Ethylene vinyl alcohol copolymer (EVOH) as a functional barrier against surrogate components migrating from recycled paperboard packaging

Presented by:
Caroline Maes
EVAL Europe nv - Kuraray
Hasselt University

Overview

- Mineral oil migration
- How can we prevent mineral oil migration?
- Experimental evaluation of mineral oil barriers
- Conclusions

Overview

- **Mineral oil migration**
  - **What are mineral oils?**
  - **Sources of mineral oil contamination**
  - **Regulation**
- **How can we prevent mineral oil migration?**
- **Experimental evaluation of mineral oil barriers**
- **Conclusions**

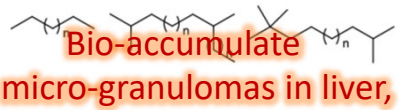
What are mineral oils?

"Mineral oils" or "Mineral oil products"

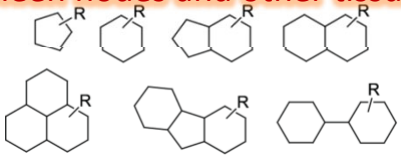
Crude oil fraction: $C_{10} - C_{50}$

MOSH

n-alkanes branched alkanes



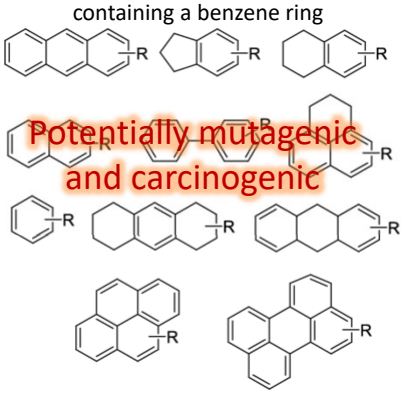
cycloalkanes



Bio-accumulate
+ micro-granulomas in liver, spleen nodes and other tissues

MOAH

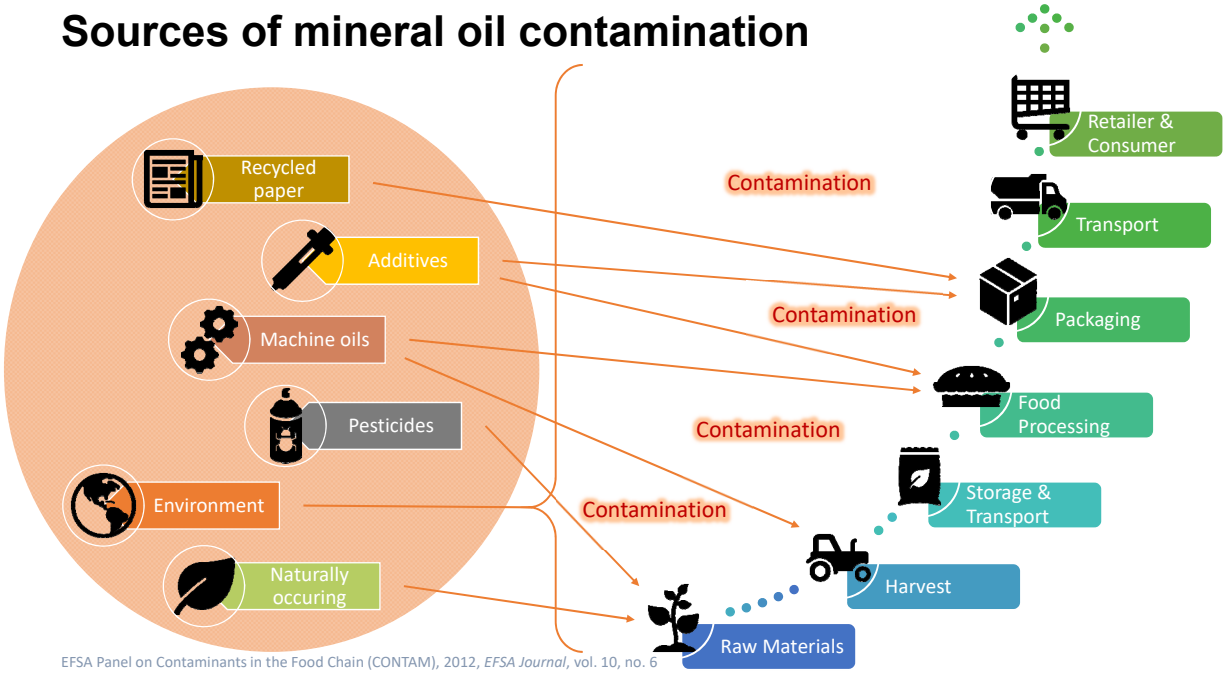
containing a benzene ring



Potentially mutagenic and carcinogenic

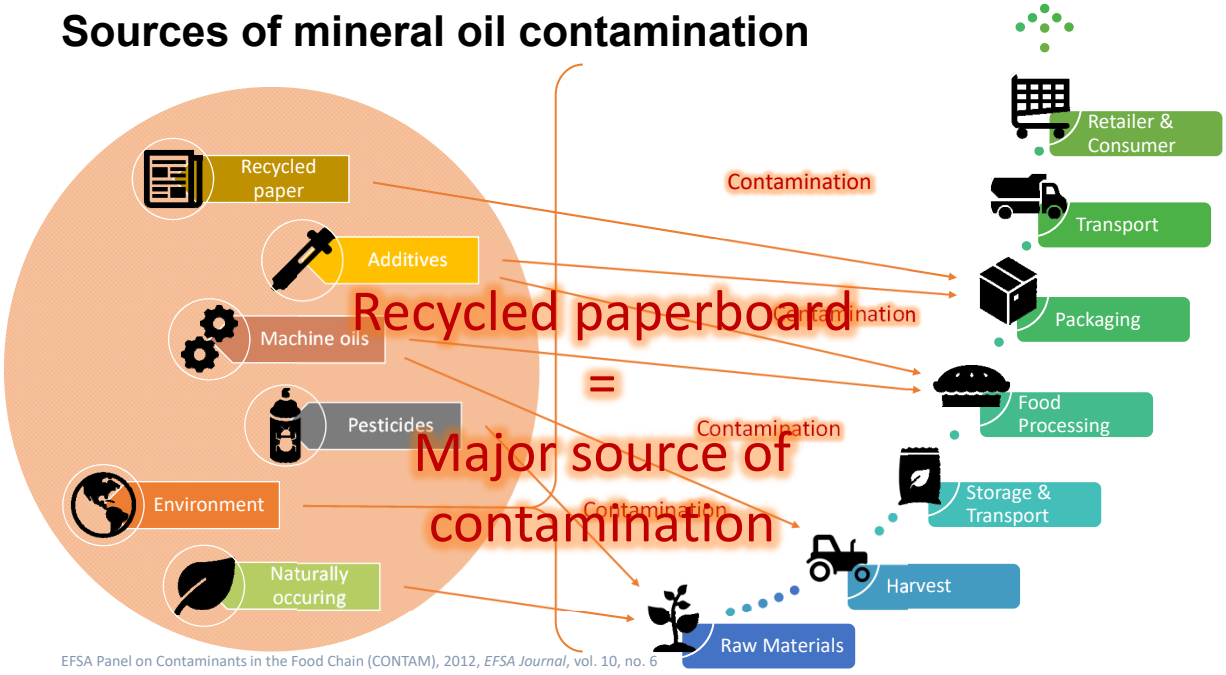
EFSA Panel on Contaminants in the Food Chain (CONTAM), 2012, *EFSA Journal*, vol. 10, no. 6
Weber et al., 2018, *Analytical Chemistry Insights*, vol. 13, pp. 1-16

Sources of mineral oil contamination



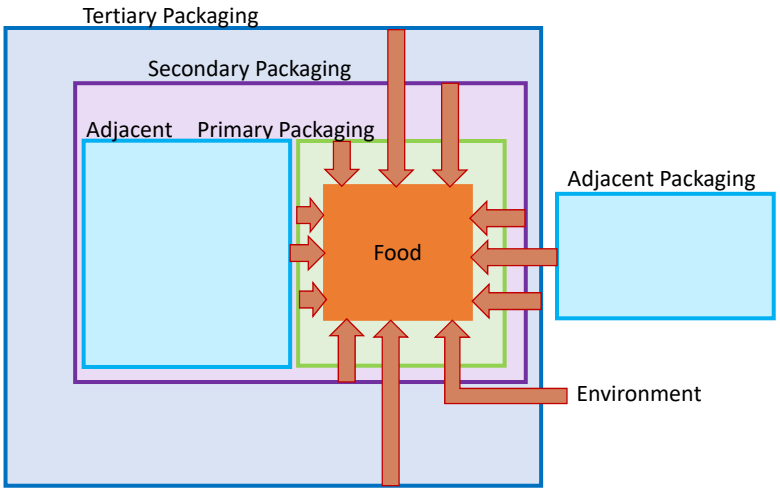
EFSA Panel on Contaminants in the Food Chain (CONTAM), 2012, *EFSA Journal*, vol. 10, no. 6

Sources of mineral oil contamination



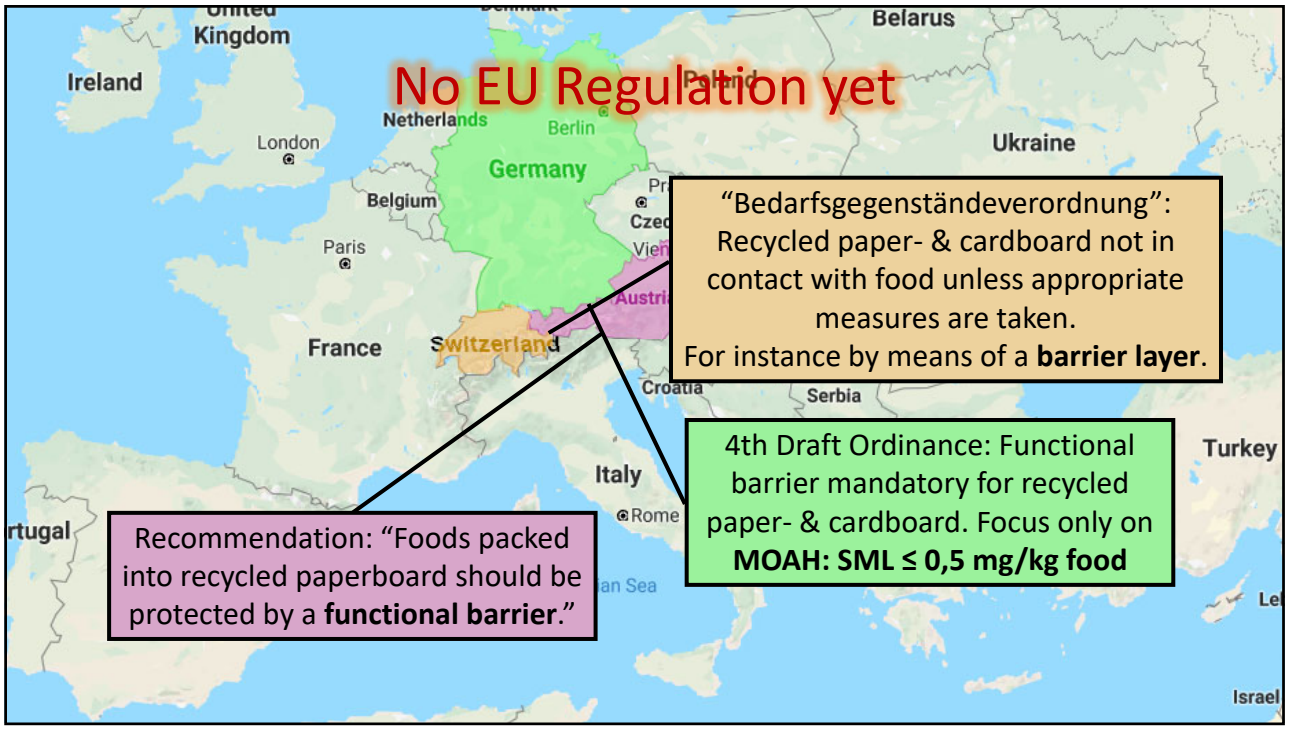
EFSA Panel on Contaminants in the Food Chain (CONTAM), 2012, *EFSA Journal*, vol. 10, no. 6

