NEW AND OPTIMIZED VACUUM COATING PROCESSES TO EXPAND METALLIZED FILMS APPLICATIONS

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OUTLINE

INTRODUCTION

PRETREATMENT TO IMPROVE METALLIZED FILM PERFORMANCE – Case A : An update

CLEAR BARRIER (AIOX coated films) PROTECTION AND CONVERTING - CASE B : An update

SELECTIVE METALLIZATION - CASE C REGISTER CONTROL

CONCLUSIONS
INTRODUCTION

TRENDS AND MOTIVATION DRIVING METALLIZING INDUSTRY GROWTH:

- GAINING OR MAINTAINING THE COMPETITIVITY EDGE
- EFFICIENCY AND ENERGY SAVING
  - FROM COMMODITY TO SPECIALITY IN THE PRODUCTION MIX
- INNOVATIVE PRODUCTS
- ECO-FRIENDLY SOCIAL AWARENESS AND TIGHTING LEGISLATION
  - 4R: Reduction, Reuse, Recovery, Recycle
    - Gauge and weight reduction
    - From multi-material to mono or chemically similar compounds
Motivations: Material saving, cost reduction, environmental friendlier solution

Metallized sealant films (m-PE, m-CPP) for packaging ply-structures reduction
CASE A: Pre-treatment for met-BOPP upgrading

- Pre-treatment
  - PLASMA
  - IN-VACUO COATING
  - SURFACE ACTIVATION by DEPOSITION «SEEDING»

- Vacuum deposition
  - PROCESS CONTROL (Vacuum, deposition, cleanliness etc.)
  - STOICHIOMETRY (reactive processes)
  - PLASMA ACTIVATED DEPOSITION (reactive processes)

- Post-treatment
  - POST-PLASMA
  - IN-VACUO TOP COATING
  - IN AIR TOP COATING

For a general description of each single process, ref to: «Adding Value to Vacuum Coated products...» presented at AIMCAL R2R Conference USA 2017.
CASE A: Pre-treatment for met-BOPP upgrading

BARRIER PROPERTIES
(examples from major manufacturers)

- Bio-Oriented PolyPropylene is the most used polymer film for Flexible packaging: approx 60% of all plastic films (source AWA 2012)
- Bio-Oriented PolyPropylene is produced in multiple composition and functionality.

Source: Published data from web site and brochures
Basic met-Bopp features:

- **Low-Polarity Polymer**
  - Low water transmission rate (Wvtr: 0.3 – 0.8 gr/m² 24h)
  - «High» gas transmission rate (O2TR: 10 -80 cc/m²/24h)
  - Different levels and methods of surface treatment

- **Presence of additives (slipping/antiblocking) and loosely bound polymer chains**
  - «Blooming»: additives migration
    - Affecting the metal adhesion
    - Affecting long term treatment retention («Dyne retention»)
  - Surface roughing and porosity
    - Affecting barrier properties

**CASE A: Pre-treatment for met-BOPP upgrading**

1: Heat sealable inner layer
2: Inner PP core
3: Metallizable outer layer (corona treated)

- **Plasma**
- **Tie-layer**
PLASMA

Plasma action on polymer surface

- Cleaning and removal of organic contamination
- Oligomers Vaporization
- Microetching, scission, crosslinking, grafting and functionalization
- Increasing wettability

Most Popular treaters categories
(in order of treatment efficiency)

- DC magnetron based plasma treaters
- AC type dual electrode plasma sources
- AC hollow cathode

«Plasma-Plus» KEY FEATURES

Construction: Dual Hollow cathodes, magnetically enhanced

Power: AC 80 KHz, quick arc detection and suppression system

Energy dose: up to 0.8 - 1 Kjoule/m²

CASE A: Pre-treatment for met-BOPP upgrading
CASE A: Pre-treatment for met-BOPP upgrading

BOPP SURFACE «SEEDING» AND «TIE LAYER» («BARRIER_MET»)

1 - Film (Bopp)
2 – «Tie» Layer
3 – Aluminium layer

Substrate, mechanical strength
✓ High bond with polymer surface (adhesion promotion)
✓ Polymer surface modification (Planarization, seeding etc.)
✓ Functional: barrier, gloss etc.

