Glaskin™ by Tetra Pak

PECVD barrier coating of plastic bottles

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Tetra Pak More than the package™

Glaskin™ by Tetra Pak

Contents

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1.Plastics as Container Material

In competition with: Glas

Metal

Paper / Paper board

Specific advantages:

- **Design shape (additional functions) and colour flexibility**
- **Unbreakable**
- **Corrosion resistance**
- **Low packaging weight**

Specific problems:

- **Recycling system for such versatile materials**
- **mechanical stability**
- **low decomposition rate**
- **partly insufficient diffusion barrier effect**

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1.1 Example: Beverage bottles

Base material (among others):

PEHD: Milk

PET: Mineral water
"Carbonated soft drinks" CSD
Beer and Juice

Advantages:

- **Design flexibility: Attractive shape**
  Colour
- **Additional functions possible (Handle, big-neck, screw closures)**
- **Light weight of packaging and cover packaging**

Problems:

- **Recycling system**
- **partly insufficient diffusion barrier effect against CO_2, O_2, H_2O, flavours, plastic constituents (acetaldehyde)**

Production:

- **Extrusion Blow Moulding**
- **Injection moulding followed by Stretch Blow Moulding**

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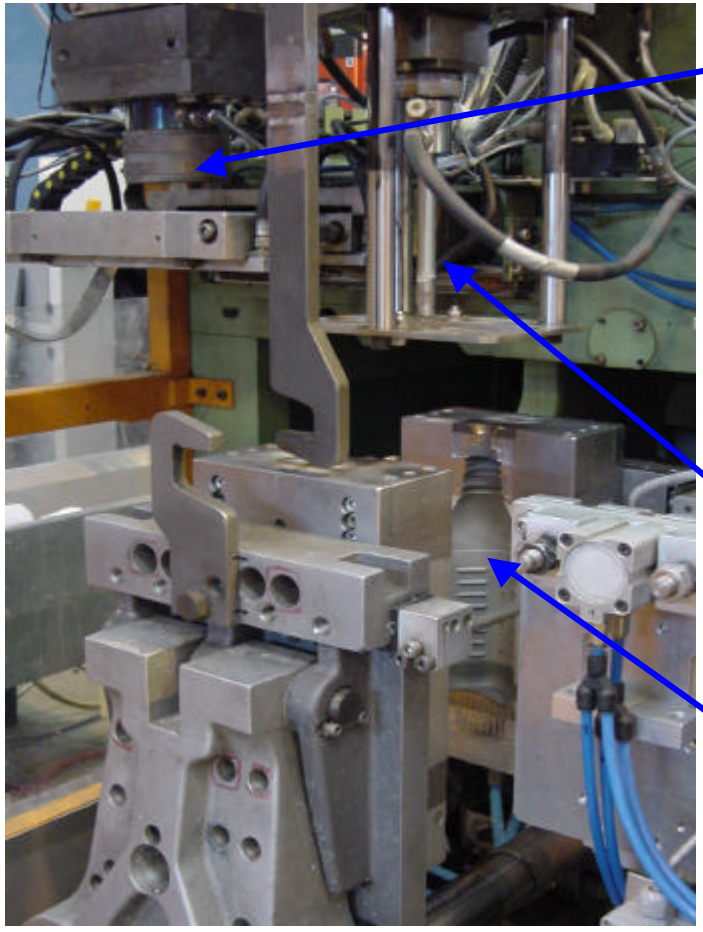
Extrusion Blow Molding



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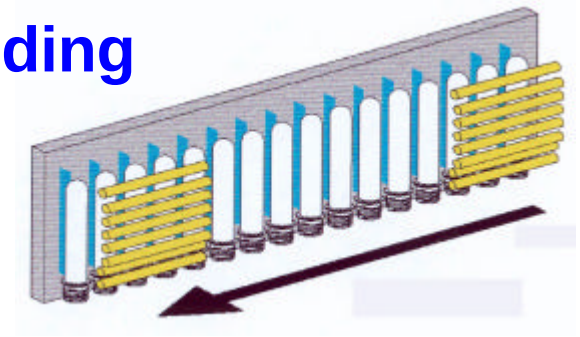
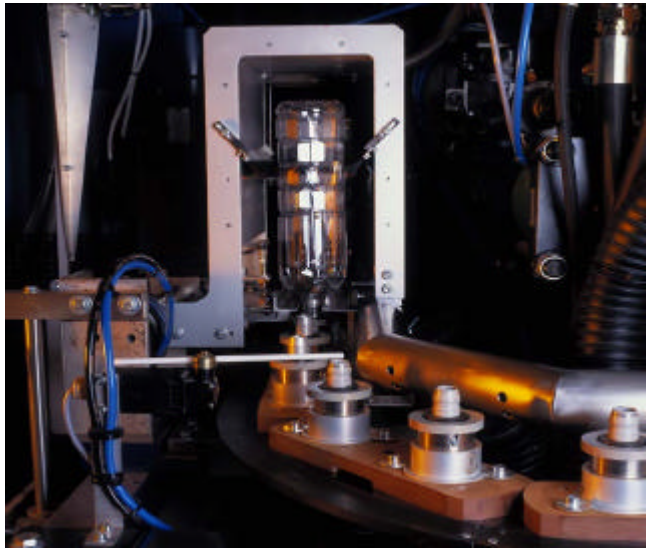
Heat-Set stretch-blow-moulding



Injection moulded preforms are taken in via a linear transport system.

During a transition period in the oven they are conditioned and taken to the moulds.

After an initial mechanical stretching and pre-blow at 10 bar, the preform is fully blown to a bottle at 40 bar.



