Advances in protection of Aluminum Oxide using inline vacuum deposited organic top coats

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- Overview transparent barrier materials
- Overview transparent vacuum deposited coatings
- Main problem with AlOx coated films
- General characteristics of inline organic top coats
- Performance of AlOx + Inline organic top coats
- Conclusion
## Transparent barrier materials: An overview

<table>
<thead>
<tr>
<th>Type</th>
<th>WVTR</th>
<th>OTR</th>
<th>Retort</th>
<th>Flexibility &amp; processing</th>
<th>Environment</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVdC</td>
<td>-</td>
<td>+</td>
<td>---</td>
<td>++</td>
<td>---</td>
<td>++</td>
</tr>
<tr>
<td>EVOH</td>
<td>---</td>
<td>++</td>
<td>---</td>
<td>++</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Oxides</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
<td>+/-</td>
<td>+++</td>
<td>-</td>
</tr>
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</table>

- PVdC Coated films offer the best price vs performance followed by EVOH.
- Main problem with PVdC is dioxin formation upon uncontrolled incineration.
- Main problem with Oxides (AlOx and SiOx) is the high price.

- There is an opportunity for transparent barrier materials that can offer the performance of Oxide coated films but at a price closer to PVdC and EVOH.
### Transparent barrier materials: Oxide coated films

<table>
<thead>
<tr>
<th>Coating</th>
<th>Barrier</th>
<th>Flexibility &amp; processing</th>
<th>Capital investment</th>
<th>Price raw materials</th>
<th>Total cost of Ownership</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOx</td>
<td>+++</td>
<td>+/-</td>
<td>---</td>
<td>--</td>
<td>-</td>
</tr>
<tr>
<td>AlOx</td>
<td>++</td>
<td>---</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
</tr>
</tbody>
</table>

- **SiOx coated films** offer a good performance but at a high price (limited use in high end applications).

- **AlOx coated films** have low cost of ownership (comparable with Al metallization) but the main problem is the high brittleness of these coatings.

- **AlOx coated films** have the potential to capture a large segment of barrier market provided that the problem of brittleness is resolved without significantly increasing the Cost of Ownership.
• Unprotected AlOx is prone to damages during downstream processing steps in particular:
  1. Printing
  2. Extrusion lamination
  3. Retort & sterilization
Main issue with AlOx: Barrier loss upon direct printing (Flexography)

- Barrier values of unprotected PET-AlOx after different stages of conversion:

  ![Effect of direct printing on barrier values of PET-AlOx](image)

- Both oxygen and water barrier are damaged after printing unprotected AlOx films, but while water barrier is somewhat recovered after lamination with PE, oxygen barrier remains low.

  **Barrier is significantly deteriorated upon direct printing on AlOx.**
Mechanism of barrier deterioration for AlOx

- Extremely thin AlOx layer (10nm) can be damaged upon downstream processing following two mechanisms:

1. **Mechanical**
   a) *Elongation*: Standard AlOx loses barrier above 1% elongation
   b) *Abrasion*: Direct contact with guide rollers resulting in scratches, i.e. loss of barrier.

2. **Chemical**: Some inks components may cause damage to AlOx layer.

- AlOx layer is prone to both mechanical and chemical damages.
Requirements for Top Coat

Ideal Top Coat for packaging applications should have the following characteristics:

• Boost the initial OTR

• Protect barrier during downstream processing steps.

• Compatibel with commercially available inks & adhesives

• Cost effective, i.e. Inline process using inexpensive material

• Compliant with FDA and EU regulations

• Ideal Top coat must comply with a set of stringent conditions
Conventionally AlOx layers have been protected by offline lacquering / priming:

- Offline Top Coat
  - AlOx
  - PET

While offline coatings are effective in protecting the AlOx layer, they result in dramatic increase of the total Cost of Ownership because of:
1. Two step process resulting in additional operational expenses.
2. Additional raw materials costs
3. Additional hardware investment
4. etc

There is a need for a cost effective inline Top coating process.

Inline coating process, branded as Freshure®, is developed by DSM.
Main characteristics of base material & general coating characteristics

- **Base materials**: Technology is based on the vapor deposition of organic compounds.

- **Regulatory**: Materials are compliant with both EU and FDA regulations for application in food packaging.

- **Coating conditions**: Physical Vapor Deposition (PVD) process executed at moderate pressure ($< 10^{-3} \text{ mbar}$) and temperatures ($< 340^\circ\text{C}$).

- **Vapor deposited layer**: Transparent crystalline layer providing excellent oxygen barrier.