The “nucleation” concept: from low-density to more densely packed thin film

Silver nucleation

Source: AIMCAL Reference Manual
CASE A : Pre-treatment for met-BOPP upgrading

BOPP SURFACE «SEEDING» AND «TIE LAYER» («BARRIER_MET»)

- A «primer» layer generation within a conventional aluminium metallization process
- An accurately controlled gas distribution for tie-layer uniformity and thickness
- Complemented by plasma treatment
Plenty of film types from diversified sources (points representing average values)

A clear indication of pretreatment positive effect in decreasing gas permeability but the plurality of film properties would prevent a more specific analysis
Factors for Barrier improvement:

- **Base Polymer Film**
  - A standard Commercial grade
  - A moderate corona treatment
  - A minimum and properly distributed anti-block additives

- **Plasma (in vacuum) pre-treatment**
  - Moderate power and efficient energy distribution

- **Barrier-met**
  - Designed for uniform and «separate» tie-layer generation

- **Machine design and Process Parameters**

The lower density of surface protruding particles translates into 30% better O2TR
The Case Study Example:

Starting point: Using Bopp 18 micron, commercial, already used on High Barrier application with very high metal thickness > 3 OD

Motivation and target: Improving the oxygen barrier and the quality consistency at more moderate OD.

Project leading factors:

✓ Use of plasma pre-treatment

✓ Use of Tie-Layer

✓ Optimizing raw material properties and process control.
CASE A: Pre-treatment for met-BOPP upgrading

PROJECT 2018: OPTIMIZING met-BOPP barrier and metal bond

Plasma System and Tie-Layer («Barrier met»)

Standard process:
> 3.2 OD; poor consistency

OD < 2.8; Tie-Layer and High Power plasma (>5Kw/m): Barrier impr.

Metal bond

OD < 2.8; Tie-Layer and Low Power plasma (<2Kw/m): Barrier Metal bond
Path to stabilize materials and processes:

a) A controlled film quality (e.g.: additives contents and distribution)

b) Solutions designed to:
   I. Uniform layer formation (gas distribution, gas nozzles position, protection for cleanliness)
   II. Stable plasma energy delivery at different power requirement
   III. Tension and web control, minimizing possible material damages
CASE A: Pre-treatment for met-BOPP upgrading
PROJECT 2018: “BARRIER-MET” FOR “DYNE RETENTION”

- Metallized Films have the tendency to lose the pristine surface tension within weeks or months from metallization.

- The dyne loss depends on the nature of the film and the storage conditions.

- The most likely cause: additives slowly moving to the film metal interface, contaminating the metal surface.

There is evidence that the metal/polymer tie-layer stabilizes the surface tension, preventing or limiting the dyne level degradation.
**Examples of diversified Polyolefine film**

<table>
<thead>
<tr>
<th>Material</th>
<th>Origin</th>
<th>Time from metallization</th>
<th>Surface tension (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bopp 18mic</td>
<td>Asia</td>
<td>18 months</td>
<td>&gt; 40</td>
</tr>
<tr>
<td>CPP 25 mic</td>
<td>Asia</td>
<td>5 months</td>
<td>&gt;40</td>
</tr>
<tr>
<td>CPP 25 mic</td>
<td>Asia</td>
<td>6 months</td>
<td>&gt;38</td>
</tr>
<tr>
<td>LDPE 25 mic</td>
<td>Europe</td>
<td>7 months</td>
<td>&gt;42</td>
</tr>
</tbody>
</table>

**Note:**
- The «dyne protection» effect is material dependant and needs to be checked on the specific film of interest
- The data collection is in progress
CASE B: Clear barrier films (AlOx) Protection & Converting
An Update

AlOx by «Reactive Evaporation»:

- Aluminium «conventional» metallizer
- A Specially Designed Gas Diffuser/Distributor
- Metered and Controlled Gas Injection
- Accurate Optical Sensors
- Oxygen Safe Pumping
- Design for Safe Operation

Basic AlOx Requirements:
Base Film: Pet
Clarity: Transparency > 90%
Barrier Properties: OTR 1-5 cc/m2/day (Film Dependant)
WVTR: 1-5 gr/m2/day (Film Dependant)
Conventional Wisdom

Oxide coatings are more brittle than metallic ones possibly leading to barrier loss during handling and converting.

