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Barrier layers on paper-based packaging

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Outline

- **Background**
  - The roles of layers, barrier demands, etc.
  - Special interest on vacuum deposited coatings
- **Approaches for solution**
  - Basic technologies (polymers, metallization)
  - Current technologies (reactive evaporation, EB-evaporation, PECVD)
  - Novel methods under investigation (roll-to-roll ALD, atmospheric)
- **Conclusions**

Background

- **We know paper is a porous material,**
  - Paper allowes the passage of gases, moistures and liquids.
- **We know paper does not stand water.**
  - Paper is a hygroscopic material.
  - When absorbing water, the fibres swell and the bonding between them disappear leading to a loss of mechanical properties.
- **Still, paper and paperboard are used in the production of barrier packaging; even liquid packaging**.
  - How?

The roles of individual layers

- **Paper or Paperboard**
  - Mechanical strength
  - Printability
  - Processability as a reel
  - Stiffness (with paperboard)
  - Opacity
  - Heat resistance

- **Polymer coating**
  - Barrier properties
  - Heat sealability

- **Additional inorganic layer**
  - Improved barrier properties!

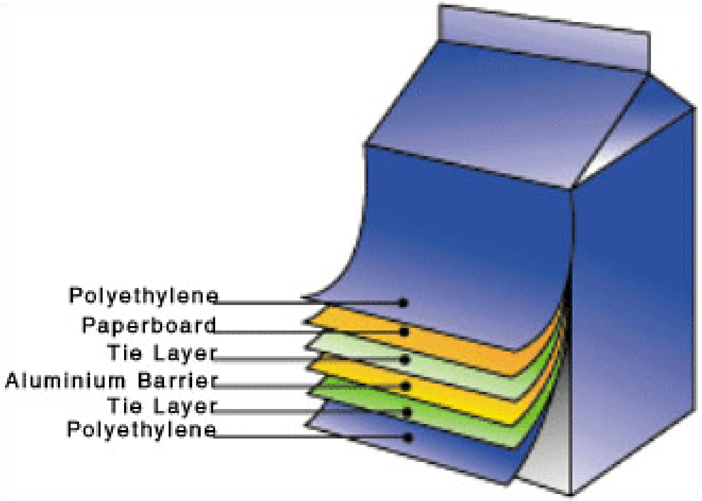
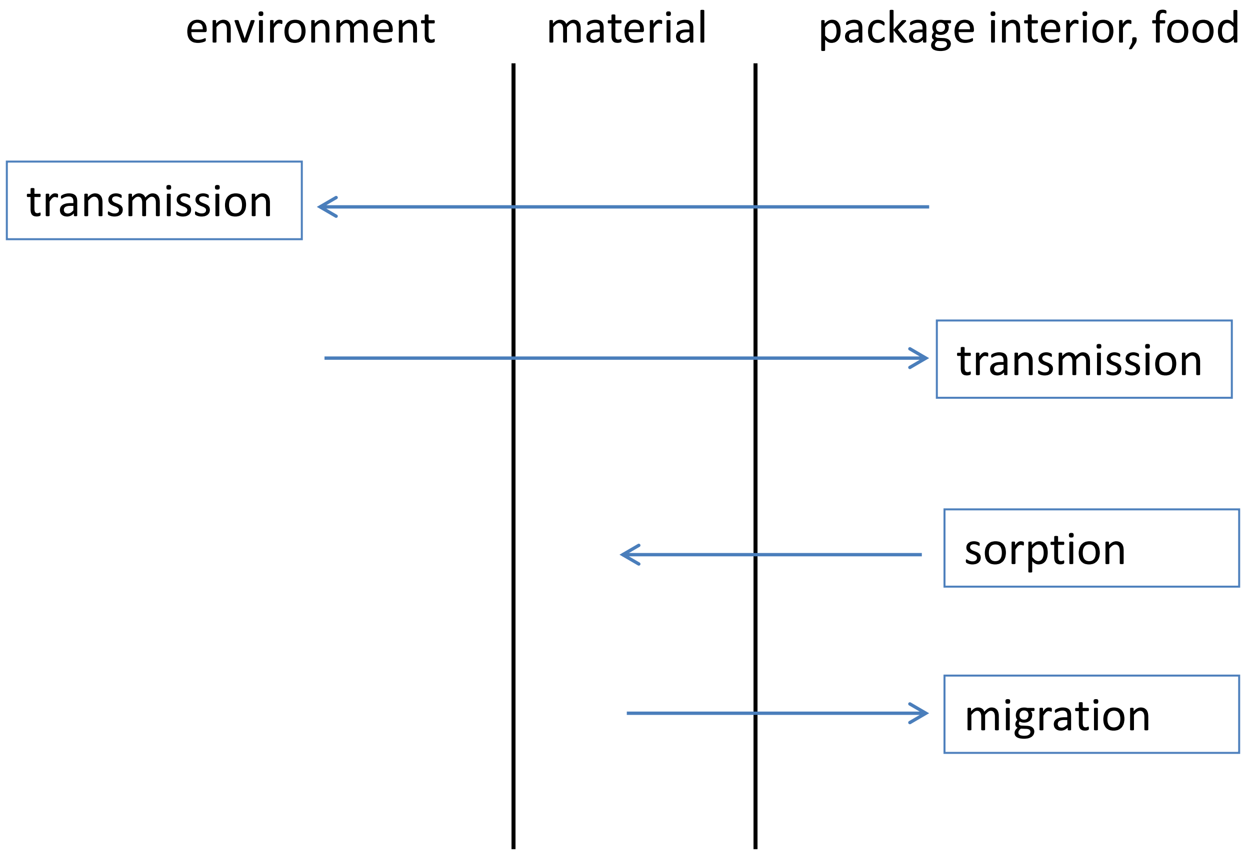


