, 38 (26): 6285-6293.

- Monteiro VAD, de Souza EF, de Azevedo MMM, Galembeck F.; Aluminum polyphosphate nanoparticles: Preparation, particle size determination and microchemistry; JOURNAL OF COLLOID AND INTERFACE SCIENCE, 1999, 217 (2): 237-248.

- De Souza EF, da Silva MDCVM, Galembeck F.; Improved latex film-glass adhesion under wet environments by using na aluminum polyphosphate filler; JOURNAL OF ADHESION SCIENCE AND TECHNOLOGY, 1999, 13 (3): 357-378.

- Azevedo MMM, Bueno MIMS, Davanzo CU, Galembeck F.; Coexistence of Liquid Phases in the Sodium Polyphosphate-Chromium Nitrate-Water System; JOURNAL OF COLLOID AND INTERFACE SCIENCE, 2002, 248 (1): 185-193.

Theses and Dissertations

- 1990: Obtenção de Novos Materiais pelo Processo Sol-Gel; Óxidos e Fosfatos de Ferro. PhD Thesis, P.P. Abreu-Filho
- 1991: Obtenção e Caracterização de Metafosfatos de Alumínio: um Novo Pigmento Branco. MSc Dissertation, Emília C.de Oliveira Lima.
- 1995: Gelificação termorreversível em soluções aquosas de polifosfato de alumínio. PhD Thesis, Emília C. de Oliveira Lima.
- 1996: Géis, vidros e compósitos de polifosfatos de cálcio, de ferro (III) e mistos. MSc Dissertation, Nancy C. Masson.
- 1996: Obtenção e caracterização de fosfatos de alumínio amorfos. MSc Dissertation, Marisa M. Beppu.
- 1998: Vítor Augusto do Rego Monteiro. Nanopartículas de polifosfato de alumínio. MSc Dissertation, V.A. do Rego Monteiro.

Patents

- 1991: Processo de Obtenção de Pigmentos Brancos, PI 9104581-9. *E.C.O. Lima and F. Galembeck*

- 1994: Processo de Síntese de Partículas Ocas de Fosfato de Alumínio. PI 9400746-2. *M.M. Beppu and F. Galembeck*

- 1995: Processo de Obtenção de Partículas Ocas de um Metafosfato Duplo de Alumínio e Cálcio em Látex Poliméricos. PI 9500522-6. *E.F. de Souza and F. Galembeck*

- 1997: Processo de síntese de partículas de fosfato e polifosfatos de ferro (III), simples duplos ou múltiplos, não-cristalinos. PI: 9700586-0. *E.F. de Souza and F. Galembeck*

Current product and process

- 2004 - Produto e Processo de Fabricação de um Pigmento Branco Baseado na Síntese de Partículas Ocas de Ortofosfato ou Polifosfato de Alumínio. PI0403713-8

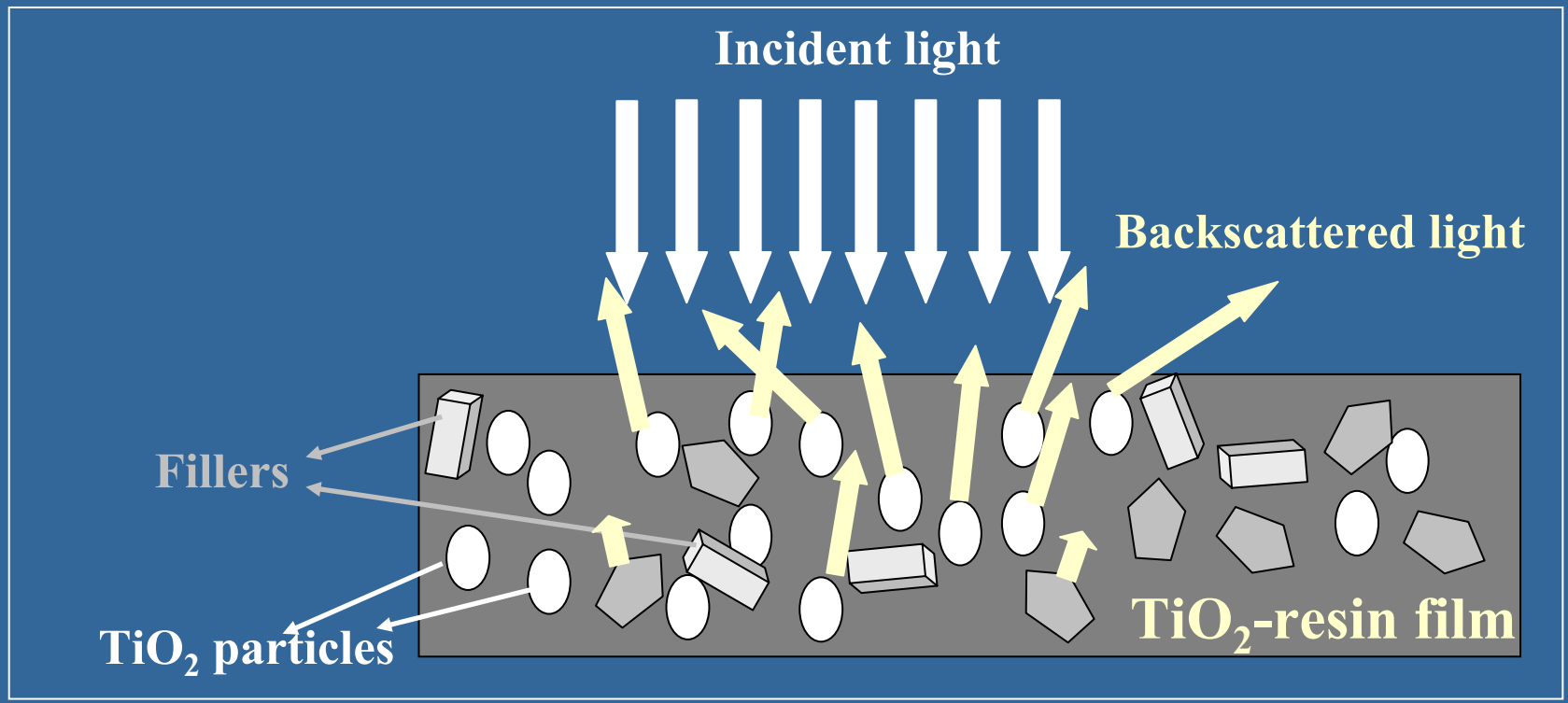
- 2005 - PCT Patent Applications: Aluminum Phosphate or Polyphosphate Particles for Use as Pigments in Paints and Method of Making Same

Inventors: F. Galembeck and J. de Brito

Assignees: Unicamp and Bunge

HOW ALUMINUM PHOSPHATES WORK?

