Conventional versus Plasma Assisted Deposited AlOx coatings on PET films in roll-to-roll metalizers.

Dr. Anye Chifen
Agenda

- Buhler Leybold Optics Business unit at a glance
- Aluminium Oxide coatings for food packaging
  - Conventional Reactive Oxidation: Aluminium and Oxygen
  - Plasma Assisted Deposition of AlOx on PET (12μm)
  - Evaluation: Barrier, shelf life, microscopy, thermal stress
- Conclusion & Analysis
Buhler Group.
Global market leader with strong local roots since 1860.

- Headquarters in Uzwil, Switzerland.
- 10,000 employees, including 500 trainees.
- 20 manufacturing sites and 24 service stations around the world.
- 70 sales & service companies.
- 100 % family owned.
Bühler Leybold Optics leader in thin film coating equipment. 164 years of experience in vacuum technology.

- Production site and headquarters in Alzenau (Germany).
- Other production sites in Beijing (China), and Cary (USA).
- Over 300 employees worldwide.
- 2,500 systems total installed base.
- Innovation leadership in key areas such as sputtering, PECVD and plasma assisted evaporation.
- Leybold Optics markets – Precision Optics, Ophthalmic Optics, Metalization, Glass, Flexible Packaging and Flexible Electronics

Productivity for competitive products.

Differentiation by providing innovative solutions.
Bühler Leybold Optics leader in thin film coating offers solutions for a variety of markets.

Precision Optics Applications
- Dielectric filters
- Narrow band pass filters
- IR coatings
- Anti-reflection coatings
- Endoscopes
- Laser mirror coatings

Ophthalmic Optics
- Anti-reflection coatings
- Anti-static coatings
- Non-color coatings
- Mirror coatings
- Super-hydrophobic coatings
- Oleophobic coatings

3D - Coating
- Reflective coating with protective layer
- Hydrophobic coating
- High reflective coating
- Reactive sputtering
- Wipe resist coating
Leybold Optics FLC 650 for Flex. Printed Circuit Boards

The hazardous chemical waste generated during electroless seed layer plating drives the FPCB marked to turn to sputter solutions.

Electro plated copper film (5 - 24 µm)

PI, PET, PEN film
12 µm – 70 µm

Sputtered Cu seed layer (150 - 200 nm)
Sputtered NiCr tie layer (ca. 30 nm)

<table>
<thead>
<tr>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Touch Panel</td>
</tr>
<tr>
<td>FPCB</td>
</tr>
<tr>
<td>Low-e / Solar Control</td>
</tr>
<tr>
<td>EC Smart Glass</td>
</tr>
<tr>
<td>SSLB</td>
</tr>
<tr>
<td>Flex PV Electrodes</td>
</tr>
<tr>
<td>OLED / Lighting Electrodes</td>
</tr>
<tr>
<td>Medical Sensors</td>
</tr>
<tr>
<td>High Barrier</td>
</tr>
<tr>
<td>ARAS (Anti Reflective Anti Static)</td>
</tr>
<tr>
<td>AR (Anti Reflective)</td>
</tr>
<tr>
<td>IMI (ITO-Metal-ITO for IR-Shielding)</td>
</tr>
<tr>
<td>Optical coatings</td>
</tr>
</tbody>
</table>
Bühler Leybold Optics leader in thin film coating offers solutions for a variety of markets.

**Architectural glass Applications**
- Architectural glass
- Display technology
- Barrier layers
- Reflectors

**Flexible Electronics**
- Aluminium metallizing on film
- Aluminium zinc metallizing on film
- Flexible printed circuit boards
- Touch panel
- Low-e window film
- High barrier

**Flexible Packaging**
- Aluminium metallizing on film
- Transparent barrier (AlOx) on film
- Aluminium metallizing on paper
- ZnS (High reflective) coating on film
Bühler Alzenau’s portfolio in LAC / web / packaging consists of the following systems.

- **Standard-rate portfolio**\(^1\) – work-horses

<table>
<thead>
<tr>
<th>LO PAK 1300</th>
<th>LO PAK 1700</th>
<th>LO PAK 2100</th>
<th>LO PAK 2500</th>
</tr>
</thead>
</table>

- **High-rate portfolio** – maximum productivity (+) / combined with specials (T+)

<table>
<thead>
<tr>
<th>LO PAK 2500 + / T+</th>
<th>LO PAK 2900 + / T+</th>
<th>LO PAK 3300 + / T+</th>
<th>LO PAK 3700 + / T+</th>
</tr>
</thead>
</table>

\(^1\) The systems of the standard-rate portfolio are also suitable for processing of paper substrates.
Aluminium Oxide coatings for food packaging

- **History:**
  - 1969: AlOx coatings disclosed by DuPont
  - 2000's: growth continues in both food and industrial applications

- **Production methods:**
  - (1) Conventional reaction of oxygen with aluminium
  - (2) Plasma Assisted/enhanced reaction of oxygen with aluminium

- **Some advantages:**
  - Improved barrier properties (gases, light, odor) → **Functional**
  - Printing & lamination processability → **Sustainable**
  - Amount of Al wire required → **Economical**
  - Transparent & fresh packaging → **Healthy**
  - Retortability / Microwaveability → **Comfortable**
Despite all these advantages,

.........Food waste is increasing at 2-3% p.a. in the EU!!!
Shelf life is the time during which all of the primary characteristics of the food remain acceptable for consumption by the consumer.
Example of high rate hybrid machine for Al and AlOx: PAK 3700 T+

- Al & AlO\textsubscript{x} Evaporator
- Superb Winding technology
- Plasma source & oxygen gas system
- Layer measuring system – MultiLMS
- Thermal management for high productivity
- Process speed: 17 m/s *
- Post-treatment Oxidation Plasma unit
- Layer Defect System

*see process description
What is important for the customer to quantify?

