Layer-by-Layer Electrostatic Self-Assembly at the Industrial Scale

Lee Boman, Chris Stoessel, Kevin Krogman, Tara Cary
Eastman Chemical Company
Agenda

- Layer-by-Layer (LbL) - What is it and how it works
- LbL - Applications
- LbL - Scale-up
- Questions
Layer by Layer
What is it and How Does it Work
Dip Layer-by-Layer (LbL)

LbL is a method of coating a substrate using the native charges of materials.

- Polycationic and polyanionic solutions
- Solutions & rinse baths, are typically aqueous
- Process times ≈ 30 minutes/cycle
- Not scalable for high layer counts
- Roll-to-Roll not feasible

Requires a new method for scaling

Flash animation courtesy J.B. Schlenoff webpage [http://www.chem.fsu.edu/multilayers/](http://www.chem.fsu.edu/multilayers/)
Spray Assisted Layer-by-Layer

- Atmospheric deposition technology
- Self-limiting = very repeatable
- Relies on electrostatic self assembly of macromolecules
- High precision and uniformity across large areas
- Aqueous based
- Produces multi-layer, multi-functional coatings
- Conformal coating
- Low stress
- Room Temperature

Positively Charged Cation

Negatively Charged Anion

Negatively Charged Substrate

Langmuir, 2007, 23, 3137-3141
**Terminology**

- **“bi-layer”**: One bi-layer is composed of a single exposure to a polymer followed by a single exposure to a nanoparticle or another polymer.

- **“film”**: Composed of multiple bi-layers, to create the targeted film thickness for desired affect.

- **“stack”**: Composed of an odd number of films, the stack defines final targeted properties.
Layer by Layer Scale

Typical LBL film containing 10-100 bi-layers approximately 100-1000nm

Typical 5 mil thick PET Film

~2 Bi-Layers Titania (~20nm/Film)

~15 Bi-Layers Silica (~300nm/Film)
Substrate Candidates

- On practically any surface that a native charge can be applied
- Anything that can be handled in a roll to roll process
  - PET, TAC, PEN, PI, PC, ETFE, COP, LDPE...
  - 25um–175+um thick
- Textured surfaces
- Porous Materials (i.e., textiles)

Pre-Treatment
ex: corona

Negative Charged
Substrate Ready for LbL
Layer by Layer

Applications
Color Coating w/LbL

- Use existing pigments with chemically modified surfaces that make them stable in aqueous dispersions.
- Pair them with a suitable cationic polymer that is used as a “mortar”
- Blend CYMK pigments to achieve desired transmission

Increased Bi-Layer Count

Cyan Magenta Yellow
Full Range of Color Demonstrated

- By blending the primary C, Y, M colors we can recreate the entire color wheel
- Cyan, magenta and yellow samples are single pigment films, the red, blue and green are ‘synthesized’ by combining C,Y,M pigments
Unique Pigment Deposition Capability

- Pigments can be deposited a mono-layer at a time
- Able to “slurry” pigments or stack single color pigment
- Allows some control over Transmitted vs. Reflected Color

“A” - Slurry Deposition

“B” – Mono Layer Deposition

Both A & B have Neutral Transmission Color

A has Neutral Reflection Color while B has Magenta Reflected Color
Conformal Coatings

Non-Woven Fibers

Electrospun nylon 3-5um diameter LbL coated with uniform layer of titania nanoparticles and polymer. Each fiber is conformally coated, regardless of orientation to deposition source.

Textured Surfaces

Etched surface of Si solar cell. 45° peaks etched into the surface by etching the <100> planes with KOH.

Same surface coated with 100nm SiO2 nanoparticle Anti-Reflective LbL coating.
What other kind of functionality characteristics can LbL impart?

- Anti-reflective
- Ion Exchange
- Gas Separation
- Anti-Fog
- Super Hydrophobicity
- Gas Barrier
- Oleophobicity
- Self Release
- Solar Rejection
- Flame Retardancy

And others...
Examples

Uniformly apply optical quality coatings to smooth or textured surfaces...

...conformally and 3-dimensionally...

...onto any surface, hydrophilic or hydrophobic, porous or planar...

...even onto materials that are soft at room temperature

Delicate proteins, small molecule drugs, catalytic metal ions...

...we can even duplicate the appearance of metal, but without metal.

All using an environmentally friendly, non-toxic, water-based technique.
Layer by Layer

Scale-up
Spray LbL Sheet-to-Sheet Evolution

From spray bottles to PLC automated large area
Spray LbL Roll-to-Roll Evolution

First R2R LbL Demonstration

v8.0 “Module 0”

v9.0: “The Dragon”

Bi-Layer based modular design*

v10.0 “Thirsty Bear 1.0”

72” Wide Web

v11.0 “Thirsty Bear 2.0”

We are on the fourth generation of R2R LbL Tools

* Embraces short run custom color designs

Bioinspir. Biomim., 8, 045005, 2013
Wide Web Capability Example

72” wide by 10,000ft pigment coating on 1mil PET

Cross Web Uniformity

T L*, Ta* & Tb* total (cross & down web) variation 1/10 of typical colored films

Modular process enables low cost short custom color campaigns
Summary

- Layer-by-Layer deposition is now scaled to full R2R process
- Key characteristics of this new coating technology are:
  - Water based
  - Self limiting
  - Uniform
  - Room temperature
  - Low stress
  - Conformal
  - Flexible platform
- Large number of coating options