Light Backscattering by TiO_2-Pigmented Resin Film

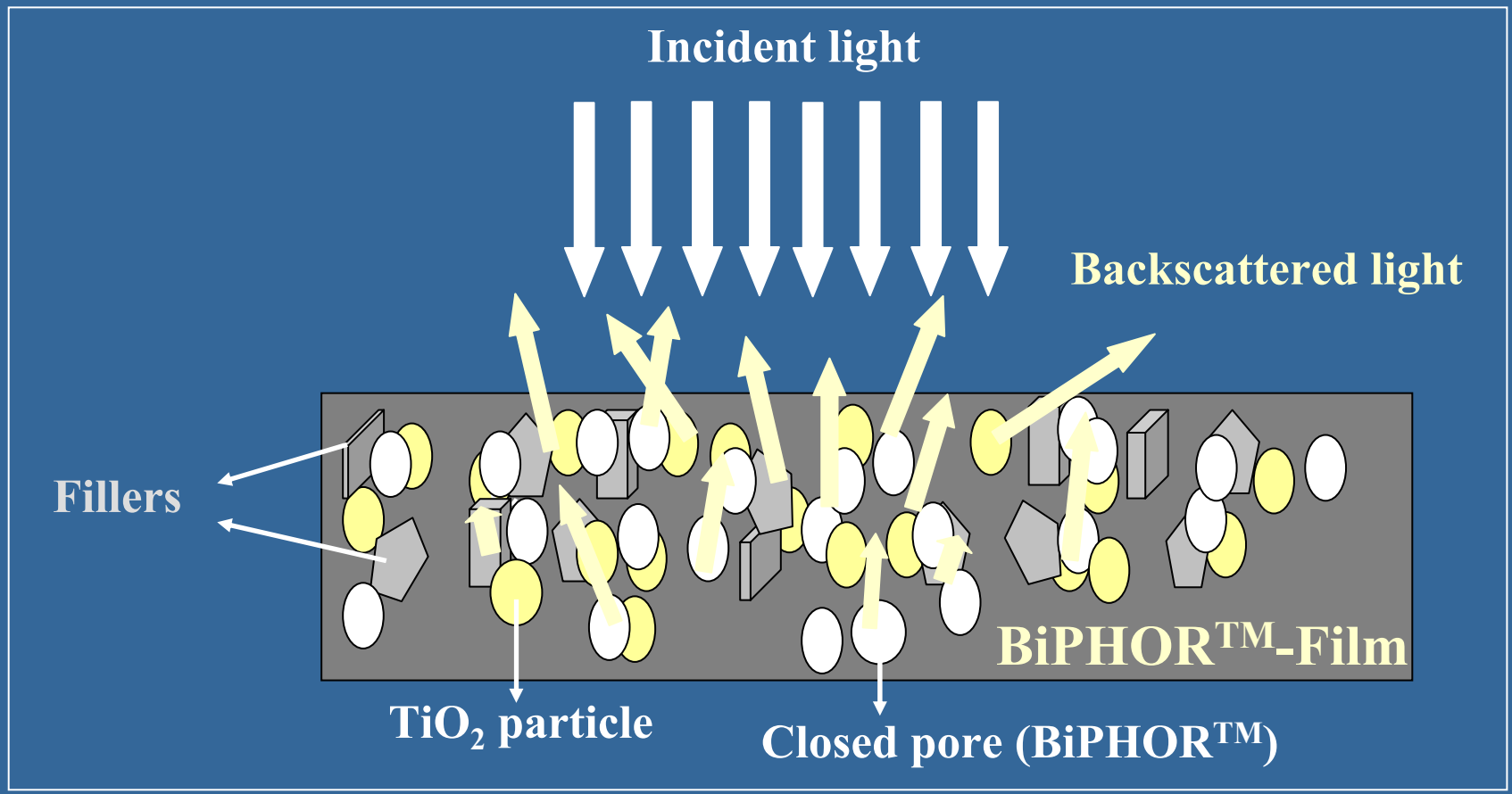


Pigment and filler particles are dispersed throughout the film and they backscatter incident light

Large refractive index difference between the resin and the particles

Near-UV light absorption

Light Backscattering by BiPHOR™-Resin Film



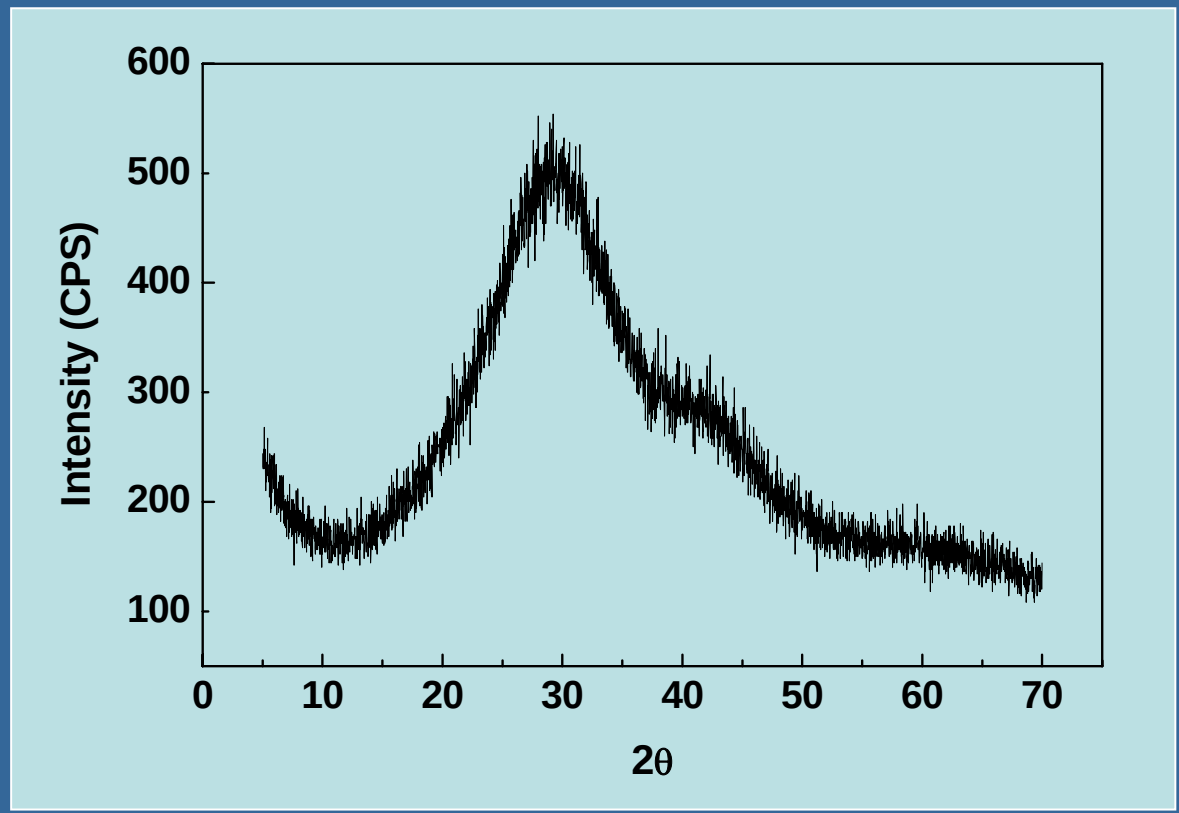
Pigment particles as well as closed pores are scattered and they backscatter incident light