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2. The industry is taking efforts to offer the best barrier technology

2.1 Effects of permeation and migration on filled beverage bottles

Substance	Diffusion from → to	Effect
O_2	outside → inside	Degradation of dyestuff, flavour and vitamine C
	wall → inside	" "
CO_2	inside → outside	recessive foam and pearl effect
H_2O	inside → outside	small (slight) fill level
	outside → inside	Moisturisation of dry goods
Flavours	inside → outside	Flavour loss
	wall → inside	Flavour transition from material
	inside → wall	Flavour transition from material
Plastic components	wall → inside	Odour debasement

Conclusion: Inside coating is preferable!

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2.2 Improvement of diffusion barrier performance

Methods	Basic Material	Barrier against	Application	Problem
Barrier plastic	PET,PEN	CO2, O2	Beverage	
	PE,PP	H2O	Fuel, cosmetics	
Copolymer	TPA-IPA	"		
Polymer mixture	PET-PEN	"		Recycling
Multilayer structure	PET,	CO2, O2	Beer	Recycling
	PET, PA			
Nano composites	PE			Recycling
	PET	CO2, O2		Opt. transmission
				Recycling
"Active" plastics	PET	O2	Beer	Long-term stability
with O2- scavenger				
Liquid coating	PET	O2	CSD, juice	Lacquer application
(Lacquer)				
"Dry"coating (in vacuum)	PET	O2, CO2	Beer, juice,CSD	Throughput

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3. Deposition of barrier layers by vacuum thin film techniques

	a) Plasma-assisted Vacuum Evaporation	b) Plasma Chemical Vapour Deposition
		(PCVD)
Basic raw material	rigid, (liquid) + gaseous	(rigid), (liquid) + gaseous
	$Si+O_2$	Si-compound, hydrocarbons
Coating material	SiO_2	SiO_2, C:H/DLC
Pressure	10^{-4} mbar	10^{-1} mbar
Vapour dispersion	directional	not directional
Coating formation	condensation	chem. reaction
Coating thickness	30-50 nm	20-30 nm/50 nm
Coating side	outside	inside or outside

3.1.PCVD coating inside PET bottles by Tetra Pak

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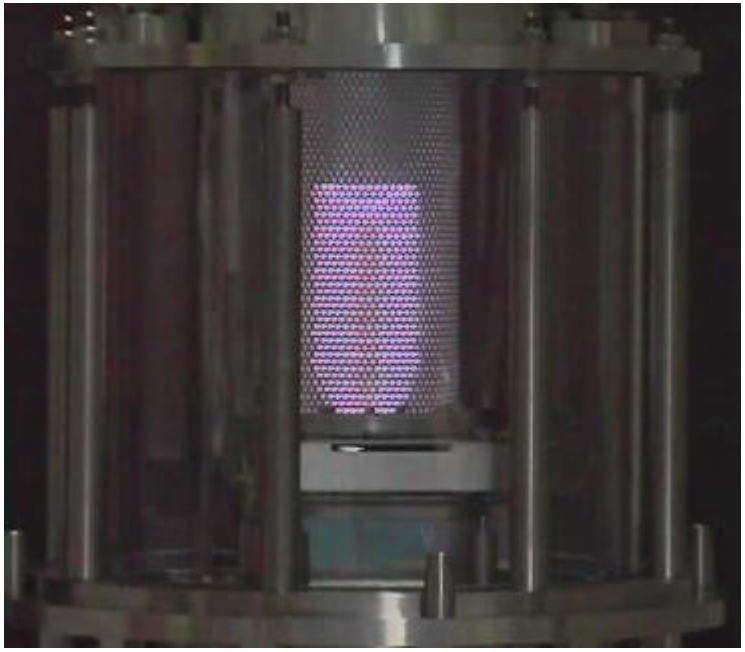

- Proprietary Tetra Pak technology
- Internal deposit of an extremely thin Silicon Oxide coating in a PET bottle
- Cold plasma deposition process

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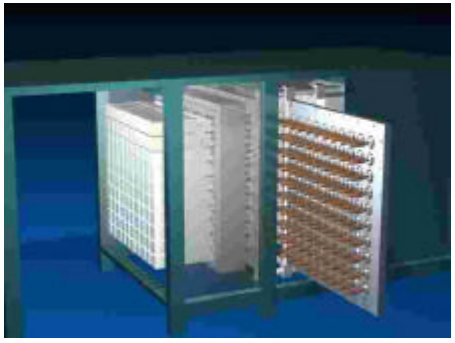
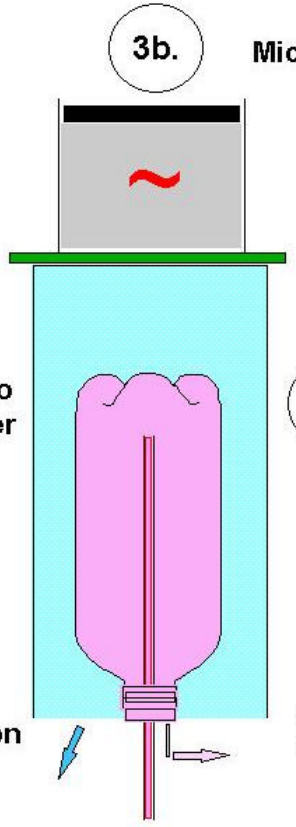
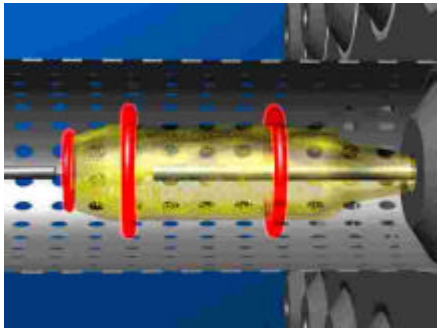
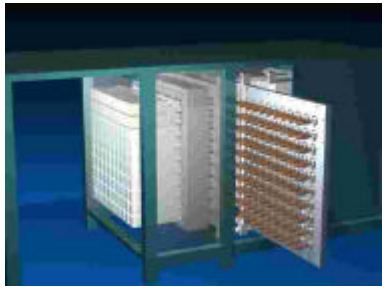
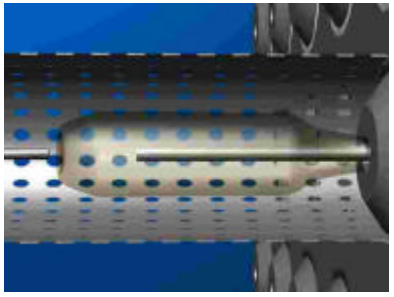
Glaskin™ Coating Process Description

