Vacuum deposited transparent barrier – a clear past, but do we need to protect the future?

AlOx – a Health & Safety warning!

Steve Jackson, Camvac Limited
Vacuum deposited transparent barrier – a clear past, but do we need to protect the future?

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• History of in-chamber protective/top-coatings

• Challenges & Developments
History of in-chamber transparent barrier coating

1969: AIOx coatings disclosed by DuPont, but little interest through 70’s and 80’s due to:
- cost v PVdC coated films
- performance due to fragile oxide coating
- thus no incentive for development

1980’s: interest in developing ceramic coatings for flexible packaging food applications grew as legislation drove more environmentally friendly packaging and thus away from PVdC (toxic) and Alu Foil (high energy content).

1990’s: major drive for AIOx emerged in the Industrial and Electronics markets with optical light emitting diodes (OLED’s) for PC’s, mobiles etc.

2000’s: growth continues in both Food and Industrial applications.
Technologies

Materials:
- Silicon Oxide (SiOx) and Aluminium Oxide (AlOx) have been the main areas of development.

Processes:
- **Reactive evaporation of Silicon Monoxide with Oxygen**: originally a relatively slow process that gave a “brown tint” to the finished product - largely died out for packaging applications.
- **Electron beam evaporation of Silicon Dioxide (quartz)**: needs expensive and dedicated equipment and is difficult to control - largely died out for packaging applications.
- **PECVD of organosilanes**: developed to an industrial scale and produces a coating with good resistance to flexing and elongation. However, organosilanes are expensive and toxic/inflammable - largely died out for packaging applications.
- **Electron beam evaporation of Aluminium Oxide**: low raw material cost but requires expensive and dedicated equipment so little used for packaging applications.
- **Plasma enhanced reactive evaporation of aluminium with oxygen**: low raw material cost, high process speed and relatively low cost non dedicated equipment, thus being the current preferred process for packaging applications.
# Technology options

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<th>MATERIAL COST</th>
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Camvac developed the first European barrier metallised pack in 1975 (Nestle potato flake). Aluminium is a highly reactive metal which oxidises rapidly if exposed to oxygen or water vapour, thus it became obvious that the barrier of metallised film was not due to the aluminium layer solely, but to the thin layer of AlOx on the surface.

A number of process routes to develop an AlOx coated film were examined in the early days:

- electron beam evaporation
- hydrolysis of aluminium metallised film using steam
- oxidisation of aluminium metallised film using hydrogen peroxide
- anodisation of aluminium metallised film
- reactive evaporation of aluminium with oxygen

Surprisingly at the time but the last option gave the most encouraging results, although initially barrier was inconsistent – an issue that was latterly improved by using a slight excess of oxygen.
Further development showed that if stoichiometric quantities of aluminium and oxygen were used then a product with good oxygen and moisture barrier and good adhesion could be produced.

**Late 80’s:**
- reaction of aluminium with oxygen generated a plasma, which improved oxide adhesion and resistance to barrier loss on flexing/elongation.
- further improvements were later achieved by using an additional plasma generator – this process was patented.
- further development work showed that if too much oxygen was introduced then barrier was affected and, if too much aluminium was used, then the product had a grey tinge.
- significant work in improving this recipe lead to us using slightly more aluminium (controlled via OD), this lead to a “greyish” tinge ex metalliser but this faded back into the correct OD spec over a short period – again, this process was patented.
Early 90’s:

- the EU recognised that it had to help European producers develop technologies otherwise the market would depend heavily on Japan for transparent barrier technology.

- thus Camvac, Hoechst and the University of Durham was awarded a three year Brite-Euram grant to help with the development of the technology.

- this lead to full width (2200mm/87”) process development.

- the mechanism for barrier loss was also heavily researched and found that although some of the oxygen barrier was lost upon elongation/flexing, it “recovered” due to the “swelling” of the oxide layer by moisture.