Sources of mineral oil contamination



- Highest migration potential: C_{16} - C_{24}
  - At ambient temperature migration substantial < C_{24} and noticeable < C_{28}
- 60-80% of < C_{24} fraction transferred into food
  - 10-20% of this fraction = MOAH
- Migration >>> ADI = 0.01 mg/kg body weight per day → 0.6 mg/kg food

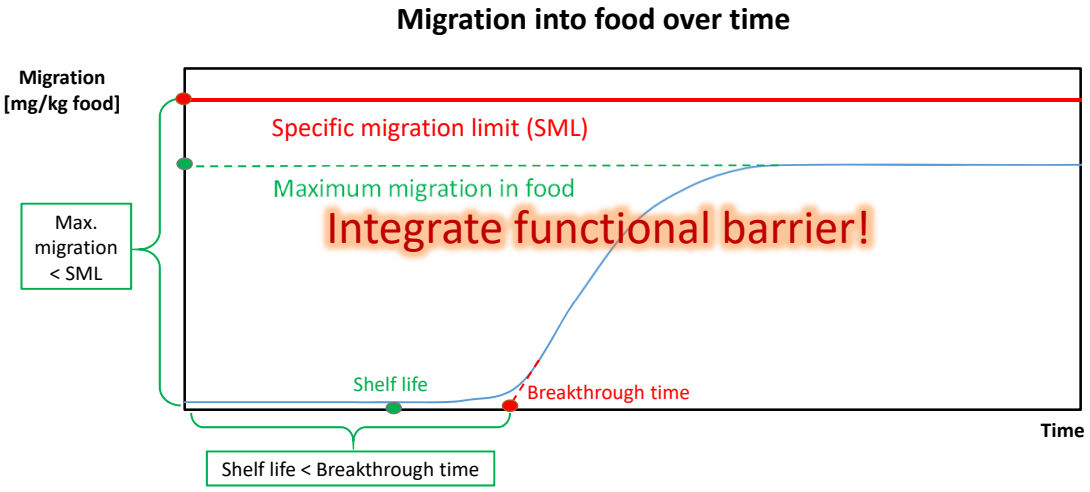
Lorenzini et al., 2010, Food Additives & Contaminants: Part A, vol. 27, no. 12, pp. 1765-1774
Vollmer et al., 2010, European Food Research & Technology, vol. 232, no. 1, pp. 175-182



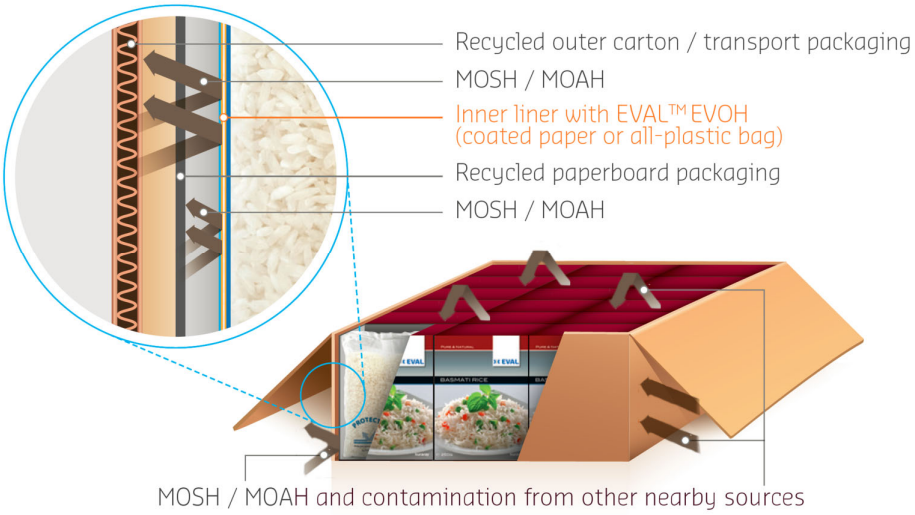
Overview

- Mineral oil migration
- How can we prevent mineral oil migration?
  - Functional barriers
  - EVOH as a solution
- Experimental evaluation of mineral oil barriers
- Conclusions

How can we prevent migration of mineral oils?