Large refractive index difference between the resin and the particles or closed pores

CHARACTERIZATION

- X-Ray Diffraction
- X-Ray Fluorescence
- Thermogravimetry
- Infrared
- Transmission Electron Microscopy
- others

X-Ray Diffraction (dry powder)



Amorphous halo (Broad bands)
Non-crystalline powder
Average P-O and Al-O distances

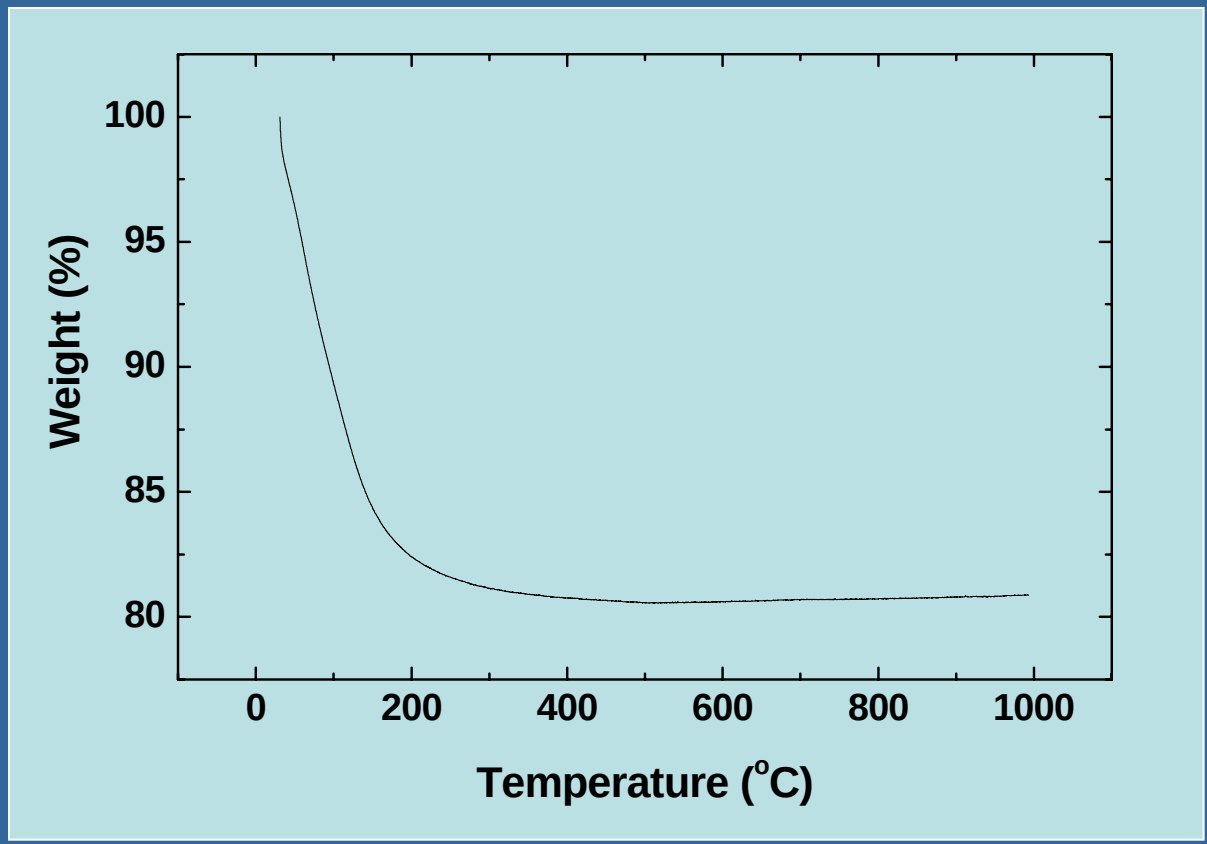
X-Ray Fluorescence

Elemental Composition of BiPHOR™ grades

Variation in P/Al Ratio

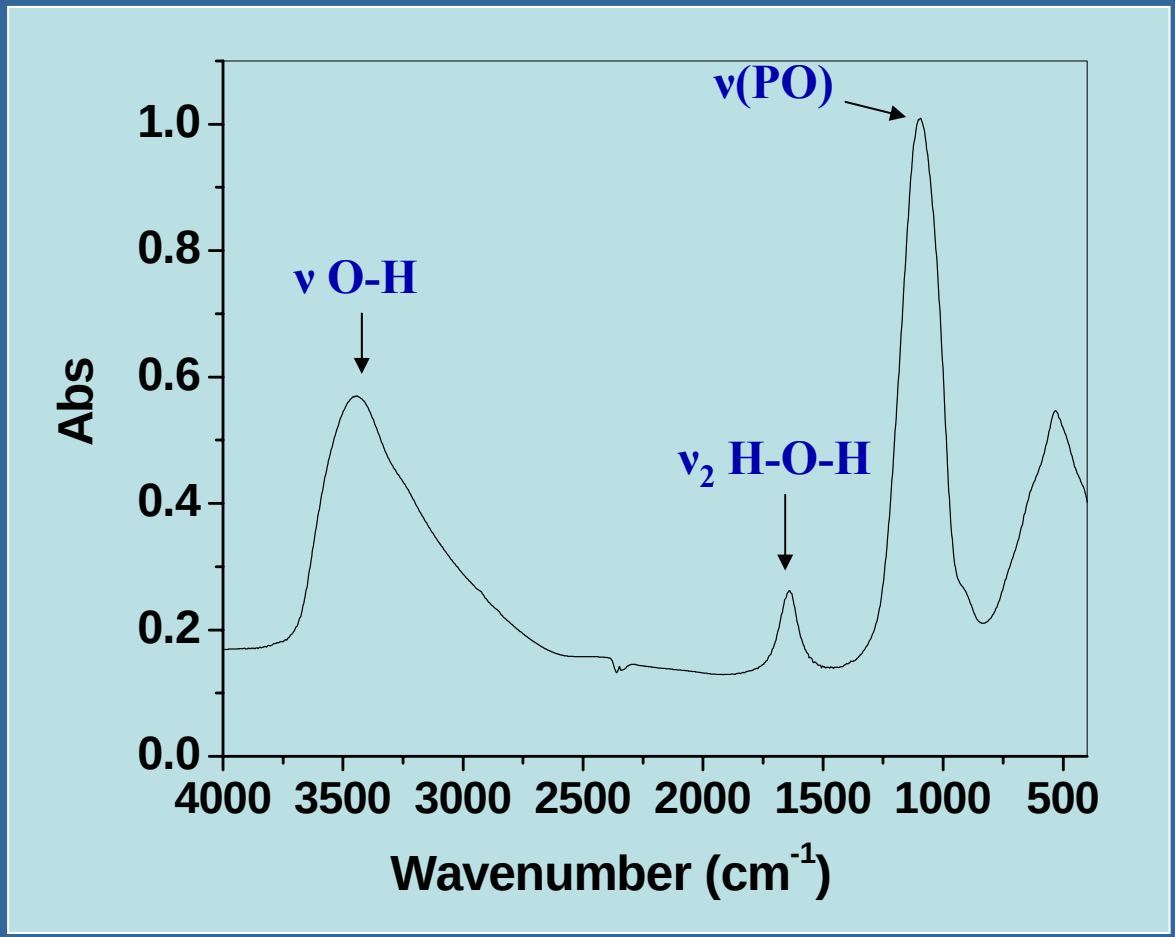
Grade	P	Al	S	Si	Fe	Ca
1	1	0.800	nil	0.067	0.0006	0.0005
2	1	0.820	nil	0.049	0.0005	0.0014
3	1	0.769	0.026	0.058	0.0007	0.0012
4	1	1.26	0.54	0.04	0.019	nil