- **Productivity**
  - Maximum process speed
  - Optimized cycle time
  - Maximum reliability & Minimum scrap

- **Quality of layer**
  - Improved uniformity
  - Minimum quantity of defects

- **Performance of barrier characteristic**
  - Optimized oxygen / water vapor barrier
Aluminium Oxide coatings for food packaging

Coventional Reactive Oxidation of AlOx

Plasma Assisted Deposition of AlOx
## General machine productivity

### Example of PET performance

<table>
<thead>
<tr>
<th>Process</th>
<th>PAK (Al)</th>
<th>PAK+ (Al High rate)</th>
<th>PAK T+ (AlOx)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>PET</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness [µm]</td>
<td>12.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Speed [m/s]</td>
<td>12</td>
<td>16-18</td>
<td>6-10</td>
</tr>
<tr>
<td>Layer thickness [OD]</td>
<td>2.2</td>
<td>2.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Layer uniformity [%]</td>
<td>± 5.0</td>
<td>± 5.0</td>
<td>± 7.0</td>
</tr>
</tbody>
</table>

Characteristics for other substrates (BOPP, CPP, PE) can be delivered upon request.
## Barrier properties: PAD vs. CRO process

<table>
<thead>
<tr>
<th>AIOx coated on</th>
<th>OTR (\text{cm}^3/(\text{m}^2\cdot\text{d} \cdot \text{bar}))</th>
<th>WVTR (\text{g}/(\text{m}^2\cdot\text{d} \cdot \text{bar}))</th>
<th>Type of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PET 12µm</strong></td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>Plasma Assisted Deposition</td>
</tr>
<tr>
<td></td>
<td>&lt; 1.0</td>
<td>&lt; 1.2</td>
<td>Conventional Reactive Oxidation</td>
</tr>
<tr>
<td>Test conditions</td>
<td>23°C, 50% RH</td>
<td>37.8°C, 90% RH</td>
<td></td>
</tr>
</tbody>
</table>

- Transparency: 90%
- Major impact for WVTR & OTR values achieved using PAD

*Base film PET: OTR = 120 \(\text{cm}^3/\text{m}^2\cdot\text{d}\) (23°C 50%), WVTR = 50 \(\text{g}/\text{m}^2\cdot\text{d}\) *(37.9°C, 85% RH)*
### Stability of transparent barrier films – Permeability

<table>
<thead>
<tr>
<th>PET / AlOx 12µm</th>
<th>OTR cm³/(m².d.bar)</th>
<th>WVTR g/(m².d.bar)</th>
<th>Shelf life</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>Day 1 (PAD)</td>
</tr>
<tr>
<td></td>
<td>&lt; 0.65</td>
<td>&lt; 0.55</td>
<td>Day 365</td>
</tr>
<tr>
<td></td>
<td>&lt; 1.0</td>
<td>&lt; 1.2</td>
<td>Day 1 (CRO)</td>
</tr>
<tr>
<td></td>
<td>&lt; 1.3</td>
<td>&lt; 1.4</td>
<td>Day 365</td>
</tr>
</tbody>
</table>

- Surface energy decreases after 365 days, higher loss with CRO than PAD films
- Stable values over a period (less ageing) for PAD than CRO process
- Defects (barrier properties) could be reduced with the amount and type of contact rollers – untreated side contact of polymer film.
Impact of surface tailoring before Al / AlOx deposition

Pre-treatment OTR WVTR

| YES (low input) | 0.12 | 1.5 |
| NO | 0.18 | 3.0 |

➢ Layer stability achieved (permeability & mechanical)

Un-treated metalized film: section analysis profile – peak heights 26.3 nm; 19.2nm; 16.3nm

Pretreated metalized film: section analysis profile – peak heights 21.9 nm; 14.3nm; 12.4nm
Effect of pretreated packaging films

Adhesion of subsequent metal is improved
Surface defects are reduced upon inline pretreatment
Stability of transparent barrier films:
Thermal stability of CRO vs. PAD films.

AFM analysis: Topography on the left side, phase contrast on the right side
Position 5, 1 μm x 1 μm

Position 1, 1 μm x 1 μm
Conclusion & Analysis

- Large scale production on PAK 3700 T+ based on Leybold Optics Know-How for PAD of AlO$_x$
- Tailored growth coating $\rightarrow$ less defect microstructure at high plasma density in evaporation zone.
- Efficient residence time of reaction to adequate high speed of oxygen and aluminium $\rightarrow$ high deposition rates at specific transmission and required densification.
- Crystallographic (point, line) defects are imminent on CRO films $\rightarrow$ mechanical (flex, brittle, durability)
- Hardness value retrieved 4 ~ 5 GPa (retrieved from force measurements AFM)
- Shelf life stability of plasma assisted reactive samples vs. conventional reaction.
  $\rightarrow$ Barrier properties: surface energy, roughness, adhesion, & transmission values.
Thank you for your attention
For further information please contact the speaker
www.buhlergroup.com
What is the time required and steps required to switch from standard Al to AlOx process?

**Conversion from the AlOx process**
1. dismantling of electrical and cooling water connections
2. removal of shieldings
3. detachment of cathodes
4. elimination of gas injection and insertion of blockage

**Setting up for Al process**
1. cleaning
2. mounting of spacer
3. fitting of water connectors
4. adjustment of evaporator height (optional)

→ **TIME REQUIRED:** ca. 30 minutes