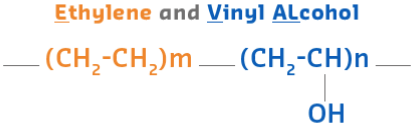
Integrate functional barrier into the primary packaging



EVAL™ EVOH is a functional barrier

Random copolymer, combining the strengths of

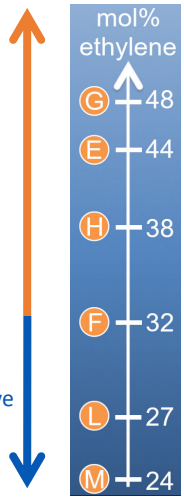
Ethylene and **Vinyl ALcohol**



- Already widely used for paper based and full plastic consumer packaging
  - Resistance to flex-crack and pinholes in folding, processing and transport
  - Oxygen barrier (extended shelf life)
  - Aroma barrier
  - Grease barrier

- More ethylene
- Thermoplastic
- Hydrophobic
- Flexible

- Less ethylene
- Higher barrier
- More RH sensitive

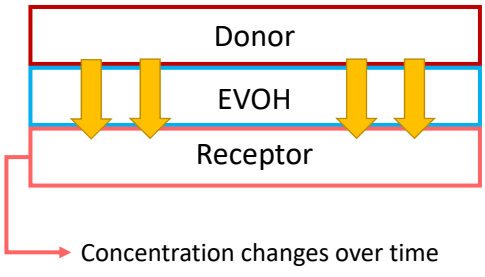


Overview

- Mineral oil migration
- How can we prevent mineral oil migration?
- **Experimental evaluation of mineral oil barriers**
  - **Dynamic Accumulation Method (Donor-Receptor)**
  - **Online Permeation Method (GC)**
- Conclusions

Methods

Dynamic Accumulation Method
Developed by Kantonales Labor Zürich
Switzerland

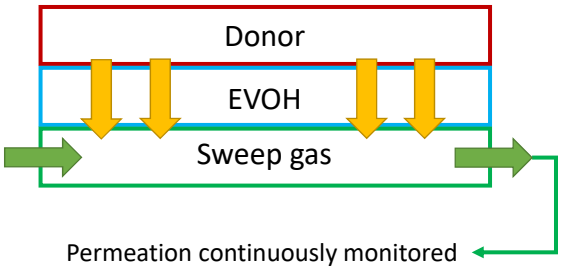


Concentration changes over time

In cooperation with
Hasselt University & SQTS

Fiselier and Grob, 2012, Packag. Technol. Sci., vol. 25, no. 5, pp. 285-301.

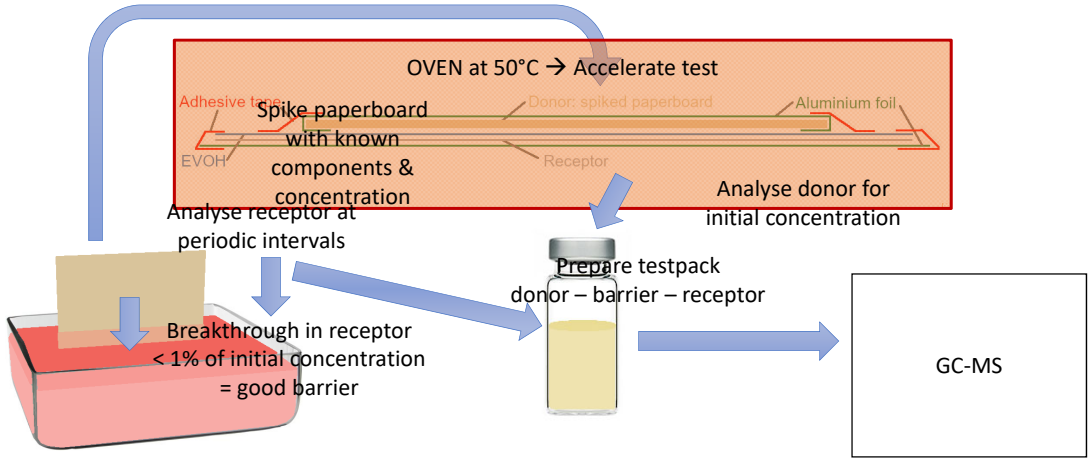
Online Permeation Method
Developed by Fraunhofer IVV
Germany