- **Hardware**: The hardware is provided by Applied Materials (TopMet Clear™)
General outline of TopMet CLEAR™

Basic System Layout (TopMet CLEAR™):
Al/AIOx + Freshure®

Image Freshure® Evaporator
There are at least 18 different product combinations possible with Freshure® for use in flexible packaging.

In this presentation we will focus on PET-AlOx-Freshure®
Effect of printing & lamination on water barrier

- With inline organic Top-coat water barrier of PET-AIox is maintained after printing & lamination.
With inline organic Top-coat oxygen barrier of PET-AI Ox is boosted and maintained after printing & lamination.
Effect of inline organic Top-coat on barrier retention

- The barrier results presented up to now were obtained using standard corona treated PET.
- Improved barrier results (< 0,5) can be obtained using special grade PET Films.
- Below barrier results are shown for special grade PET coated with AlOx + Inline Organic Top Coat measured after different stages of conversion:

![Graph showing OTR values for different stages of conversion](image)

- Improving surface smoothness of PET film results in higher barrier values after coating with AlOx + Inline Organic Top Coat.
Barrier of unprotected AlOx deteriorates upon elongation.

Inline Top Coat (thickness < 0.01µ) protects the barrier up to 3% elongation with the same performance as offline Top coated AlOx films (thickness > 0.4µ).

Inline organic Top-coat protects AlOx at a fraction of coating thickness as compared with offline coated AlOx.
Effect of elongation on PET coated only with Inline organic Top-coat (without AlOx)

Inline organic Top-coat provide intrinsic oxygen barrier stable upon elongation up to 4%.
Laminated PET-AlOx with and without inline organic Top-coat were subjected to retort process (30 minutes at 121°C):

<table>
<thead>
<tr>
<th>12µPET-AlOx</th>
<th>OTR (cc/m²/day @23°C; 85% RH)</th>
<th>WVTR (gr/m²/day @ 38°C; 90%RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without inline organic Top-coat</td>
<td>With inline organic Top-coat</td>
</tr>
<tr>
<td>After slitting and lamination*)</td>
<td>&lt; 2</td>
<td>&lt; 1.0</td>
</tr>
<tr>
<td>After retort (30 min at 121°C)</td>
<td>&gt; 5</td>
<td>&lt; 1.0</td>
</tr>
</tbody>
</table>

*) Laminated with BOPA//CPP. Top coated films were laminated on industrial lines whereas results on AlOx without inline organic Top-coat are generated using hand laminates.

- Without inline organic Top-coat barrier properties of PET-AlOx are significantly deteriorated after retort process.
- With inline organic Top-coat barrier properties are boosted and most importantly preserved after retort.

**Inline organic Top-coat protects AlOx during retort process.**
Compatibility of Inline organic Top-coat with commercial inks & adhesives

<table>
<thead>
<tr>
<th>PET</th>
<th>PE (Sealant layer)</th>
<th>Adhesive</th>
<th>White Ink</th>
<th>Color Inks</th>
<th>Inline organic Top-coat</th>
<th>AIOx</th>
</tr>
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<table>
<thead>
<tr>
<th>Adhesive type</th>
<th>Heat sealing</th>
<th>Bond strength (gram/25mm)</th>
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<tr>
<td></td>
<td></td>
<td>White</td>
<td>Color on White</td>
</tr>
<tr>
<td>Solvent based</td>
<td>Before</td>
<td>204,0</td>
<td>595,0</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>425,0</td>
<td>816,0</td>
</tr>
<tr>
<td>Solventless</td>
<td>Before</td>
<td>527,0</td>
<td>476,0</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>799,0</td>
<td>867,0</td>
</tr>
</tbody>
</table>

For most applications bond strength above 200 gram/25mm is sufficient.

**Typical reverse printed laminate structure**

- With the right selection of inks & adhesives bond strengths can be achieved well above threshold value of 200 gram/25mm both in combination with white and color on white prints.

- Heat sealing has a positive effect on bond strength.

- **Inline top coat is compatible with a wide range of commercially available inks & adhesives.**
Conclusions

- AlOx needs to be protected to withstand downstream processing steps in particular direct printing.

- Currently there are two options available in the market for AlOx protection; i.e. offline lacquering and inline organic top coat (Freshure®).

- In this presentation we have demonstrated that inline organic Top-coat protects AlOx during various downstream processing such as direct printing and retort.

- With inline organic Top-coat barrier values below 0.5 for finished laminates are achievable with bond strength > 300 gram/25 mm.

- For large scale penetration of AlOx coated films in transparent barrier market, inline top coating is the preferred option.