Fig: www.elopak.com

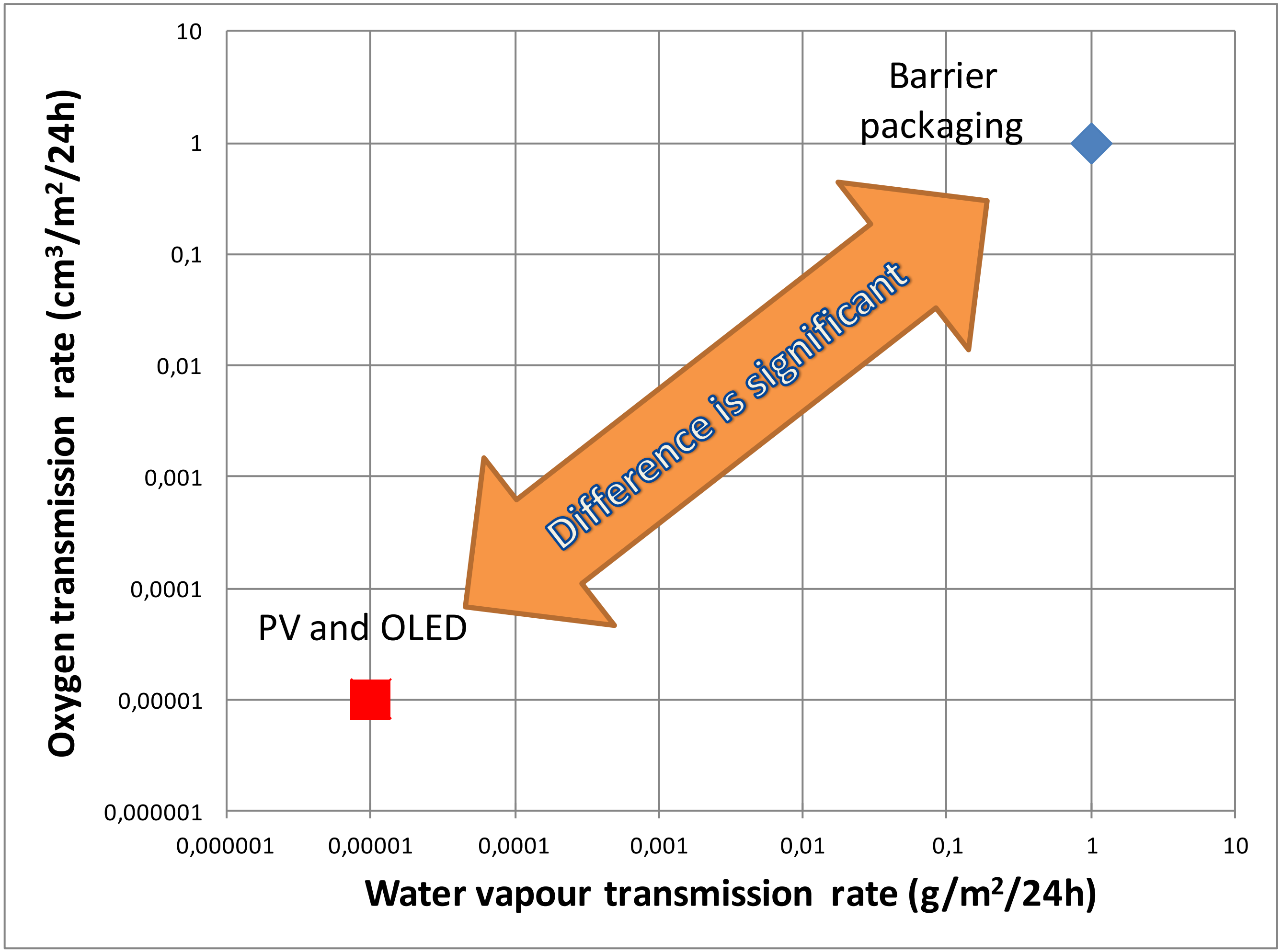
Food packaging

- In fibre-based food packaging, the role of barrier is to prevent food spoilage.
- **Moisture barrier**
  - Food lose or gain moisture before the package inlay achieves the food's equilibrium relative humidity.
  - To prevent leakage (liquid package), loss of crispiness (dry package), etc.
- **Oxygen barrier**
  - Presence of oxygen often leads to food deterioration.
  - To prevent oxidation of food components, growth of microbes, etc.
- **Others**
  - Grease barrier to pack fatty foods.
  - Aroma barrier to prevent changes in food aroma.

Transmission of substances



Difference in barrier demands (packaging vs PV)



Objective, target and motivation

- **Objective** is to use thin inorganic coatings as barrier layers in flexible packaging.

- **Target** is to obtain a ”foil-like” barrier for a material without using Al-foil.
  - Typically, Al-foil is used when a super barrier against permeating substances is needed (practically 0 transmission).

- **Motivation** is to use less Al-foil in packaging due to cost effectiveness, environmental issues and future trends.
  - Al-foil is replaced.
  - The amount of polymer is reduced.

Approaches for solution

- **Basic concept**
  - What can be done with polymers?
  - Thermal evaporation (metallization)

- **Current SoA technologies**
  - Reactive evaporation
  - Electron beam evaporation (E-beam)
  - Plasma-enhanced chemical vapour deposition (PECVD)

- **Future technologies under development**
  - Roll-to-roll ALD
  - Atmospheric technologies

Basic concept

- **What can be done with polymers?**
  - Extrusion coating
  - Barrier polymers

- **Metallization through thermal evaporation of Al**
  - PVD process
  - Barrier properties

What can be done with polymers?

- The polymer barrier layer is typically produced in an extrusion coating process.

- For moisture barrier
  - Low-density polyethylene (LDPE)
  - High-density polyethylene (HDPE)
  - Polypropylene (PP)
  - Cyclo-olefin copolymer (COC)

- For oxygen barrier
  - Polyethylene terephtalate (PET)
  - Polyamide (PA)
  - Ethylene vinyl alcohol (EVOH)