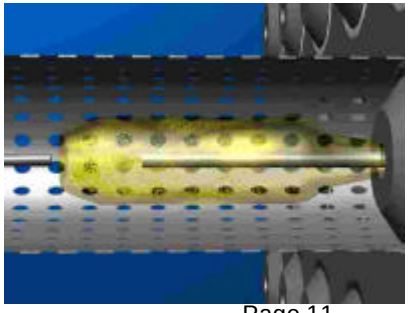




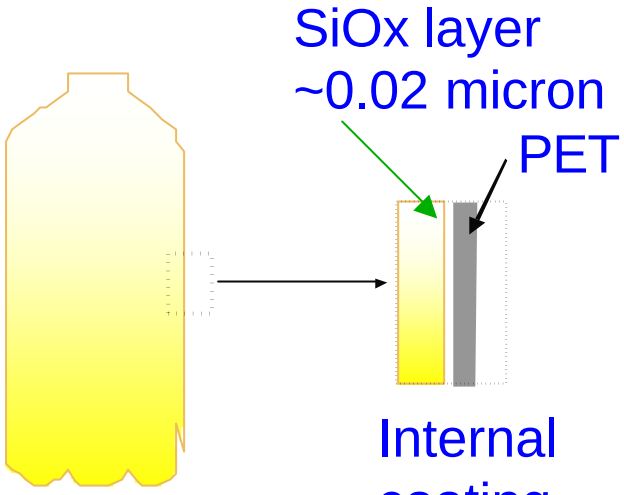








Glaskin™ Coating is thin!



Thinner Coatings have

- more flexibility
- lower stress

One newspaper sheet = 3500 Glaskin™ coating layers

Newspaper sheet thickness = 0.07mm= 70 microns

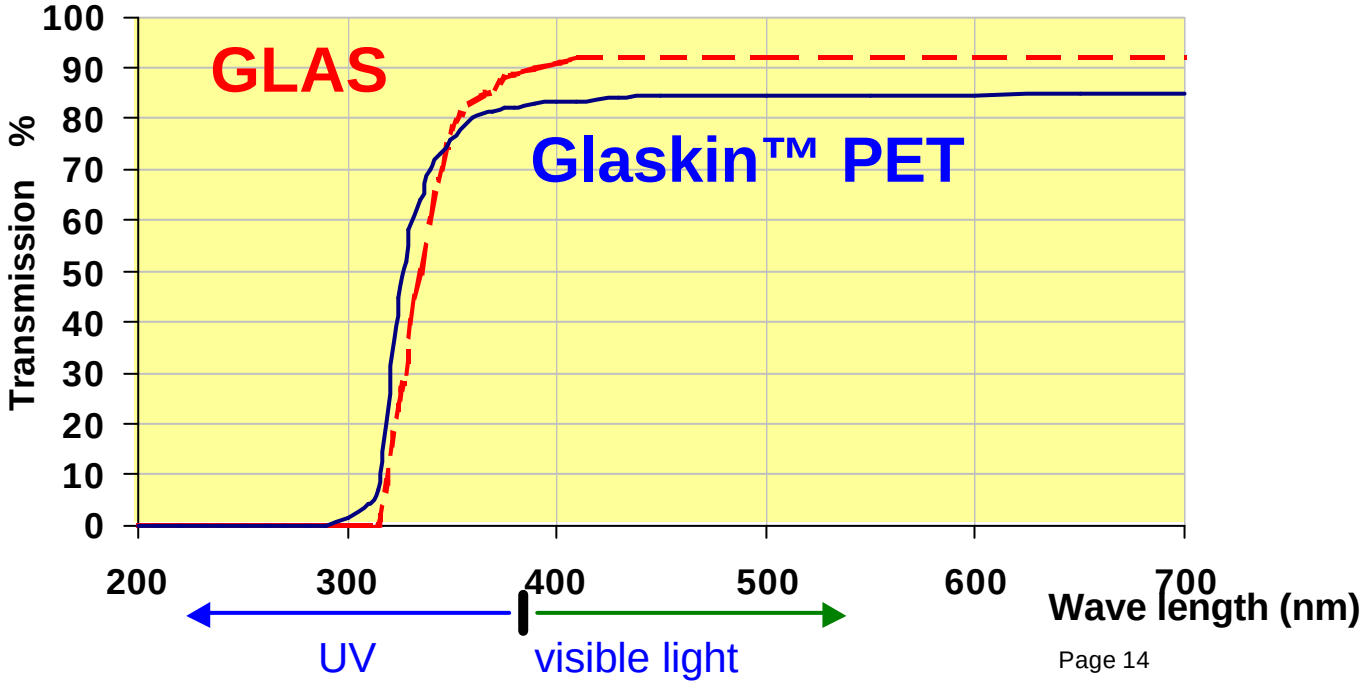
Glaskin™ coating = 0.02 microns

Glaskin™ coating is

- is a glass-like, colourless coating
- an inert food contact surface
- is a high barrier performance
- strong in minimising migration
- compliance with food legislation

Glaskin™ is transparent!