Thermogravimetry



Water strongly bound to the ionic network

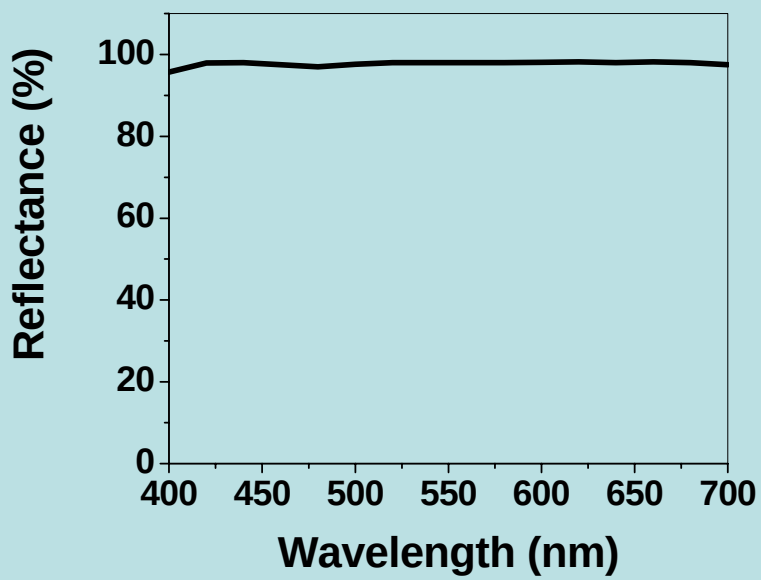
Infrared spectrum of dry powder in KBr



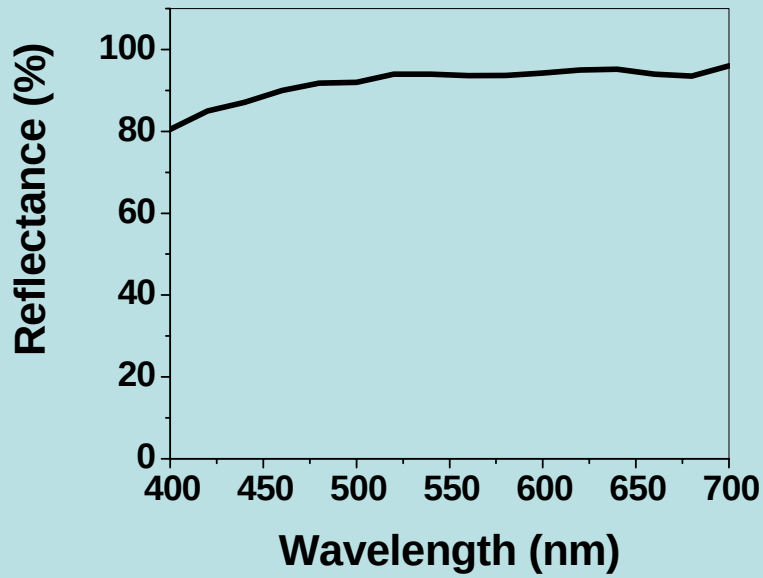
The large band at 3700-2700 cm^{-1} is due to the extensive hydration of the particles