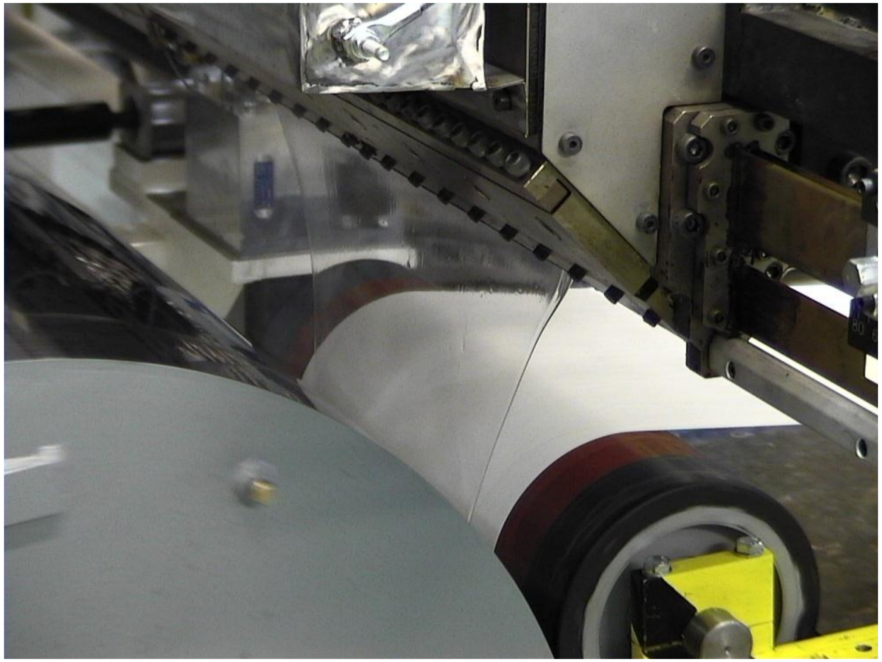
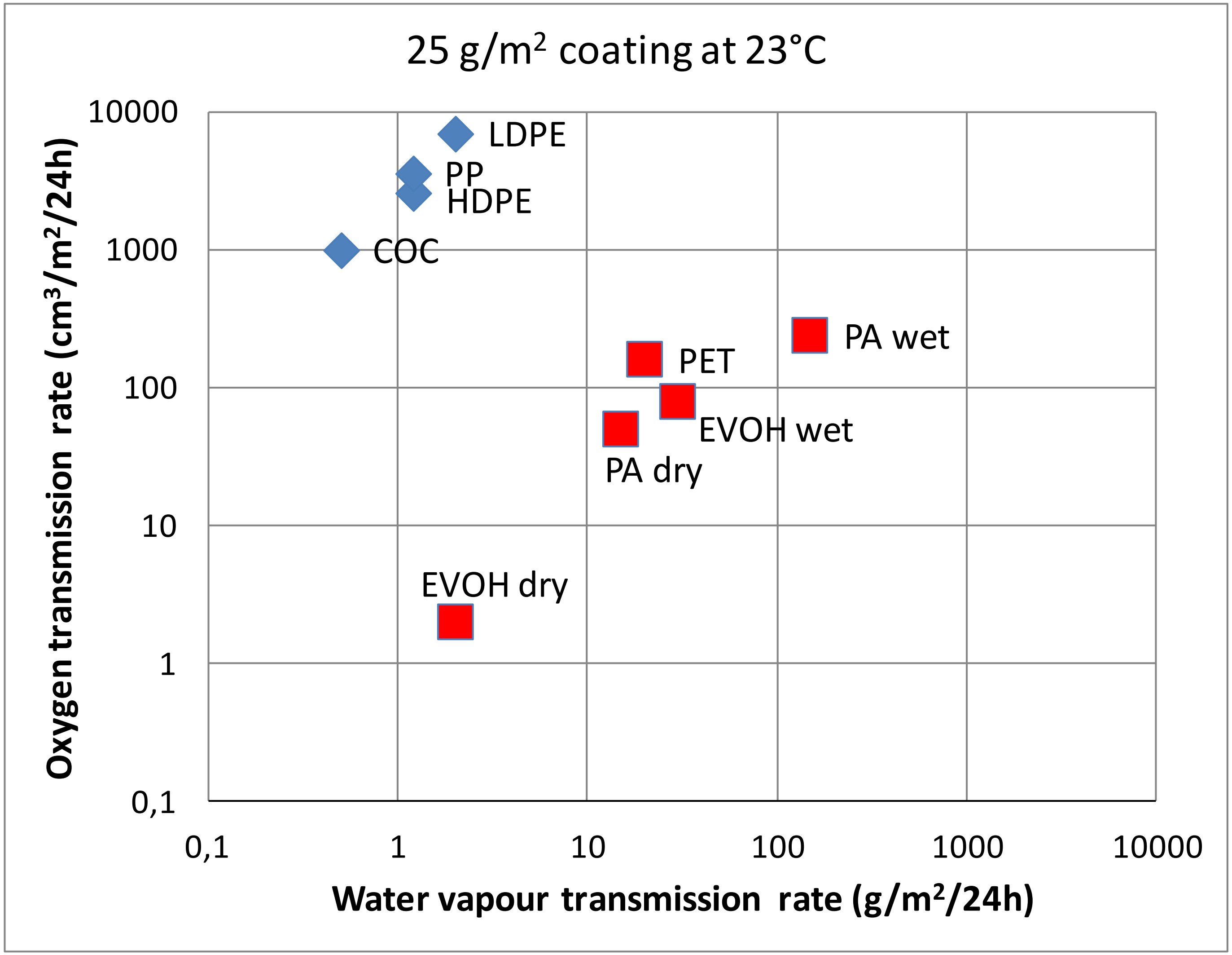


Fig: TUT / Paper converting pilot-line

(co-extruded layer structures are possible)