- ✓Transparent Glaskin™ bottles have the same light transmission as transparent glass bottles
- ✓ Glaskin™ coating is 100% transparent
- ✓ No changes of bottle transparency after coating (no clouding of bottles)

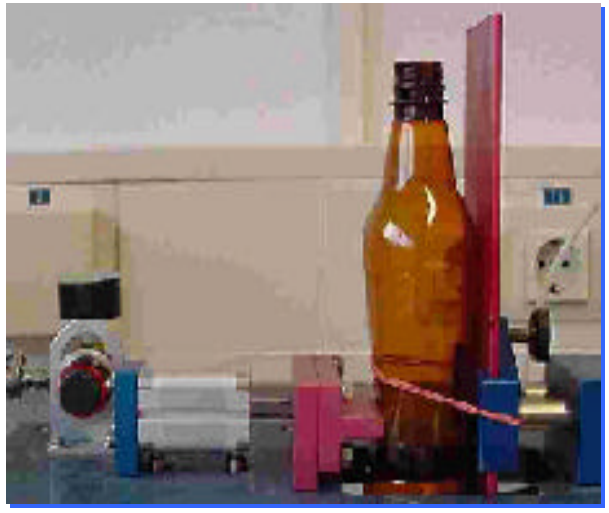


Glaskin ™ mechanical characteristics

Glaskin™ coating is extremely thin and therefore flexible and can resist a high mechanical load with no impact on the barrier performance

Drop tests:
A free fall from a height of 1,5 m has no impact on filled bottles

Deformation tests:
20% deformation of bottle diameter shows no impact on the properties

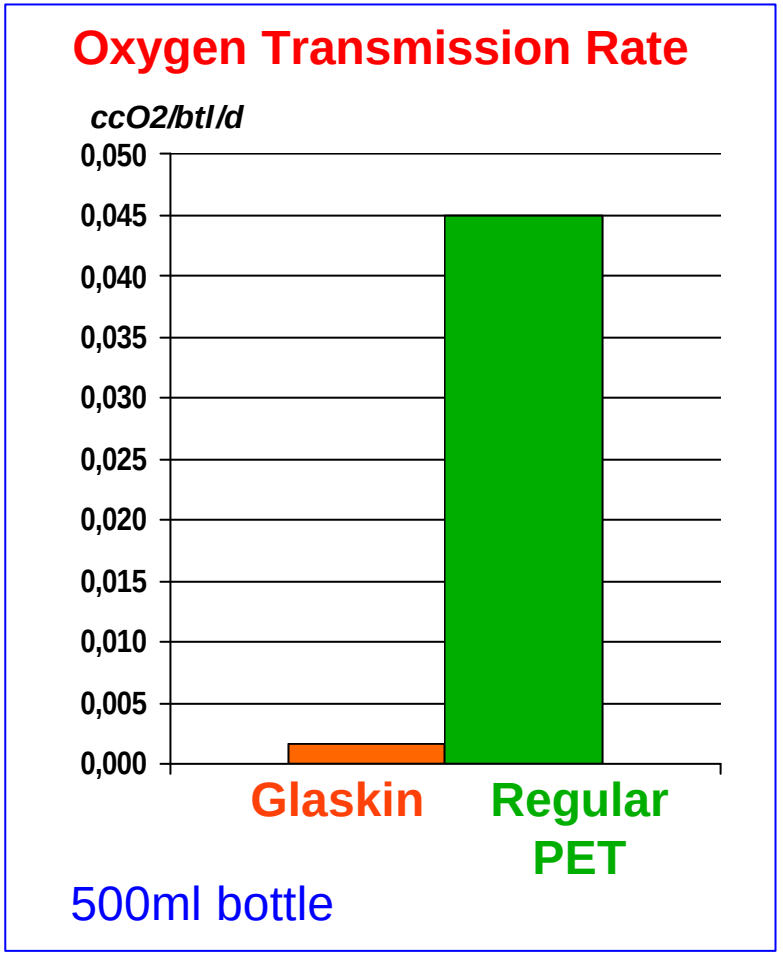


Glaskin bottle gives high O_2 barrier for demanding products

Glaskin bottles have in various tests proven to have barrier properties as low as **0.0015 cc O2 /bottle / day**