- details of the Camclear® process was disclosed in a paper presented at SVC by Roger Kelly.
AlOx developments:

- Camclear® O – OTR
- Camclear® M - WVTR
- Camclear® XL - extra light (combined with plasma treatment)
- Camclear® - “convertibility”
The AlOx Process

PLASMA PRE-TREATMENT

OXYGEN FLOW VALVE

OXIDE DEPOSITION

FROM UW

TO RW

OD METER

WINDING ZONE / METALLISATION ZONE SEPARATION

WCR

FEEDBACK LOOP

CAMVAC

O2
OTR & WVTR

OTR 3.0 0.19
WVTR 2.0 0.13

Camclear®

OTR - 23/50  WVTR - 38/90
Advantages of AlOx

- Chlorine free barrier coating
- Excellent clarity and haze values
- High oxygen and moisture barrier
- Generally lower cost than alternatives
- Barrier independent of polyester gauge
- Lower gauge than PVdC therefore increasing machine efficiencies and area cost
- High surface tension thus printable
- Sterilisable (depends on conditions)
- Pasteurisable
- Microwaveable
- Metal detector transparent

**Excellent elongation with Camclear® - 4%**
Who?

- Toppan
- Dai Nippon
- Ultimet
- Amcor - Ceramis
- Uflex
- Camvac
- JBF
- Machinery suppliers
AlOx applications
Vacuum deposited transparent barrier – a clear past, but do we need to protect the future?
So, after:
- c. 25 years of production
- X ‘000 tonnes of external sales
- X ‘000 tonnes of internal lamination
- numerous external converters experiences
- etc. etc.

There is still undoubtedly a perception and a fear that the AlOx surface can be damaged during conversion.

And maybe also a desire for higher barrier.
1990’s: Initial trials conducted with Catalina Coatings, Sigma Technologies and Galileo (EB curing).

2000’s: Ideas/discussions/thoughts etc. “Look-see” at a machinery manufacturer.

Initial investigations with the late Bernard Henry at Oxford University (EB polymerisation).

Regular trials at Oxford University - main obstacle being adhesion.

Breakthrough on adhesion.

Started work with John Topping of MFN Technologies (plasma polymerisation).  
**Breakthrough with high energy curing.**
Installed pilot machine at Camvac.

Commissioning of new pilot line.  
Improving unit design.  
**Breakthrough on distributing the “coating” and on adhesion.**
2010’s: Continual design and process improvements and refinements

Scaled up to 2200mm/87”

Achieved very high barriers

Refining wide width process (v original pilot scale)

Pilot machine working on variants

Variants scaled up to wide width

Breakthrough on delivery system

Customer trials

FCA & FDA compliance

In line thickness monitoring

New pumps and injector designs
Coating distribution:
  resolved with injection design
  nozzle design
  internal design of boiler & slot gap

Thickness measurement:
  spectral reflectometry – existing system couldn’t measure our coating levels, thus
  work needed to write specific software and develop an in-line system.

Barrier measurement:
  initially out sourced testing as our equipment not sensitive enough.
  new test procedures introduced to record OTR barriers down to 0.005 cm³/m²/day.
  new test equipment being designed.
During the development stages three key strands were followed:

**Planarising Layers:**
- Camplus Extra®: – Al Barrier
- Camclear Extra®: – AlOx Barrier

**Polymer Multi-layers (PML’s):**
- Camquest® – Al Barrier

**Protective Top Coats:**
- Camshield® M – Al Barrier
- Camshield® T – AlOx Barrier
• Organic monomer (typically an acrylate) is fed into delivery unit.

• Flash vaporisation of monomer at ~250 °C.

• Monomer deposited onto moving substrate (typically a polymer web).

• Monomer plasma polymerised and cured.

• In line barrier layers added either pre and/or post IVC coating.
The Process – Camshield® T

ALTERNATIVE POSITION FOR OD METER

TO RW

PLASMA CURING

FROM UW

ORGANIC COATING DELIVERY

OD METER

WCR

WINDING ZONE / METALLISATION ZONE SEPARATION

OXYGEN FLOW VALVE

O₂

OXIDE DEPOSITION

FEEDBACK LOOP

PLASMA PRE-TREATMENT
OTR & WVTR

OTR - 23/50 WVTR - 38/90

Camshield® T

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<tr>
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</table>
- DCM / Knowfort
- Sigma Technologies
- Celplast
- UFlex
- Camvac
- Others.....??
Applications - Food
Applications - Specialities

- TV screen
- Packaging material
- Various products
Food Contact Approval
Oxide coated films have been in production since the early 90's.