Polymer barriers



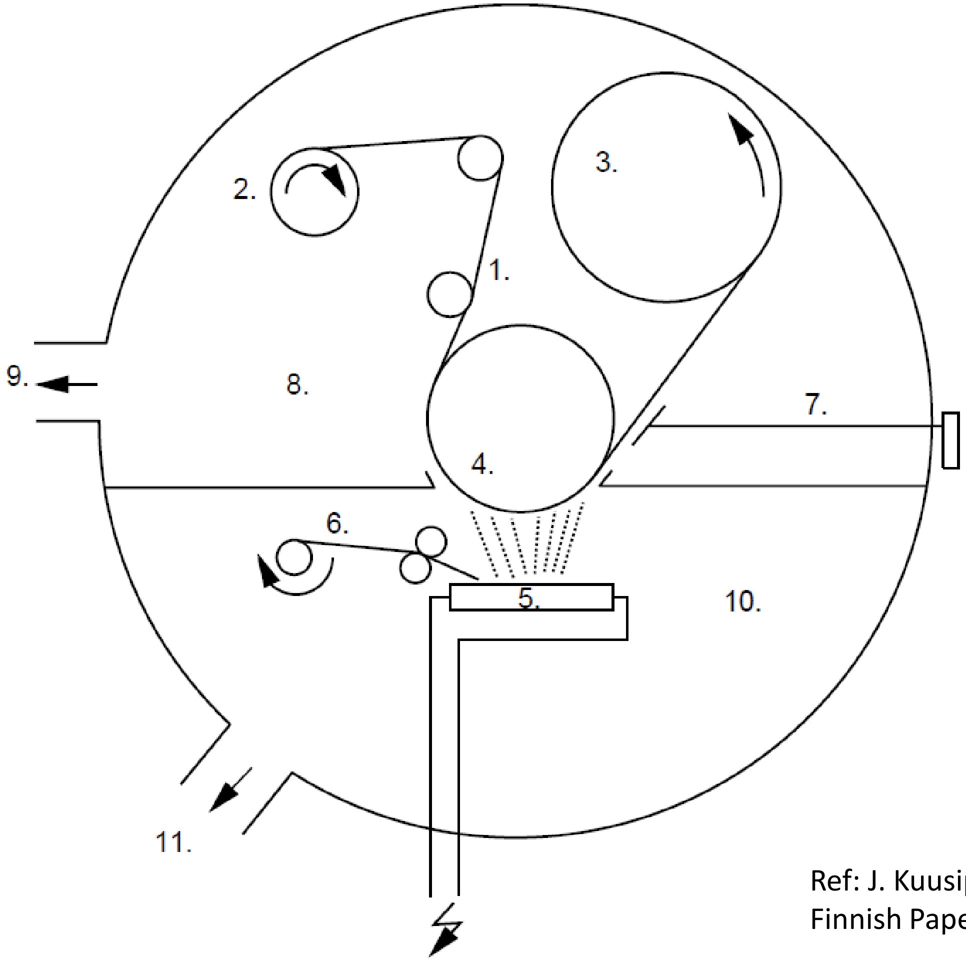
Metallization

- In general, metallization means the thermal evaporation of aluminium.

- Metal is heated and evaporated under vacuum. This substance condenses on the cold polymer film.
  - Typical layer thickness: 200-500 nm
  - Oriented polypropylene (PP) and polyester (PET) films are the most common substrates for metallization. Polymer-coated papers as well.

- Barrier levels obtained through metallization
  - supersede those of commercial barrier polymers.
  - approaches those of aluminium foil.

Metallization



1. metallized web
2. unwinding
3. rewinding
4. chill-roll
5. crucible
6. feeding of aluminum-wire
7. measuring of resistance
8. upper chamber
9. vacuum suction to upper chamber
10. lower chamber
11. vacuum suction to lower chamber

Ref: J. Kuusipalo, Paper and Paperboard Converting, 2. ed. Finnish Paper Engineers' Association, Helsinki, 2008.

Barrier properties of metallized film

	WVTR (38°C, 90% RH) $g/m^2/24h$	O_2TR (23°C, 50% RH) $cm^3/m^2/24h$
PET film, 48 µm	43	70
Metallized PET	0,08	0,19
Aluminum foil, 6 µm	0	0

Ref1: Du Pont Teijin Films website
Ref2: L. Webb, Tappi Innovations in Barrier Packaging Symposium, 7-8 June 2006, Atlanta, GA.
Ref3: European Aluminium Foil Association

Current vacuum technologies

Company	Deposition process	Material
Camvac, UK	Reactive evaporation of aluminium & oxygen, PECVD (carbon)	Al_2O_3, metallized, carbon
Dai Nippon	Electron Beam Evaporation (alumina), PECVD of organo silanes (silica)	Al_2O_3, SiOx
Toppan	Electron Beam Evaporation	Al_2O_3, SiOx
Toyo	Reactive evaporation of aluminium & oxygen	Al_2O_3
Reiko	Evaporation	Al_2O_3
Amcor Flexibles	Electron beam Evaporation	SiOx
Tetra Pak	PECVD of organo silanes	SiOx
Mitsubishi	Electron Beam Evaporation	SiOx
Oike	Electron Beam Evaporation	SiOx
Toyobo	Electron Beam Evaporation (co-evaporation)	Al_2O_3, SiOx

Common Barrier technologies

- **Reactive evaporation of aluminium**
  - Al_2O_3
- **Electron Beam Evaporation of organo silanes (E-beam)**
  - SiOx
- **Plasma-enhanced chemical vapour deposition (PECVD)**
  - SiOx and hydrocarbons
- Others
  - Reactive EB Evaporation for Al_2O_3
  - Thermal Evaporation for SiOx

Reactive evaporation of aluminium

- Aluminium is evaporated, it reacts with oxygen and the Al_2O_3 coating is formed onto the substrate.