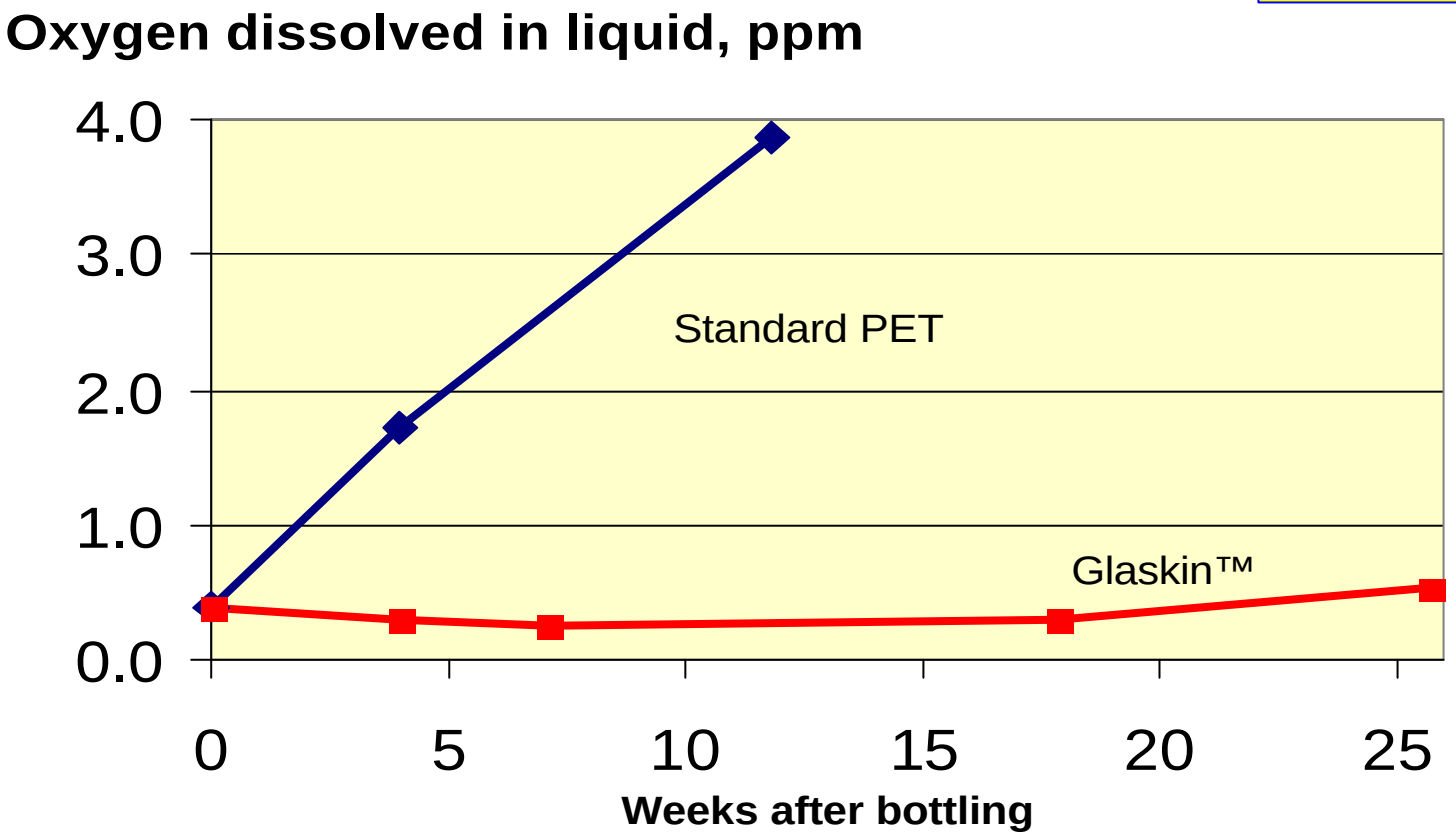
Barrier Improvement Factor (BIF) **10-30 times** compared to regular PET

BIF factor depends on performance of regular PET bottle, bottle shape, weight etc.