Absence of absorption in the visible range

Dried Powder

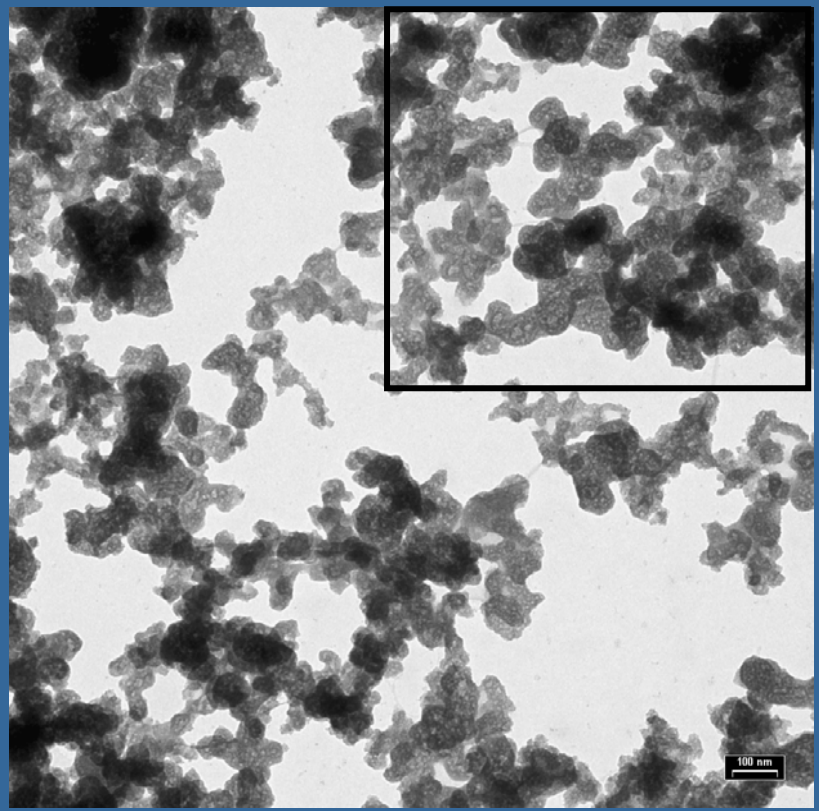


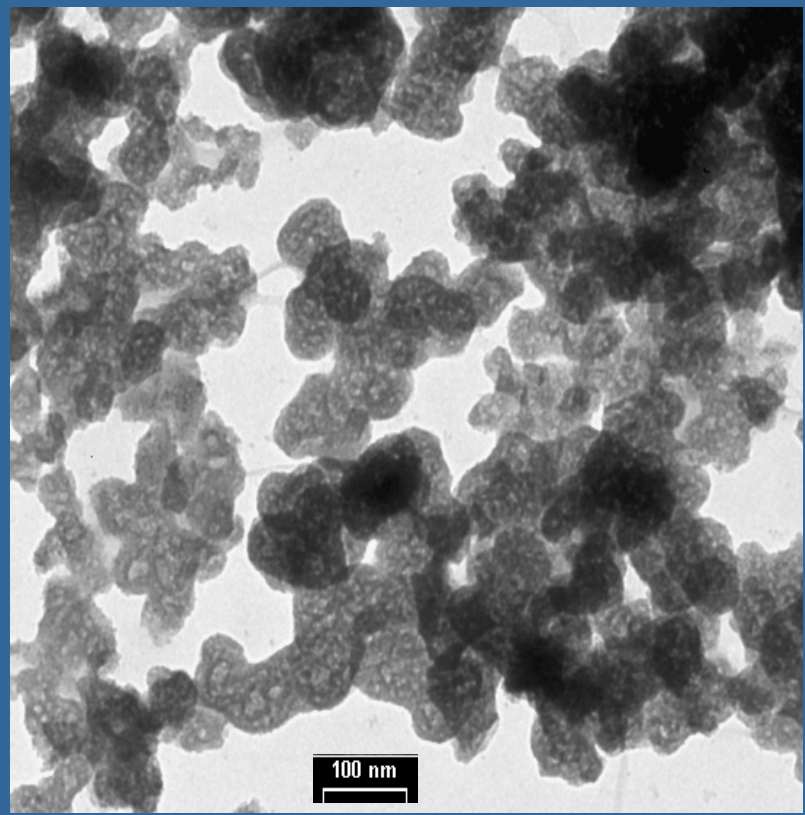
BiPHOR™



TiO_2

Transmission Electron Microscopy

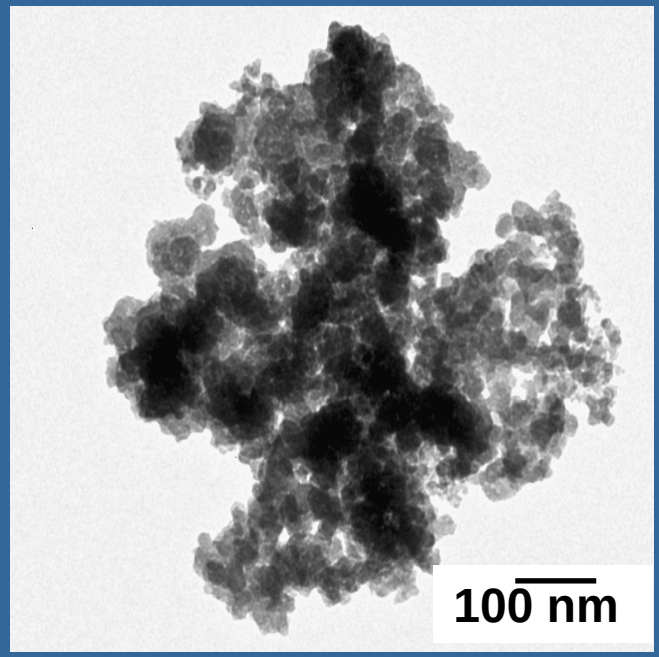


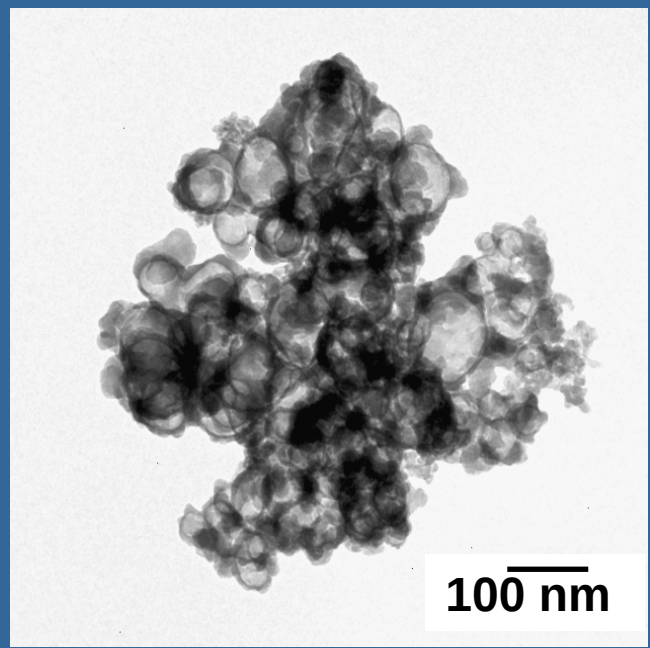


hollow particles (closed pores)

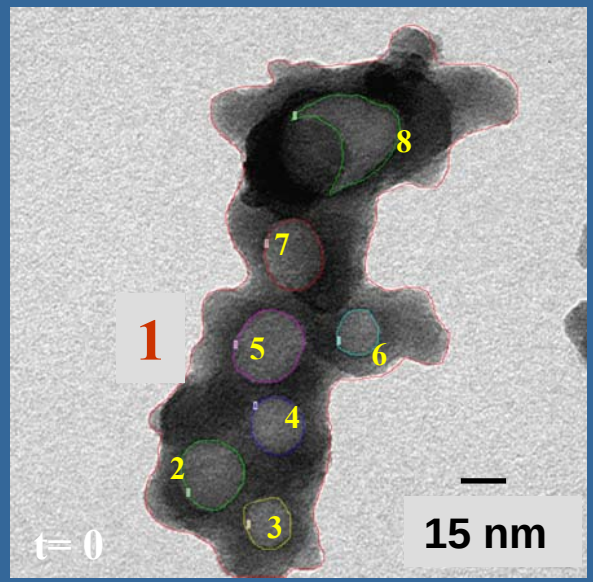
Evidence for Core-Shell Structure

- Particles under the microscope beam loose material from the bulk without major outer volume changes
- Larger voids are formed
- Plastic interiors, stiffer walls