- Advantages
  - Low material costs
  - High productivity
  - Low investment

- Disadvantages
  - Difficult to control the process
  - Layer sensitive to elongation
  - Medium barrier properties

Camvac, Toyo

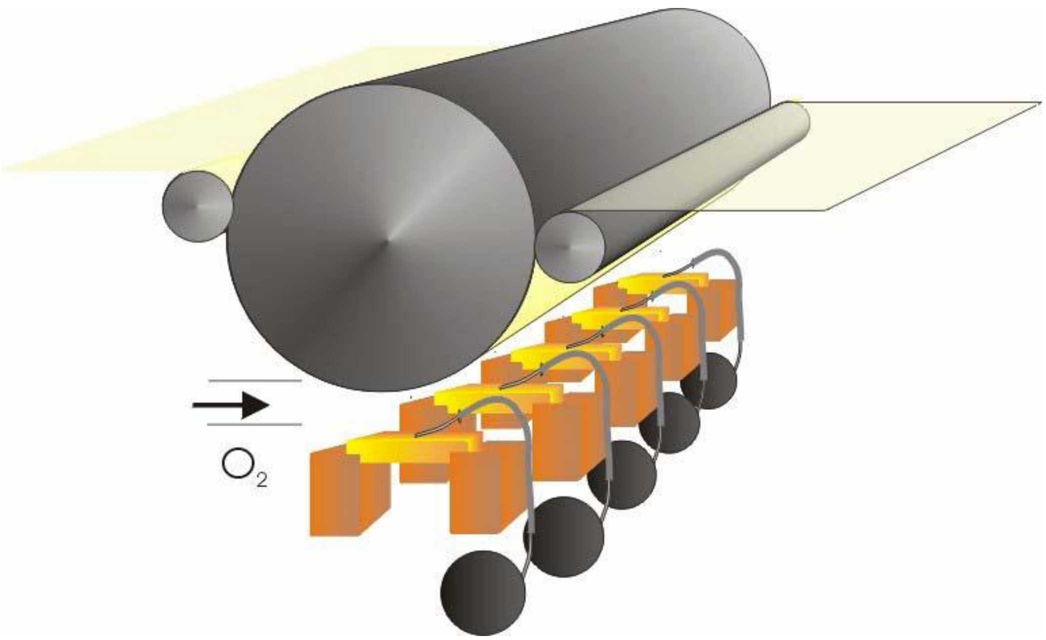


Fig: T. Glaw, Amcor Flexibles Kreuzlingen,
TAPPI 11th European PLACE Conference, Athens, 2007.

E-beam evaporation of silicon oxide

- The solid silicon oxide is heated up by an electron beam and evaporates as glass vapour. It condenses again on the film and forms the glass layer.
- Advantages
  - Low material costs
  - High productivity
  - Good barrier properties
- Disadvantages
  - High investment
  - X-ray generation