Permeation continuously monitored

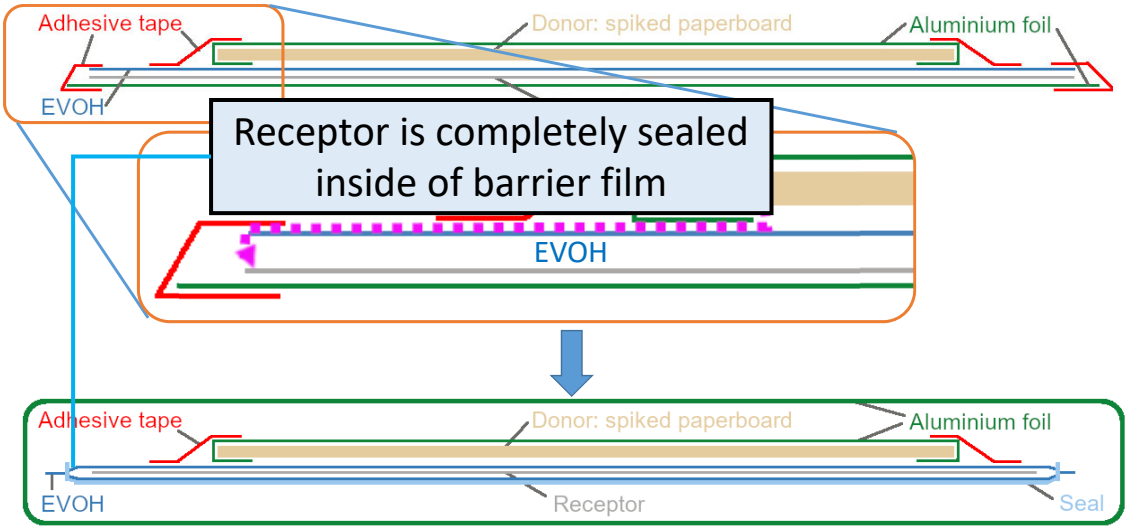
Ewender, Franz and Welle, 2013, Packag. Technol. and Sci., vol. 26, no. 7, pp. 423-434.

Principle of Dynamic Accumulation Method

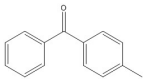
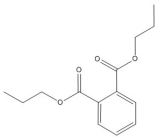
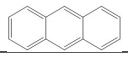


Fiselier and Grob, 2012, Packag. Technol. Sci., vol. 25, no. 5, pp. 285-301.
Biedermann-Brem, Biedermann and Grob, 2017, Packag. Technol. Sci., vol. 30, no. 3, pp. 91-102.
"Schweizerisches Verpackungsinstitut SVI Guideline 01.2015_Internal bags"

Test Packs



Surrogate components

Name	Abbrev.	Structure	Simulant for
4-methyl benzophenone (1)	**MBP**		Photo-initiator
di-*n*-propyl phthalate (1)	**DPP**		Plasticiser
n-heptadecane (1)	**C17**		MOSH
perylene (2)	**PER**		MOAH
anthracene (2)	**ANT**		MOAH

(1) Biedermann-Brem, Biedermann and Grob, 2017, Packag. Technol. Sci., vol. 30, no. 3, pp. 91-102. and "Schweizerisches Verpackungsinstitut SVI Guideline 01.2015_Internal bags"
(2) Additional components added for this study

Samples

Barrier	Mol-% ethylene	Average layer distribution LDPE/tie/**Barrier**/tie/LDPE [µm]
EVAL™ L171B	27	22/5/**3**/5/21
EVAL™ F171B	32	21/5/**3**/5/20
EVAL™ F171B	32	21/4/**5**/5/20
PA6/6.6	/	20/5/**3**/4/18
PET	/	**12**

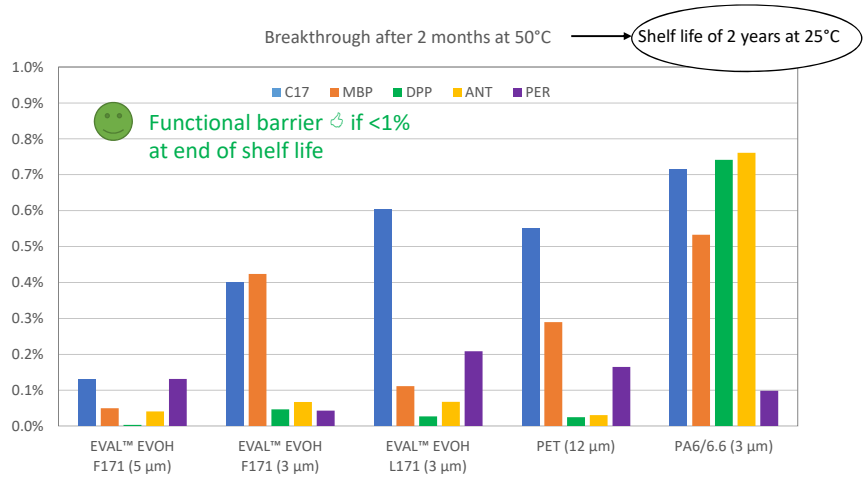
Films extruded on Dr. Collin 5-layer blown film pilot line
Layer distribution determined by microscopic analysis
O_2GTR determined on MOCON OXTRAN® 2/21 (ASTM F1927)

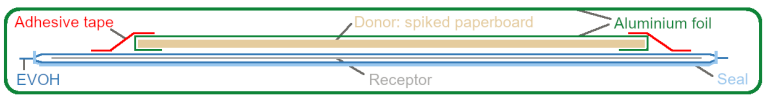
Samples

Barrier	Mol-% ethylene	Average layer distribution LDPE/tie/Barrier/tie/LDPE [µm]	O_2GTR @ 20°C, 65% RH [cm³/(m².day.atm)]
EVAL™ L171B	27	22/5/**3**/5/21	**0.7**
EVAL™ F171B	32	21/5/**3**/5/20	**1.7**
EVAL™ F171B	32	21/4/**5**/5/20	**0.7**
PA6/6.6	/	20/5/**3**/4/18	**479**
OPET	/	**12**	**91**