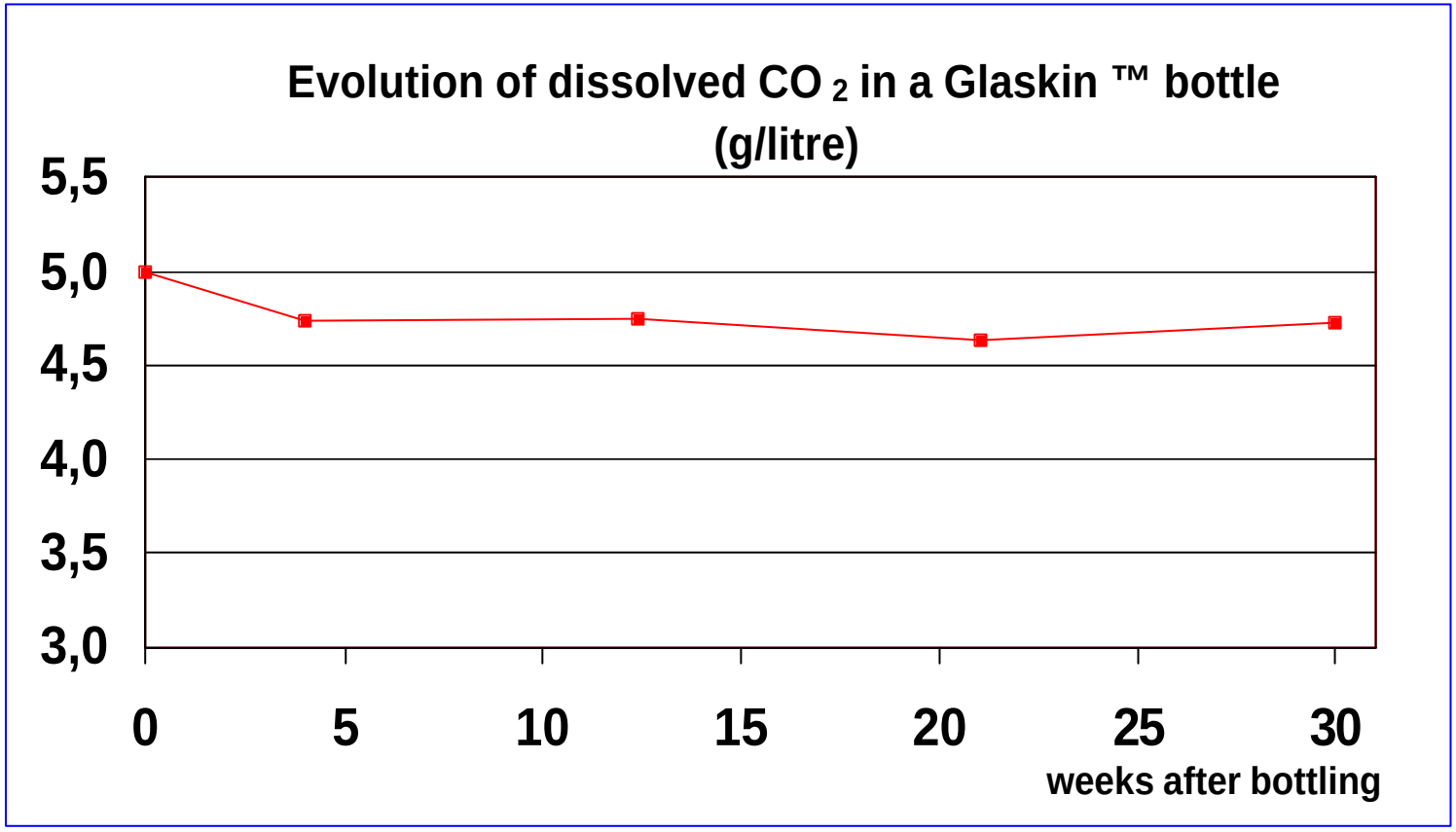
Glaskin keeps oxygen out longer

Carbonated water



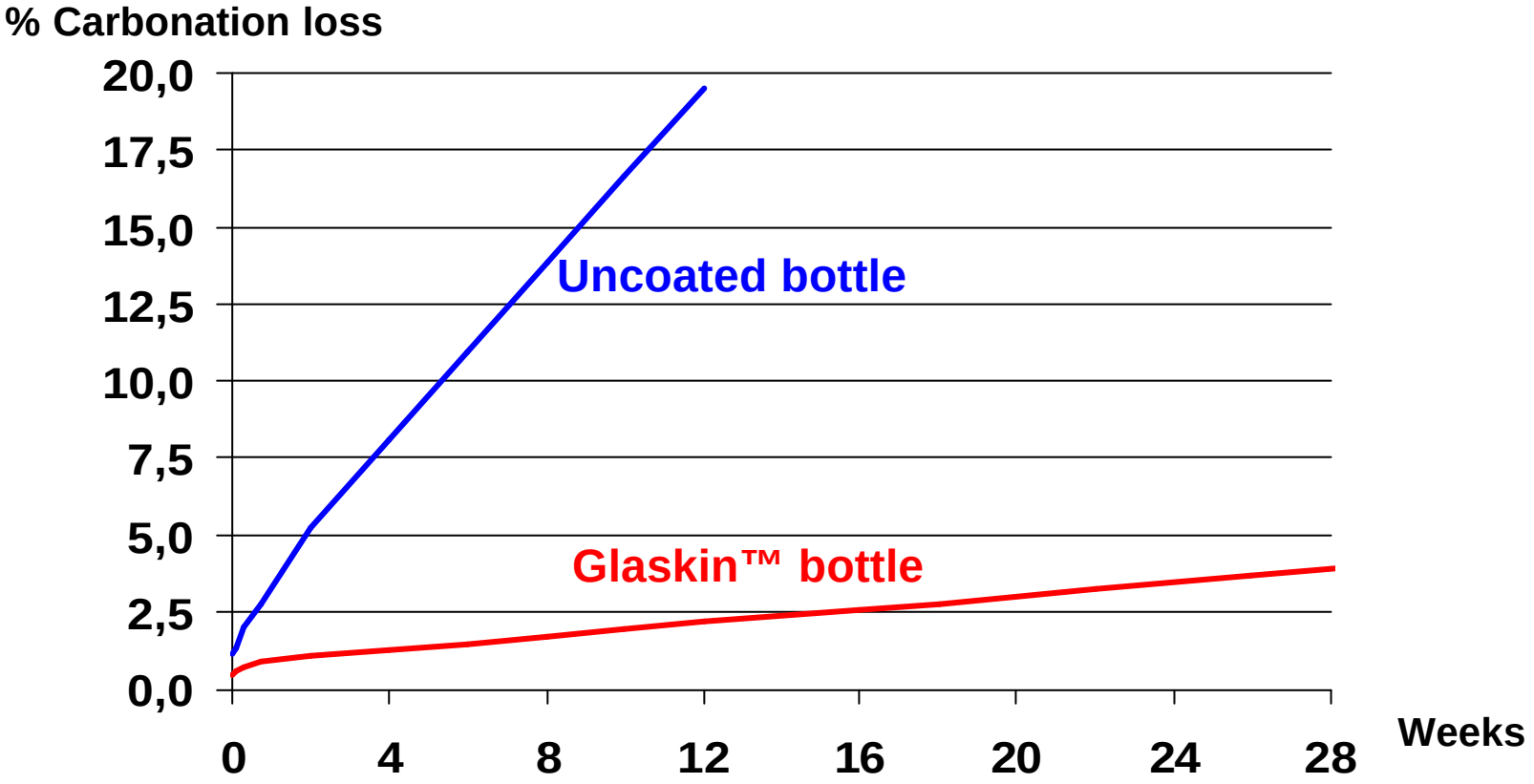
Test basis: Orbisphere analysis, 500ml bottles filled in a commercial line with deaerated carbonated water, barrier cap with 0_2 scavenger

Glaskin bottles have high CO_2 retention



Test basis: Orbisphere analysis, 500ml bottles filled in a commercial line with beer, barrier cap with 0_2 scavenger, storage at 23°C

Glaskin bottles have high CO_2 retention



Method: Coca Cola FTIR method for CO_2 retention
Conditions: Storage at 23°C, 500 ml bottle, capped empty bottle
Carbonation to approx. 8 g/liter (4 vol/vol)

Glaskin™ reduces water loss

PET transmits water vapour

Loss depends on temperature and humidity

Water loss 0,5 – 1,0 ml/month at room temperature and 50 % relative humidity (500 ml standard PET bottle)

Glaskin™ coating reduces water loss by more than a half compared to a standard PET bottle

Migration from the liquid into the bottle

Test:

Coated and uncoated bottles were filled with orange juice and stored at 40°C – then analysed by Gas Chromotography.