Amcor Flexibles, Oike, Toyobo

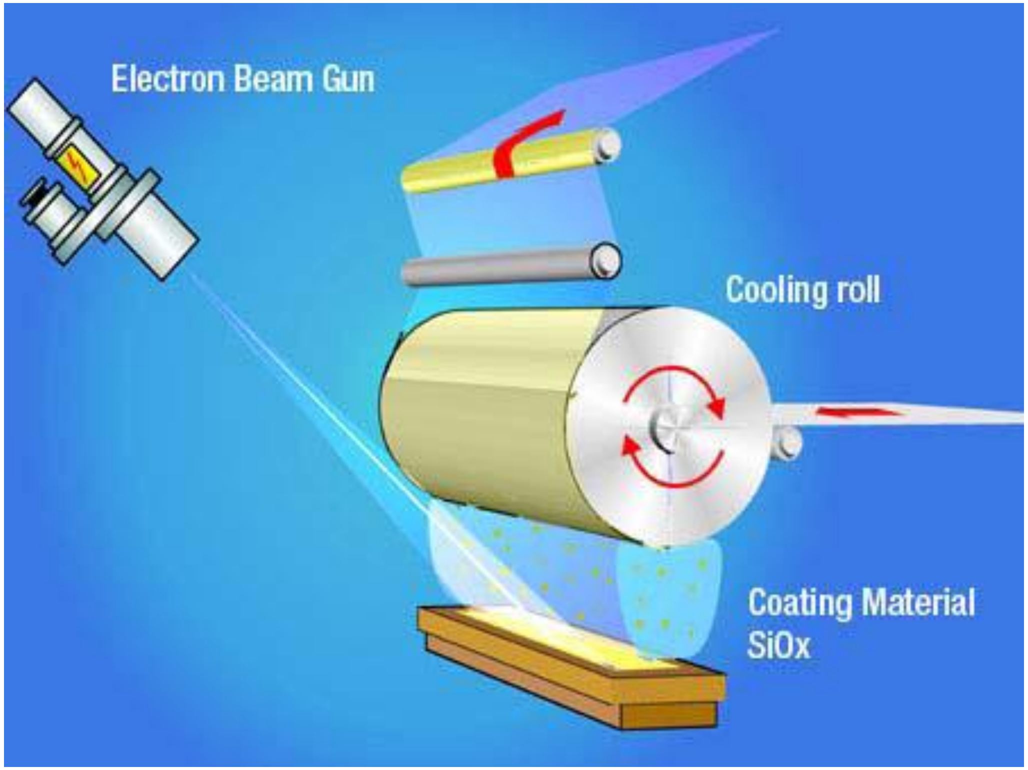


Fig: T. Glaw, Amcor Flexibles Kreuzlingen,
TAPPI 11th European PLACE Conference, Athens, 2007.

PECVD of organo silanes

- Plasma assists HMDSO and oxygen to react on the surface. Removal of methyl radicals from disiloxane followed by reaction with oxygen. → SiOx coating

- Advantages
  - Low material costs
  - Good barrier properties
  - Low heat input

- Disadvantages
  - High investment
  - Medium productivity
  - Difficult process control

Tetra Pak, Dai Nippon

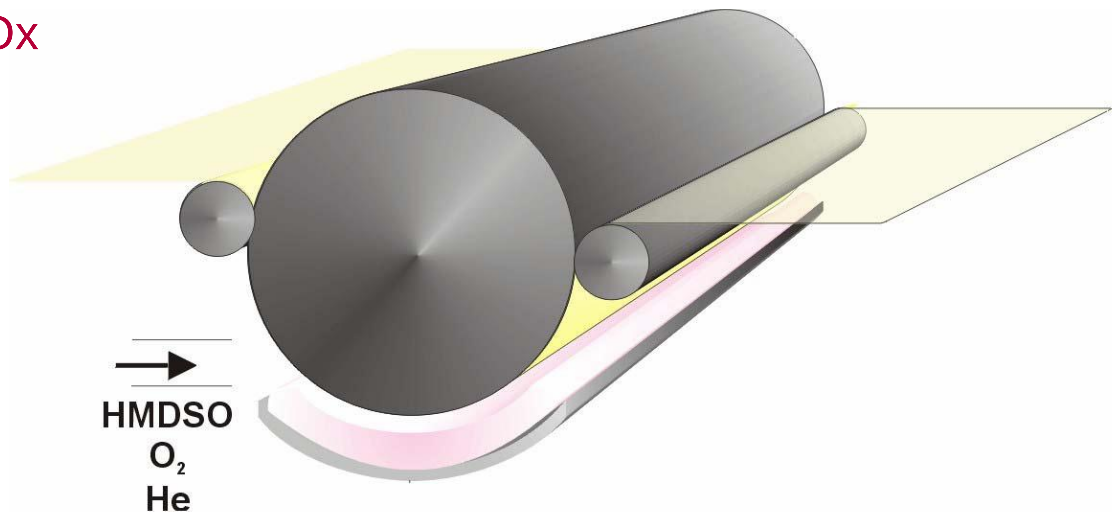


Fig: T. Glaw, Amcor Flexibles Kreuzlingen,
TAPPI 11th European PLACE Conference, Athens, 2007.

Barrier of single coated films

Barrier Material	Thickness	O_2TR^* ($cm^3/m^2/24h$)	$WVTR^*$ ($g/m^2/24h$)	Deposition process
PET	12 µm	100	64	
Aluminized PET	~ 30 nm	0,31 - 1,55	0,31 - 1,55	Evaporation
SiOx on PET	10 – 80 nm	0,35 – 10	0,46 - 1,24	Evaporation
SiOx on PET	10 – 80 nm	0,08 – 1,55	0,5 – 5,0	PECVD
Al_2O_3 on PET	20 nm	1,5	5,0	Reactive Evaporation
Diamond-like carbon on PET	20 nm	2	1,5	PECVD
* Depending on the used process and measuring conditions.				

Table: B. M. Henry, TAPPI Innovations in Barrier Packaging Symposium, Atlanta, GA, 2006.

Characteristics for vacuum coatings

- Fast deposition rates already achieved.
  - E-beam evaporation: 1000 m/min
  - PECVD: 200 m/min (Tetra Pak)
- The films are transparent and thinner comparing to metallization.
- Evaporated coatings are more sensitive to strain than plasma deposited.
  - Less strain needed for barrier loss.
- The gas transmission rates can fulfil the demands of packaging.
  - Single layer coating is enough for packaging.
  - Further improvements are needed for displays and PVs by 1) reducing the number of defects, 2) applying multiple barrier layers or 3) using more sophisticated coating methods.