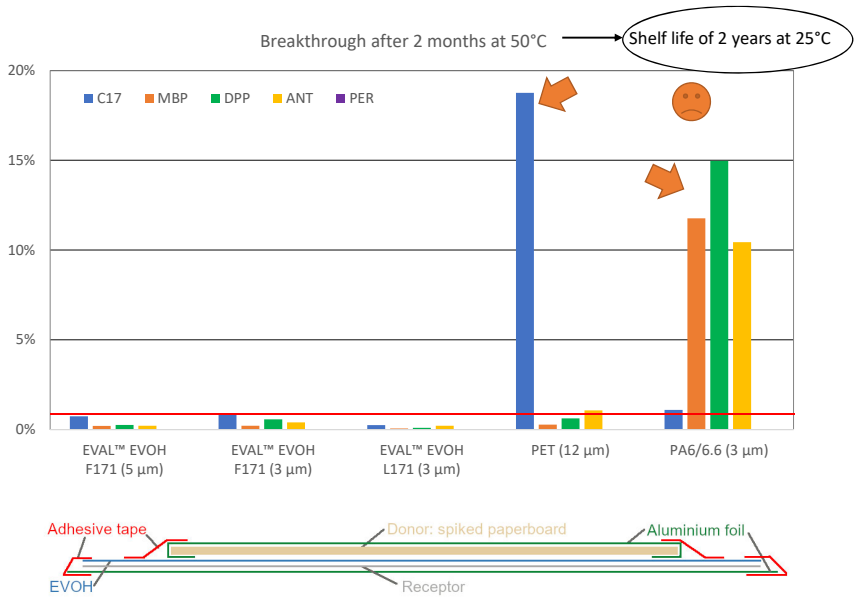
Films extruded on Dr. Collin 5-layer blown film pilot line
Layer distribution determined by microscopic analysis
O_2GTR determined on MOCON OXTRAN® 2/21 (ASTM F1927)

Breakthrough at 50°C – Hasselt University

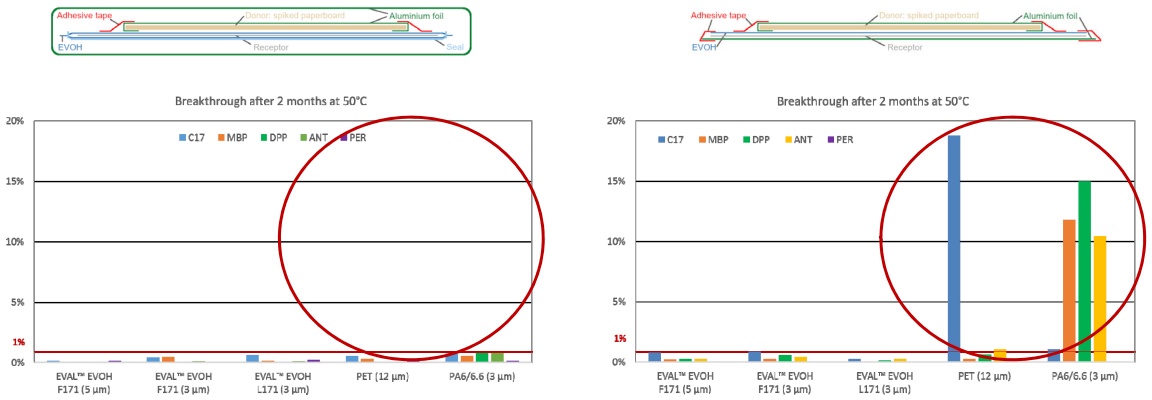




Breakthrough at 50°C – SQTS independent lab



Conclusion of Dynamic Accumulation Method



Discrepancy between tests

Nevertheless, it can be concluded that EVOH is a good barrier in both tests

Methods

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Developed by Kantonales Labor Zürich
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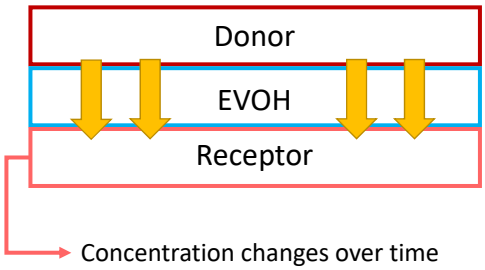
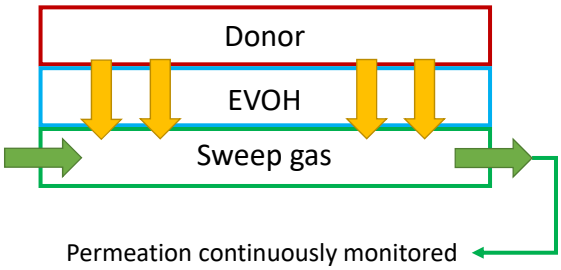