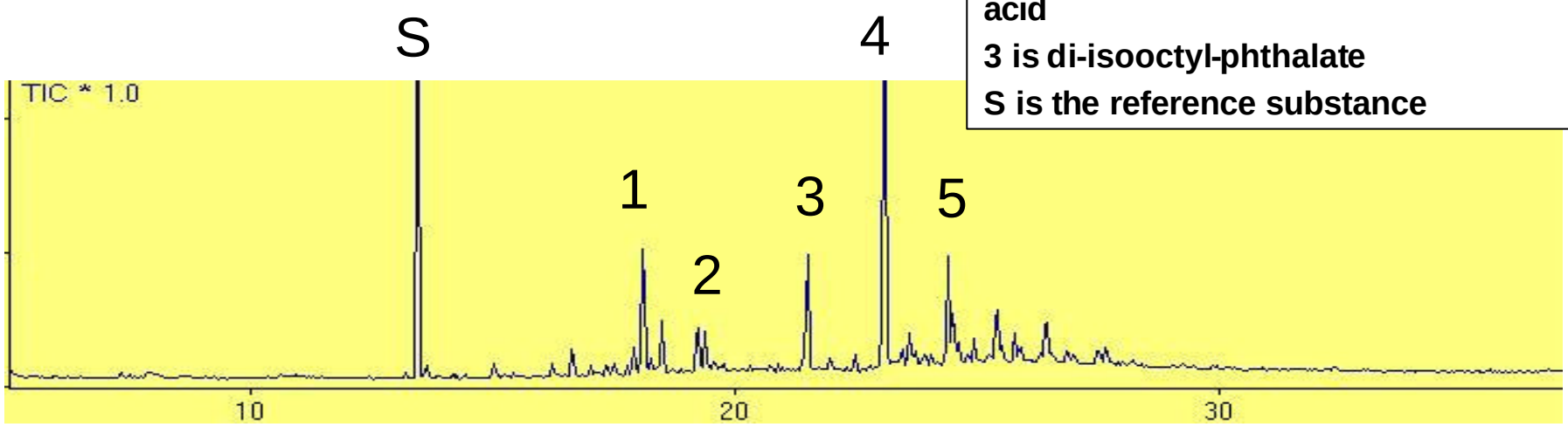
Result:

The migration from product constituents (d-limonene) into the Glaskin coated bottle wall is not considerable being

→ **15.000 times** less than Mono- PET

Results: Monolayer PET – bottle, uncoated

Substances migrated into product



Peaks 1and 5 are esters of saturated acids

2 and 4 are alkyl-esters of unsaturated fatty acid

3 is di-isooctyl-phthalate

S is the reference substance

Concentration : 1=10-20 µg/bottle, 2= 1-10 µg/bottle, 3= 5-15 µg/bottle, 4=100-150 µg/bottle, 5=10-20 µg/bottle

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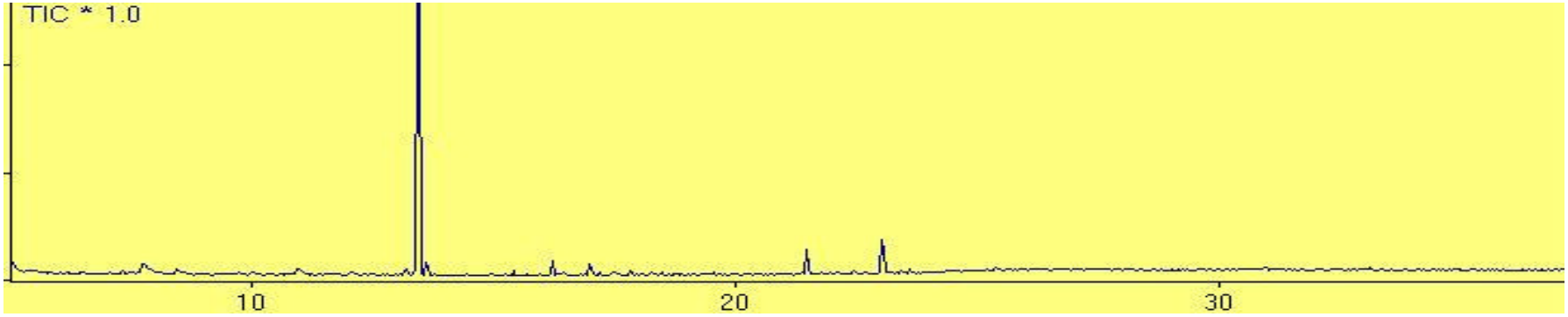
Result: Glaskin™ inside coated - bottle

Nearly nothing has migrated into the product



Also, acetaldehyde (AA) concentration was reduced at least by 50%

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Glaskin™ coating stops migration from PET walls into product

Tests:

- Coated and non-coated bottles tested
- Bottles filled with 95% ethanol, stored for 1, 5,10 and 20 days at 40°C
- Ethanol solution emptied and analysed by Gas Chromotograhpy (GC)

Results:

Non-coated bottles*:* substances migrate from PET surface into ethanol solution

Glaskin™coated bottles: virtually nothing detected by GC

Tests by FABES Research Institute, Germany

Product Launches

Spendrups Beer, Sweden:

450 & 500ml bottle, 28mm neck

Two brands in 2 bottle shapes

Supermarket distribution

State liquor store distribution

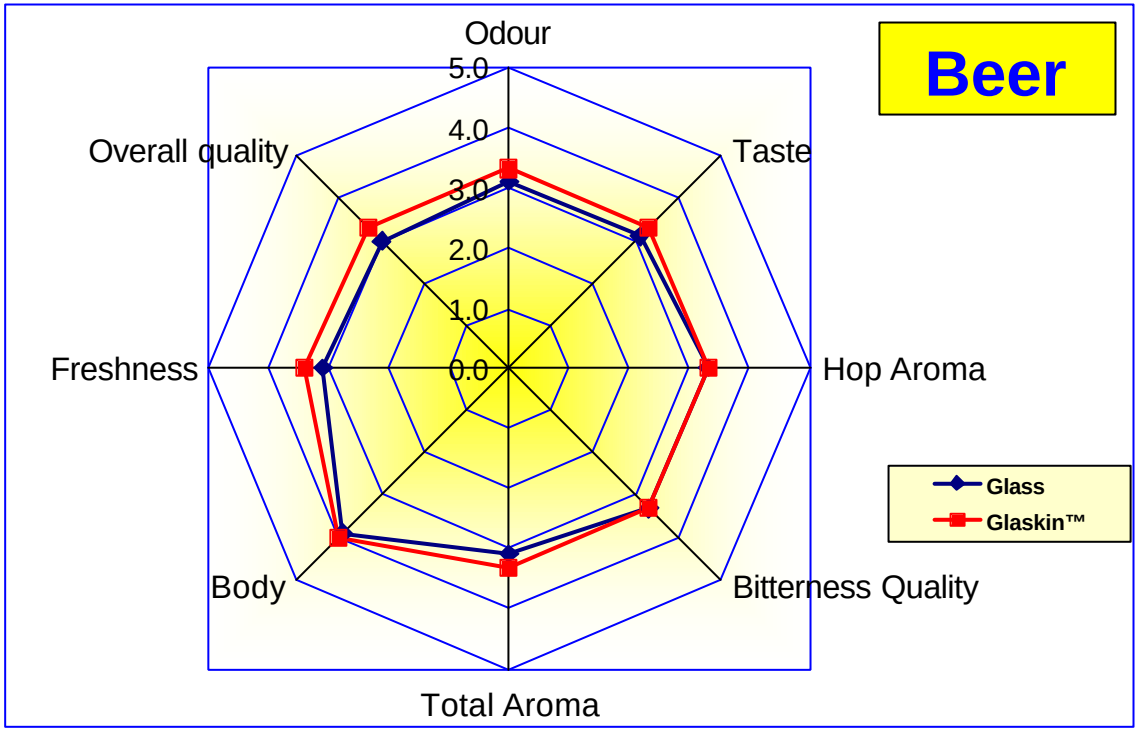
Launched in the first part of 2000

Picture: First beer in Glaskin™ bottles. Spendrup's "Norrlands Guld" launched March 2000 in Sweden. Second label Spendrup's "Original" launched July 2000.

Proven Product Quality :

Beer in Glaskin™ rated equivalent to beer in Glass after 9 months

- Panel of 8 tasters from TUM Weihenstephan
- Blind comparison of glass and Glaskin™ bottles
- 500 ml bottles, filled in a commercial line with a 12 plato flash pasteurised beer.
- Barrier Cap with O2 scavenger



Example: 500ml beer bottle

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Product Launches

Bitburger Beer, Germany:

- 500ml bottle, 38mm neck
- Convenience stores and garage forecourt distribution
- Launched in May 2000
- Shelf life = 9 months

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Product Launches

Zipfer (Brauunion), Austria

330ml bottle, 28mm neck

Events

Launched in August 2001

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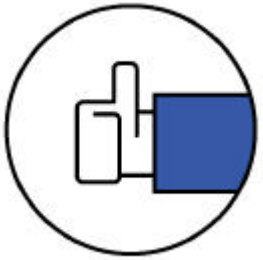
Status of Tetra Pak Recycling Activities



Glaskin™ coating has no effect on PET recycling

Bottle-to-Bottle recycling test with 100 % Glaskin™ was successful

Direct re-injection of 20 % Glaskin™ production regrind tested successfull

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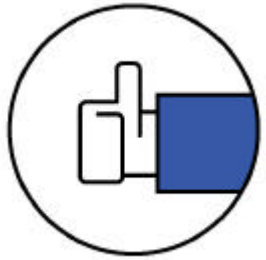
Results of B-to-B Recycling



100% R-PET content:

No effect on **any** processing **parameters attributable to residual Glaskin™ coating.**

The bottles looked and performed in a virtually identical way compared to bottles from virgin PET.

Bottles were **not visually different** from the control bottles in yellowness.

Conclusion: Glaskin™ coated recycled PET behaves like standard recycled PET

Source: PTI 2000

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5. Conclusion

- Plastic with favourable application properties has been widely-used as material for containers, especially in beverage industry.
- Expectations on the barrier performance can be met with very different techniques
- Vacuum deposited thin film barrier coatings proved to be especially effective and recycling-friendly.

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