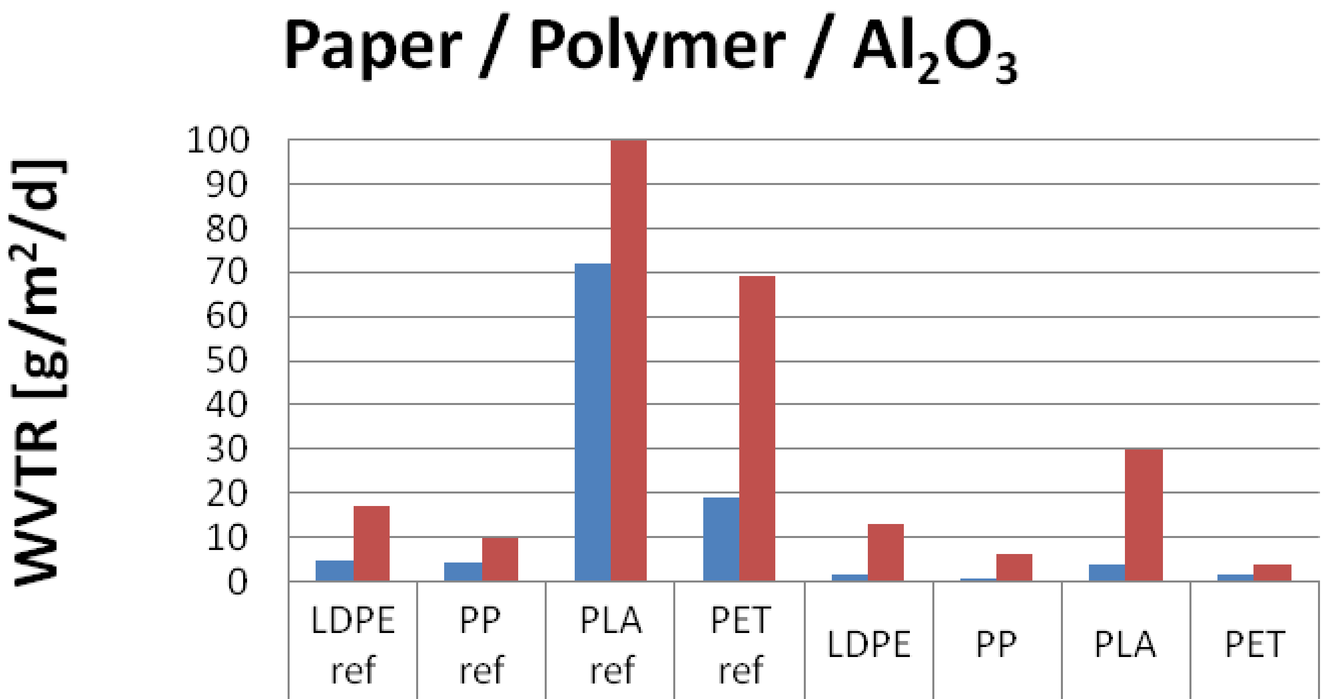
New technologies under investigation

- **Roll-to-roll atomic layer deposition (R2R ALD) for Al_2O_3**
  - TMA and the oxygen source react only on the substrate's surface.
  - All the ALD-cycles are made under one by-pass (roll-to-roll).
  - In theory, the coating is as thin and as dense as it possible gets.

- **Technologies applicable in atmospheric pressure**
  - Atmospheric plasma deposition, atmospheric ALD, etc.
  - Huge benefits from avoiding the vacuum.
  - Difficult to obtain conformal coatings.

- REF: Session 5 in MIICS 2012, Thursday morning.
  - Roll-to-roll ALD
  - Atmospheric ALD

Barriers achieved for paper with CALD



	LDPE ref	PP ref	PLA ref	PET ref	LDPE	PP	PLA	PET
23°C 50% RH	4,6	4,2	72	19	1,4	0,5	3,8	1,4
38°C 90% RH	17	10	290	69	13	6	30	4

Fig: P. Johansson et al., TAPPI 13th European PLACE Conference, Bregenz, Austria, 2011.

Conclusions

- **A single layer deposition offers good enough barrier properties** for most of the packaging applications. Further development is needed for OLEDs and PVs.

- **Commonly used technologies are**
  - Basic: Metallization
  - Current SoA: Reactive evaporation, E-beam evaporation and PECVD of oxides

- **Possible technologies in the future**
  - Roll-to-roll ALD
  - Atmospheric technologies

Main references

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TEKES

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