Online Permeation Method
Developed by Fraunhofer IVV
Germany



In cooperation with Fraunhofer IVV

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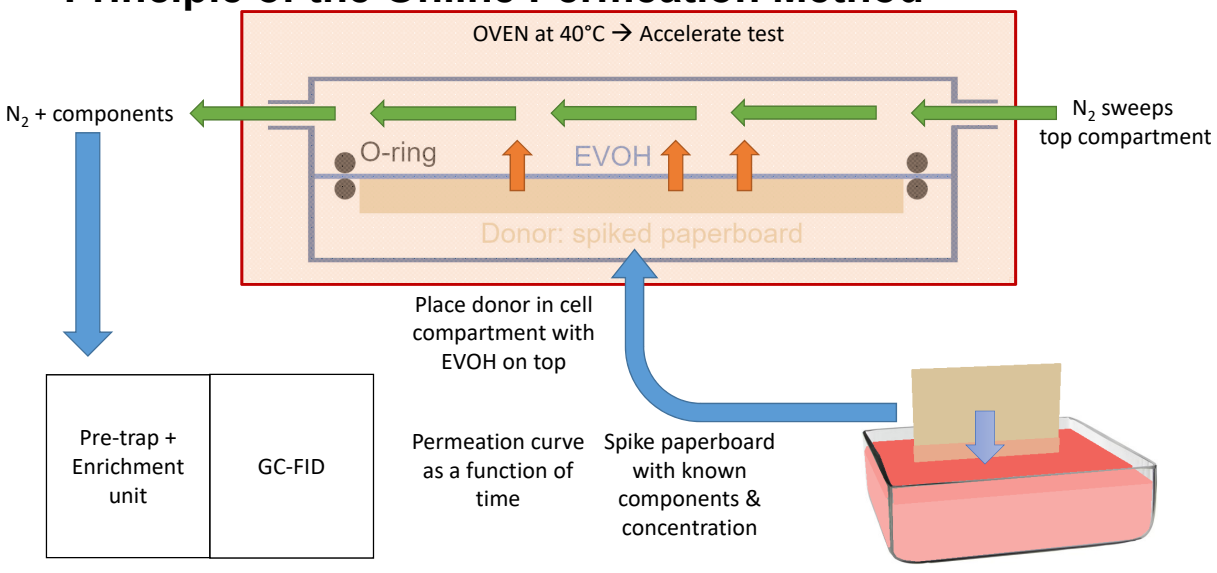
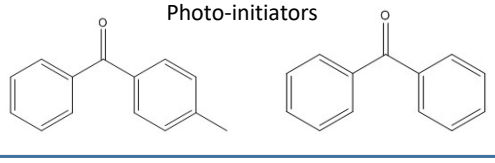
Principle of the Online Permeation Method



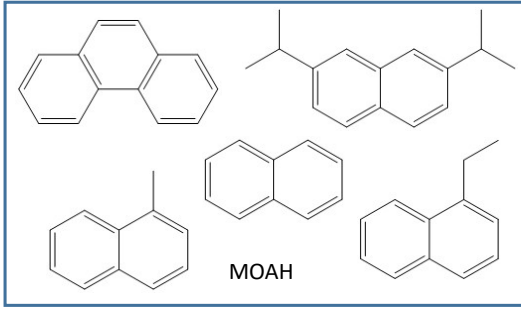
Ewender, Franz and Welle, 2013, Packag. Technol. and Sci., vol. 26, no. 7, pp. 423-434.

Surrogate components and Samples

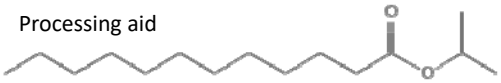
Photo-initiators



MOAH



Processing aid



MOSH

EVOH32 (5µm) **EVOH27 (3µm)** **OPET (12µm)**

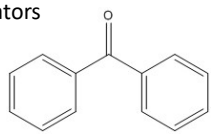
EVOH32 (3µm) **PA6/6.6 (3µm)**

DL < 0.002 µg/dm²·day
DL < 0.003 µg/dm²·day (processing aid)

Permeation of components – EVOH32 (5 µm)

Photo-initiators

≤ 0.004



All below DL

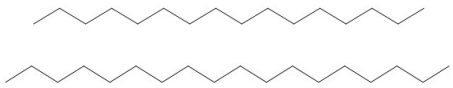
MOAH

Processing aid

Below DL

MOSH

0.006-0.007



0.005-0.006

EVOH32 (5µm) **EVOH27 (3µm)** **OPET (12µm)**

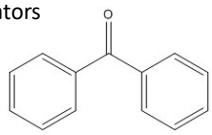
EVOH32 (3µm) **PA6/6.6 (3µm)**

DL < 0.002 µg/dm²·day
DL < 0.003 µg/dm²·day (processing aid)

Permeation of components – EVOH32 (3 µm)

Photo-initiators

0.002-0.004



All below DL

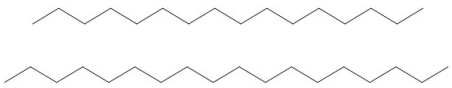
MOAH

Processing aid

Below DL

MOSH

0.006



0.005-0.006

EVOH32 (5µm) **EVOH27 (3µm)** **OPET (12µm)**

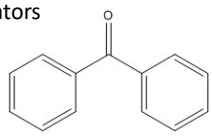
EVOH32 (3µm) **PA6/6.6 (3µm)**

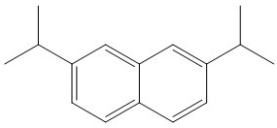
DL < 0.002 µg/dm²·day
DL < 0.003 µg/dm²·day (processing aid)

Permeation of components – EVOH27 (3 µm)

Photo-initiators

≤ 0.003





≤ 0.003

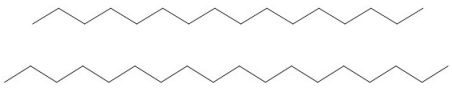
MOAH

Processing aid

Below DL

MOSH

0.007-0.008



0.006

EVOH32 (5µm) **EVOH27 (3µm)** **OPET (12µm)**

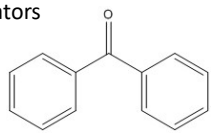
EVOH32 (3µm) **PA6/6.6 (3µm)**

DL < 0.002 µg/dm²·day
DL < 0.003 µg/dm²·day (processing aid)

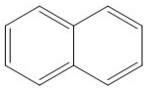
Permeation of components – PA6/6.6 (3 µm)