They have demonstrated strong growth - mainly fresh and chilled food applications, but have also been used for dry food, liquid and some industrial applications.

They have been successfully converted (printing, slitting and lamination) by numerous companies over the years, with good OTR and WVTR being maintained, thus demonstrating the ability to survive flexing/elongation.
• However, top/protective coated oxide films are probably an inevitable next stage for many applications.

• Off-line top/protective coatings are available but by nature are probably not ideal, nor cost competitive.

• In-chamber coatings have been/are being developed by a select few companies.

• They offer far more versatility than off-line coatings.

• They offer protection for the oxide (and metallised) layer.

• They provide even higher OTR and WVTR.

• Indirect food contact can be/has been achieved.

• However, the technology is still new and development is ongoing.
AIoX – a Health & Safety warning!

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For a fire to thrive and spread, it requires 3 things:

- **Fuel** for the fire to burn
- **Air** for the fire to breathe
- **Heat** for the fire to continue burning

Removal of any one of the sides of the *Fire Triangle* will extinguish the fire.
Shale can ignite – what is shale?

- Shale is the evaporated aluminium that does not deposit on the web.
- It is a rich source of aluminium, but the surface quickly oxidises to prevent reaction of the core of the shale.
- AlOx shale has aluminium and oxygen embedded within the structure of aluminium oxide.
- Trapped aluminium and oxygen want to react with each other and do so slowly as they are controlled by the barrier of the oxide.
Why shale fires?

- Aluminium reacts with oxygen (AlOx production) exothermically

\[
4 \text{Al} + 3 \text{O}_2 \rightarrow 2 \text{Al}_2\text{O}_3 + \text{HEAT}
\]

- Aluminium also reacts with water exothermically

\[
2 \text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2 + \text{HEAT}
\]

- If both occur and produce enough heat, the free hydrogen will ignite explosively and if left unchecked, the reaction will self-sustain and cannot be extinguished.
There are **two main hazards** with a shale fire:

- **Flames** indicating that the hydrogen has ignited.
- If in a contained vessel, this can have explosive consequences and has blown drum lids into our neighbours yard!

- **Heat** from aluminium fire: the hydrogen ignition can speed up the ignition of the aluminium fire itself and this will burn at >1000°C.
Control measures

- **Shale Alarms**
  - Having conducted experiments on the speed of ignition of a shale fire, it has been determined that a difference of only a few degrees from ambient indicates an ignition could be imminent.
  - These give operators an early warning to get the bins outside *before* they catch fire.

![Diagram of sensor setup](image)
Bin Lids

- These work on the same principle as cigarette ash trays and circulate the vapours to smother themselves.

- The lids suppress the flames given off by the hydrogen burning, but allow any explosive pressure to dissipate safely.

- The lids have been designed to be in place at all times other than dispensing into the collection drums: shale can be swept up and disposed of through the lid and the gap is large enough to allow the extinguisher wand to penetrate.
**Control measures**

- **Fire Extinguishers**
  - Class D Powder extinguisher with low pressure wand.
  - Suppresses the flames, in order to take bin outside. **Do not use the extinguisher and leave the fire unattended in the building as it WILL REIGNITE!**

- **SOP**
  - Please read and follow the procedure instructions as they are the safest way to deal with the Shale.

- **House Keeping**
  - Camclear (AlOx) shale is most dangerous when fresh and if swept up in a pile as this allows the heat from the oxidation reaction to be contained and build up.
  - Although it may sound counter intuitive part of the SOP instructs the operator to leave Camclear (AlOx) shale on the floor for 30mins before sweeping up. This time allows the shale to slowly react with atmospheric oxygen and moisture without heat building up in one place risking a fire.
Control measures

• Containment

– As the shale is collected, it is taken outside and stored for a minimum of 2 weeks in a 30ft container.

– The time period should be more than enough to allow the AlOx shale to react and become as safe as standard shale.

– The drum lids are left loose until the end of the time period and holes are drilled in the tops of the drums to allow any hydrogen to escape.

– Should anything explode, the container will protect anyone in the vicinity.

– Note: The container doors are left open to ensure no build up of explosive hydrogen in the container.
Special thanks to

[Images of individuals and a product]
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AlOx – a Health & Safety perspective

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