- By deposition process control: until 2% stretching no significant barrier loss occurs.
- For a more secure durability:

  TOP COATING AND/OR LAMINATION
CASE B: Clear barrier films (AIOx) Protection & Converting
PROJECT 2017: SCOUTING DIFFERENT TOP COATING

- 3 products: «A», «B», «C», all water base from different sources
- All topcoatings increase the AIOx original barrier
- All topcoatings are resistant to mechanical stretching
CASE B: Clear barrier films (AlOx) Protection & Converting

PROJECT 2018 : TOP COATING AND CONVERTING INDUSTRIAL TESTS

A purpose-formulated coating:

- Significant barrier improvement
- Superior Protection and Robustness

![Graph showing OTR (cm³/m²·24h·bar) for different treatments: Before Treatment, Stretching (2%), Abrasion Test, and Gelboflex-50.](image)

- No Top-Coat
- Traditional Top-Coat
- Henkel's Top-Coat

From: Caimmi, Kolbach: New Design-Enabling Technologies Flexible Packaging – AIMCAL –EU 2018
CASE B: Clear barrier films (AlOx) Protection & Converting

PROJECT 2018: TOP COATING AND CONVERTING INDUSTRIAL TESTS

Top coating ("BC") effect on AlOx- Pet Through converting

- AlOx
- BC top coat
- Gravure print
- Lamination

- ALOX: 600 m/min
- BC top coat: 150 - 200 m/min, 0.5 - 0.7 gr/m2
- Gravure print: 150 - 200 m/min, Standard inks
- Lamination: 150 - 200 m/min, Solventless glue, 50mic LDPE
CASE B: Clear barrier films (AIOx) Protection & Converting
PROJECT 2018 : AIOx on BOPP – Work in Progress

- BOPP COMMODITY
- MIXED (medium/poor) BARRIER IMPROVEMENT RESULTS WITH PURE AIOX
- BARRIER TOP COATING (BC) EFFECTIVE IN REDUCING OXYGEN PERMEABILITY - still mixed results
- MARGINAL PRINT EFFECT ON IMPROVING BARRIER
- LAMINATION (bopp-AIOX//bopp) very effective in reducing gas permeation
Solutions for consistent AlOx on Bopp:

- Use of a «special» skin PP
- Combining primer and top coating
CASE C: SELECTIVE METALLIZATION «IN-REGISTER»
Vast Variety of potential Applications

Packaging

Security

Others
CASE C: SELECTIVE METALLIZATION «IN-REGISTER»

Standard Design: Selective metallization for plain film
CASE C: SELECTIVE METALLIZATION «IN-REGISTER»
Project 2018: Selective metallization for pre-printed film

Unwind
Anilox Roller and Oil Boiler
Print Roller

Rewind
Winding zone
Evaporation zone
5 × 10^{-4} mbar
CASE C: SELECTIVE METALLIZATION «IN-REGISTER»
Project 2018: Selective metallization for pre-printed film

PRINT RESOLUTION AND ACCURACY

SYSTEM CAPABILITY:

Print Resolution: 50 micron

Registration control (across/along): avg. 0.2 mm +/- 0.1mm

Detection capability: Ink/embossing mark
Presented three examples of recent promising development to extend metallizing scope and applications:

- Vacuum pre-treatments to improve polyolephine performance
- Vacuum + atmospheric coating for superior clear barrier Pet AlOx performance and stconversion. Work-in-progress for Bopp-AlOx
- Selective metallization for pre-printed materials – Work-in-Progress