Photo-initiators

0.002-0.004



0.055-0.098



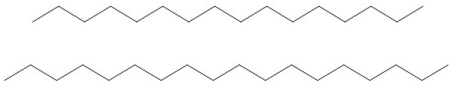
MOAH

Processing aid

Below DL

MOSH

0.005-0.007



0.004

EVOH32 (5µm) **EVOH27 (3µm)** **OPET (12µm)**

EVOH32 (3µm) **PA6/6.6 (3µm)**

DL < 0.002 µg/dm²·day

DL < 0.003 µg/dm²·day (processing aid)

Permeation of components – OPET (12 µm)

Photo-initiators

All below DL

All below DL

MOAH

Processing aid

Below DL

MOSH

All below DL

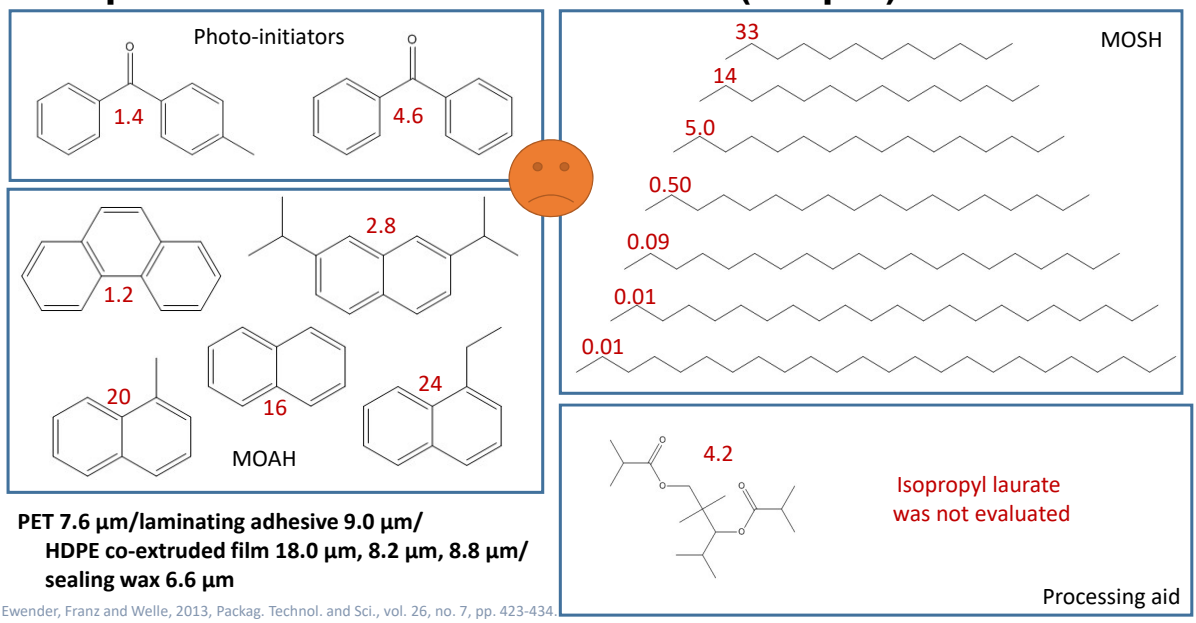
EVOH32 (5µm) **EVOH27 (3µm)** **OPET (12µm)**

EVOH32 (3µm) **PA6/6.6 (3µm)**

DL < 0.002 µg/dm²·day

DL < 0.003 µg/dm²·day (processing aid)

Comparative data of laminated PET (7.6 µm) - Fraunhofer



PET 7.6 µm/laminating adhesive 9.0 µm/
HDPE co-extruded film 18.0 µm, 8.2 µm, 8.8 µm/
sealing wax 6.6 µm

Ewender, Franz and Welle, 2013, Packag. Technol. and Sci., vol. 26, no. 7, pp. 423-434.

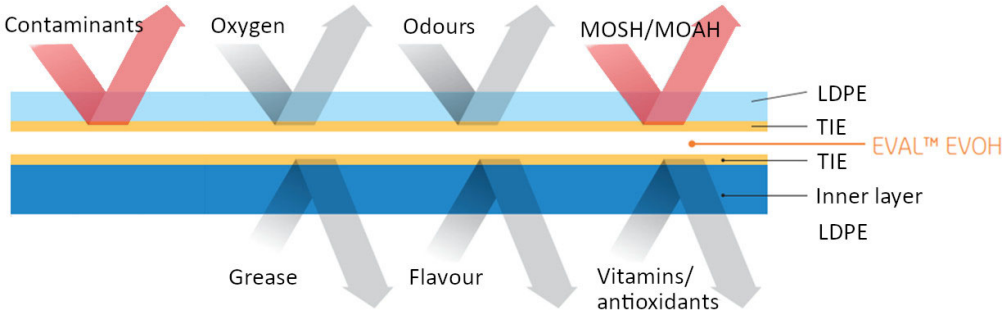
Overview

- Mineral oil migration
  - What are mineral oils?
  - Sources of mineral oil contamination
  - Regulation
- How can we prevent mineral oil migration?
  - Functional barriers
  - EVOH as a solution
- Experimental evaluation of mineral oil barriers
- **Conclusions**

Conclusions

EVOH = Multifunctional solution

for protecting food products which need additional barrier functions
(e.g. oxygen sensitive, fatty or aromatic foods)



And this study also proves

EVOH = an excellent barrier against mineral oils
and other contaminants

Thank you for your attention!

Presented by:
Caroline Maes
caroline.maes@kuraray.com

For more info contact:
Dr. Naomi Winckelmans
naomi.winckelmans@kuraray.com

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