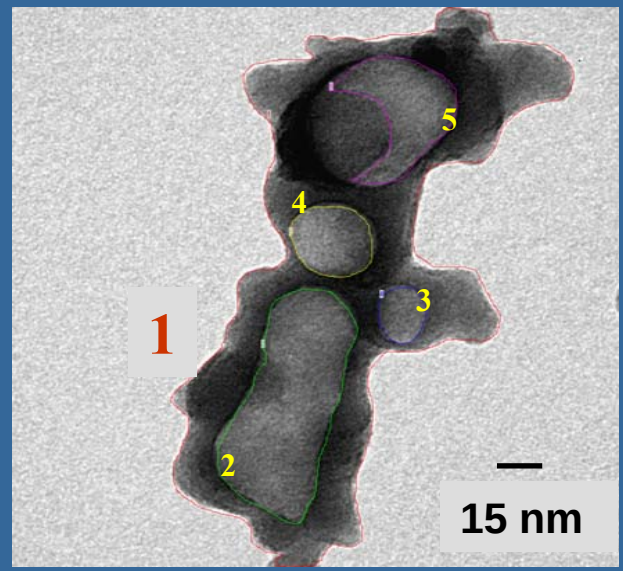




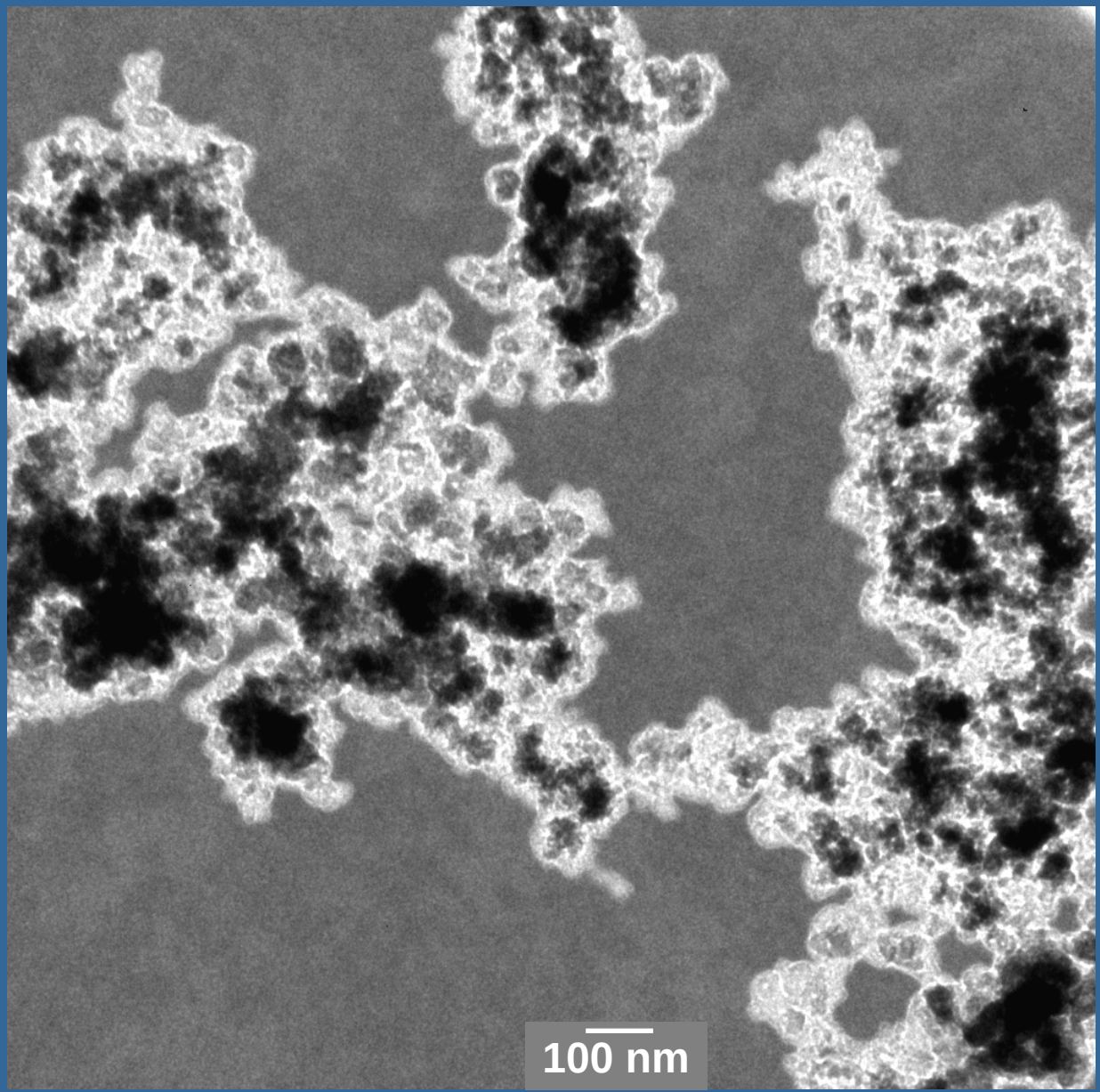
The perimeter of shells remains unaltered while the interior voids become larger with electron beam effect



electron beam

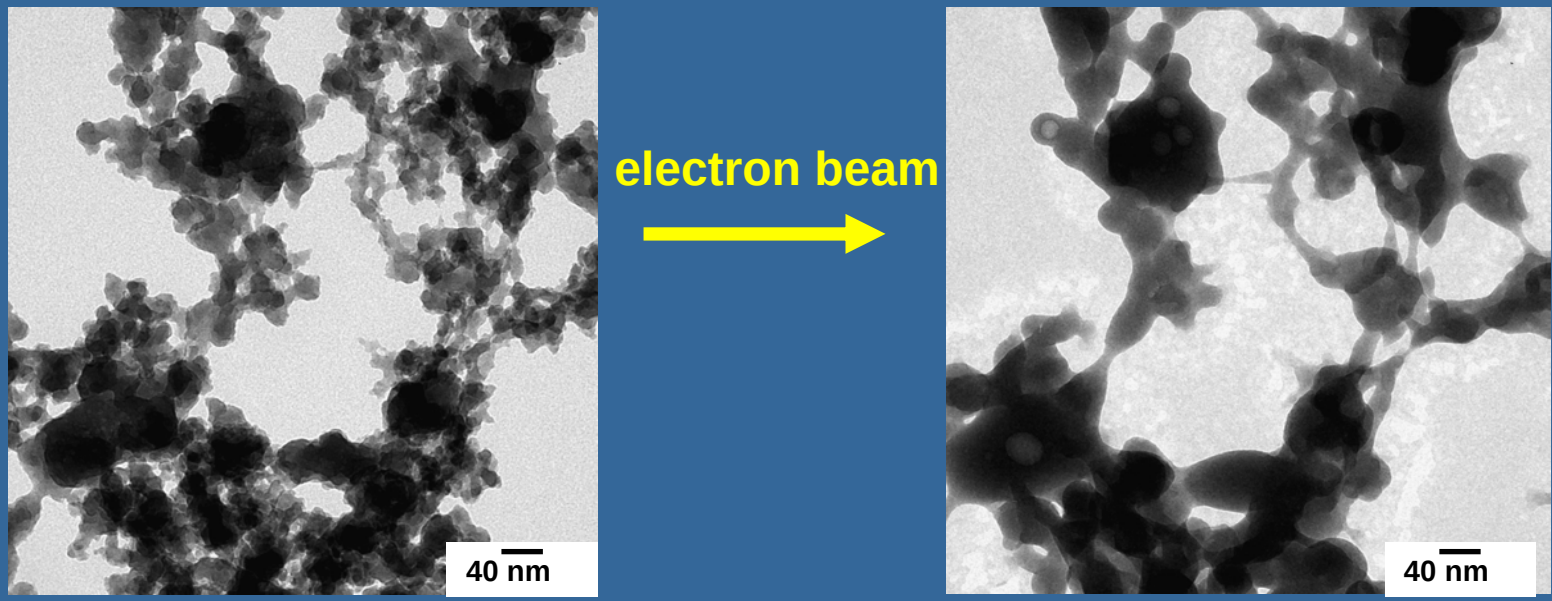


Perimeter (nm) / Area (nm²)	
Before exposure to electron beam	*After exposure to beam*
1) 733.8 / 11.718	1) 733.5 / 11.975
2) 85 / 407 3) 62 / 229 4) 71 / 283 5) 91 / 457 } 309 / 1.376	2) 229 / 2.283
6) 57 / 179	3) 65 / 240
7) 82 / 384	4) 99 / 557
8) 137 / 602	5) 180 / 899



Another evidence, from plasmon imaging: particle contours are brighter than the particle interiors

Amorphous aluminum phosphate (P/Al =2.5) following Hem´s procedure. (Vaccine, 2001, 19, 275)



- Dry particles do not show small voids by TEM
- The particles undergo large morphological changes upon heating
- The extensive formation of “necks”, where the particle surfaces are very deformable

BiPHOR™ Slurry Specifications

Description	*BiPHOR™*
Hegman Grind	7H (ASTM D 1210)
Density (at 26% solids)	1.3 ± 0.1 g/mL (ASTM D1475)
Viscosity (at 26% solids)	53 ± 2 KU (ASTM D 562)
Non-volatile %	34 ± 1 (ASTM D 1644)
pH	> 6.5 (ASTM D 4584)
Opacity (%)	94.1 ± 0.2 (ASTM D 2805)
Reflectance (%)	90.7 from 400 to 700 nm (ASTM E 1331) *l* = 96.5; *a* = -0.2; *b* = + 0.5
Yellowness (%)	0.4 (ASTM E 313)
Whiteness (%)	95.9 (ASTM E 313)
Particle size diameter	200-2000 nm (light dynamic scattering)

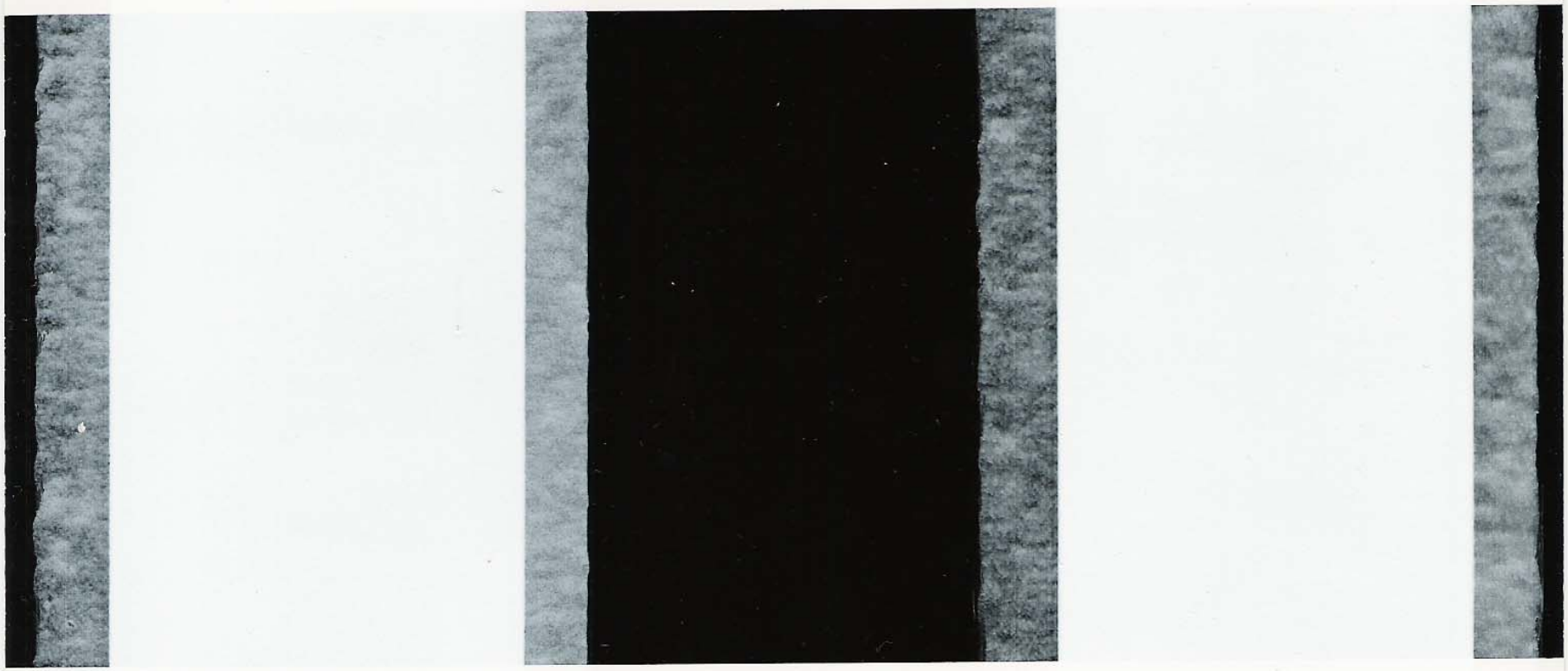
Formulating with Biphor

Component	*Standard Formula (g)*	*Formula using BiPHOR™ slurry (g)*
Water	839.79	361.86
Propyleneglycol	30.00	30.00
Thickener/rheology modifier	84.00	4.50
Antifoaming/Coalescing agent	0.60/60.00	1.17/43.47
Tetrapyrophosphate/Dispersant	0.87/20.94	9.00/11.00
Anti-oxidant	0.87	0.90
AFE anionic	7.86	7.86
Biocides	9.00	9.00
NH_4OH 25%	7.11	15.00
Titanium dioxide	534.00	267.00
BiPHOR™ slurry 35%		763.00
Inorganic Fillers	690.96	690.96
Acrylic resin	735.00	591.00
Total	3030.00	2816.72

Excellent hiding power

Control: 100% TiO_2

50% BiPHOR™



Performance tests

- 50% TiO_2 replacement on formulas of testing laboratories
  - DL Labs, Inc. 74 Kent Street Brooklyn, New York
  - Stonebridge Technical Services. 6223 Linden Road, Fenton, MI, USA
- 50% TiO_2 replacement on premium formulations used in Brazil.

TEST	*Standard Formula*	*Formula using BiPHOR™ slurry*
Description	**100% TiO_2**	**50% BiPHOR™ + 50% TiO_2**
Hiding		
At 9.8 m^2/L (%)	**92.5**	**92.1**
At 6.6 m^2/L (%)	**94.4**	**94.5**
At 6.6 m^2/L (%)		
Reflectance (%)	**90.1**	**90.1**
Whiteness Index (%)	**79**	**78.8**
Yellowness Index (%)	**4.0**	**4.2**
Gloss - 60° (units)	**2**	**2**
Sheen - 85° (units)	**1**	**2**
Washability – Reflectance Recovery		
Before washing (%)	**87.6**	**87.0**
After washing (%)	**54.0**	**53.1**
Reflectance Recovery (%)	**61.7**	**61.0**

Source: DL Labs, Inc. 74 Kent Street Brooklyn, New York.

TEST	*Standard Formula*	*Formula using BiPHOR™ slurry*
Description	**100% TiO_2**	**50% BiPHOR™ Slurry + 50% TiO_2**
Fineness of Grind (Hegman)	**5**	**4**
% Non-volatile	**58.3**	**53.6**
Density	**12.0**	**11.4**
Stormer Viscosity (KU)	**96**	**99**
<u>0.003" Drawdowns</u>		
85 °C	**1.0**	**1.1**
Contrast Ratio	**0.9207**	**0.9108**
Reflectance (white)	**0.9086**	**0.9082**
Yellowing Index (D1925)	**3.76**	**3.76**
Yellowing Index (E313)	**3.33**	**3.34**
Whiteness Index (E313)	**78.79**	**78.76**
<u>0.0015" Drawdowns</u>		
Contrast Ratio	**0.7763**	**0.7632**
Reflectance (white)	**0.8807**	**0.8800**

Source: Stonebridge Technical Services. 6223 Linden Road, Fenton, MI, USA.

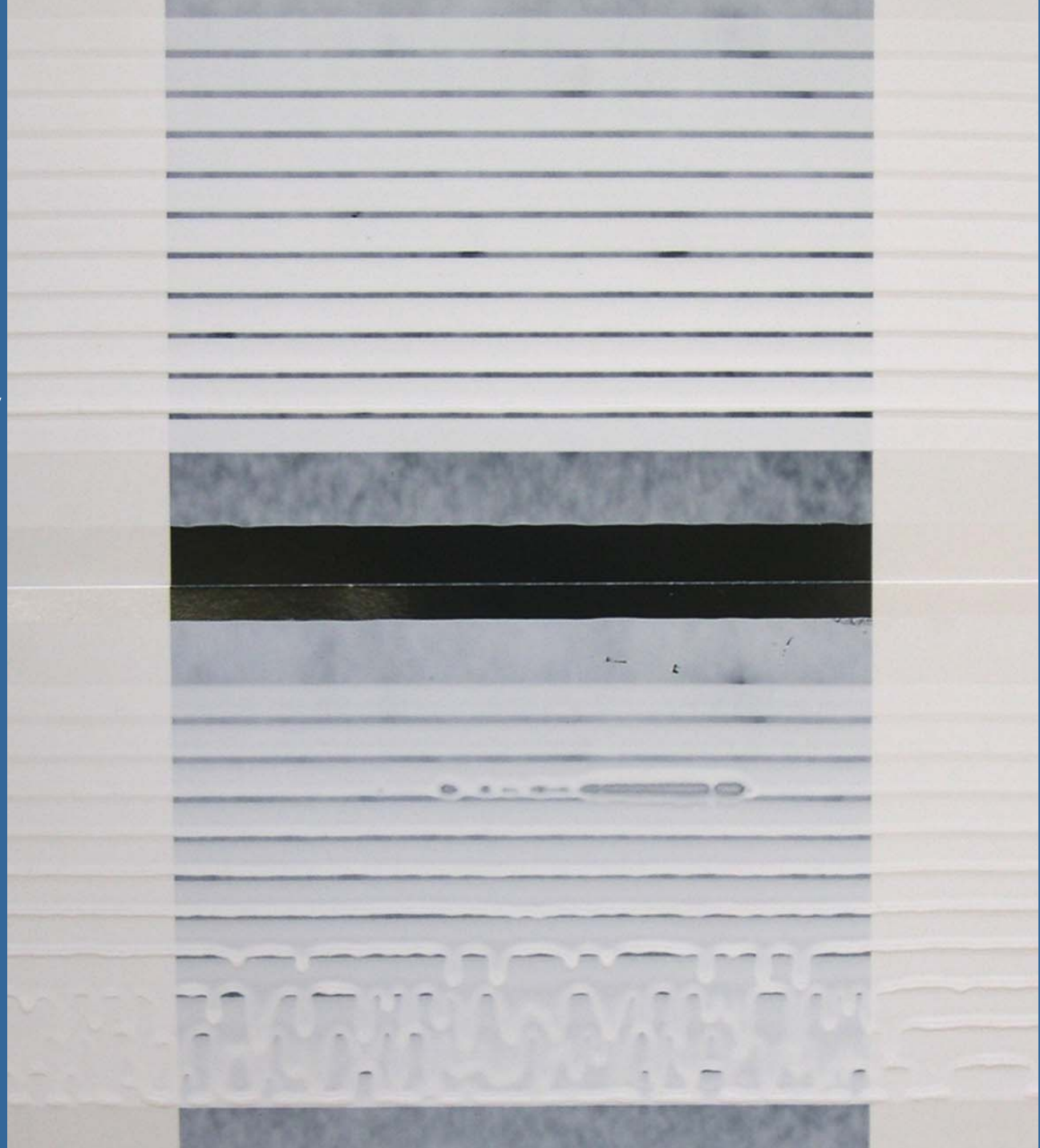
TEST	*Standard Formula*	*Formula using BiPHOR™ slurry*
Block resistance	**6**	**8-9**
Color Acceptance		
ΔE_{XYZ} Wet-on-Wet Rub	**0.39**	**0.38**
ΔE_{XYZ} Wet-on-Dry Rub	**0.46**	**0.85**
ΔE_{XYZ} Wet-on-Dry Brush	**0.34**	**0.44**
Y-Reflectance Drawdown Black	**0.4870**	**0.4772**
Y-Reflectance Drawdown White	**0.4873**	**0.4781**
Y-Reflectance Wet-on-Wet Rub	**0.4842**	**0.4802**
Y-Reflectance Wet-on-Dry Rub	**0.4906**	**0.4701**
Y-Reflectance Wet-on-Dry Brush	**0.4909**	**0.4728**
Washability		
Y-Reflectance (before/after)	**0.8839/0.4335**	**0.8790/0.3402**
Gloss (before/after)	**1.8/2.6**	**2.2/4.2**
Leveling (NYPC Drawdown)	**7**	**7**
Sag Resistance	**5.6**	**8.4**

Source: Stonebridge Technical Services. 6223 Linden Road, Fenton, MI, USA.

50% BiPHOR™ paint

Considerably less sag

Control formula



Field application test: a house painted with a BiPHOR™-based paint

To sum up

- Outstanding performance at high levels of TiO_2 replacement
- Absence of UV absorption and catalytic resin photo-oxidation
- Ample supply of raw materials
- Environmentally friendly process and product
- For further details: *www.biphorpigments.com*

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