



# EVAL™ EVOH as a functional Barrier against Mineral Oil Migration from Cardboard Packaging

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Seminar on Migration – 11/09/2018, Ghent



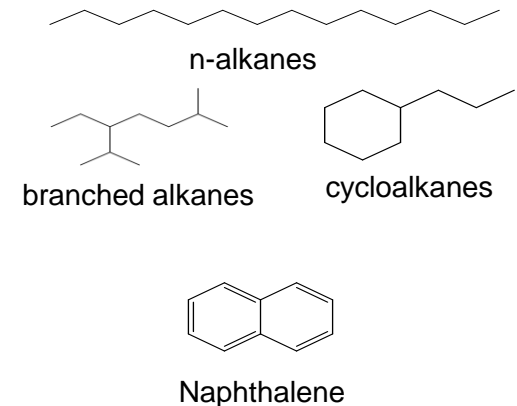
kuraray

# Outline

- Mineral oil migration
  - What is the issue?
  - Toxicological concerns
  - Regulation
- How can we prevent mineral oil migration?
  - Functional barriers
  - EVAL™ as a solution
- Experimental evaluation of mineral oil barrier
- Conclusion

# What are mineral oils?

- “Mineral oils” or “Mineral oil products”
  - Mineral oil hydrocarbons (MOH)
  - Carbon number:  $C_{10} - C_{50}$
  - Crude oil fraction
- Mineral oil contamination in food
  - Mineral oil **saturated** hydrocarbons (MOSH)
    - Single bonded carbon chains or rings
    - e.g.: n-alkanes, branched alkanes, cycloalkanes
  - Mineral oil **aromatic** hydrocarbons (MOAH)
    - Containing at least 1 benzene ring
    - e.g.: naphthalene



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

# What is the problem?

- Major source mineral oil contamination in food
  - Migration from recycled paperboard
  - Even secondary/tertiary packaging!!!
- Fraction responsible for contamination in food
  - 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  $\ggg$  ADI = 0.01 mg/kg body weight per day  $\rightarrow$  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

# Toxicological concerns



Germany

*BfR Opinion No. 008/2010  
(December 2009)*

“Animal studies have shown that mineral oil mixtures are stored in the body and can lead to damage in the liver and lymph nodes.”

“BfR finds that the **migration of mineral oil** from recycled paper and cardboard to foodstuffs should be **minimized immediately.**”



*EFSA Scientific Opinion  
(June 2012)*

“**MOSH** from C<sub>16</sub> to C<sub>35</sub> may accumulate and cause micro-granulomas in several tissues including lymph nodes, spleen and liver.” “Foodborne **MOAH** may be mutagenic and carcinogenic, and therefore of **potential concern. Revision of the existing acceptable daily intake** for some food grade **MOSH** is warranted on the basis of new toxicological information.”

BfR logo: <https://www.bfr.bund.de/en/home.html>

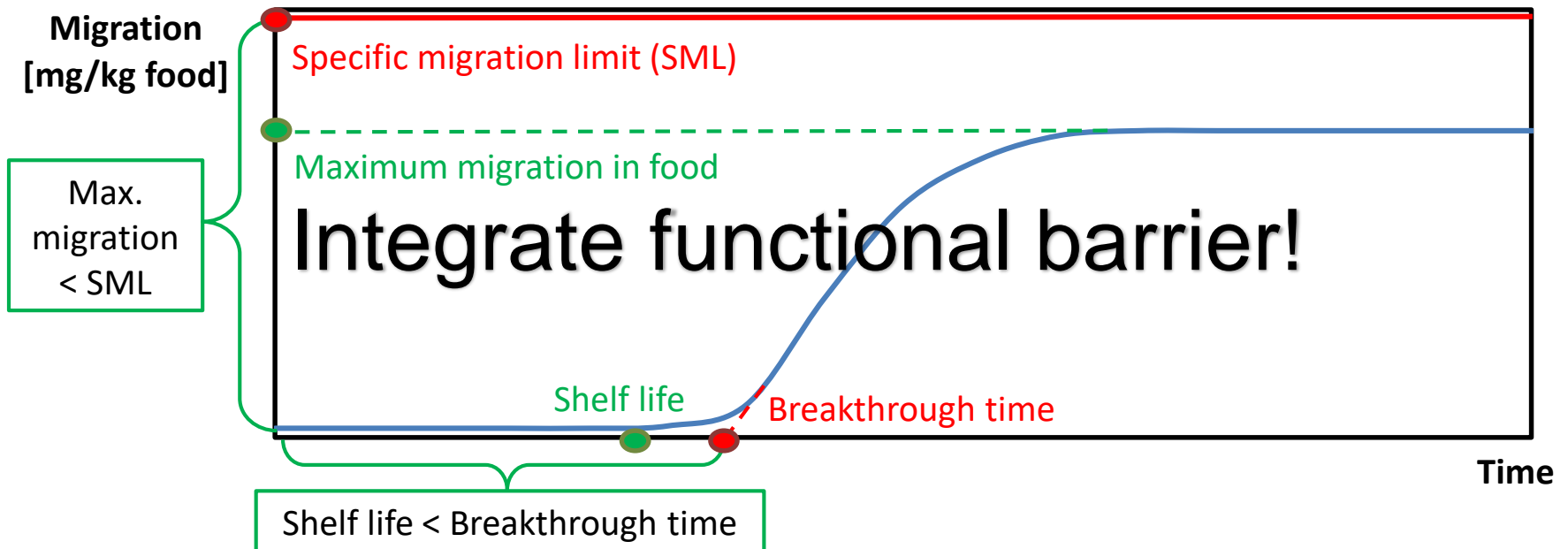
EFSA logo: <http://www.efsa.europa.eu/>

# Regulation – Not yet harmonized

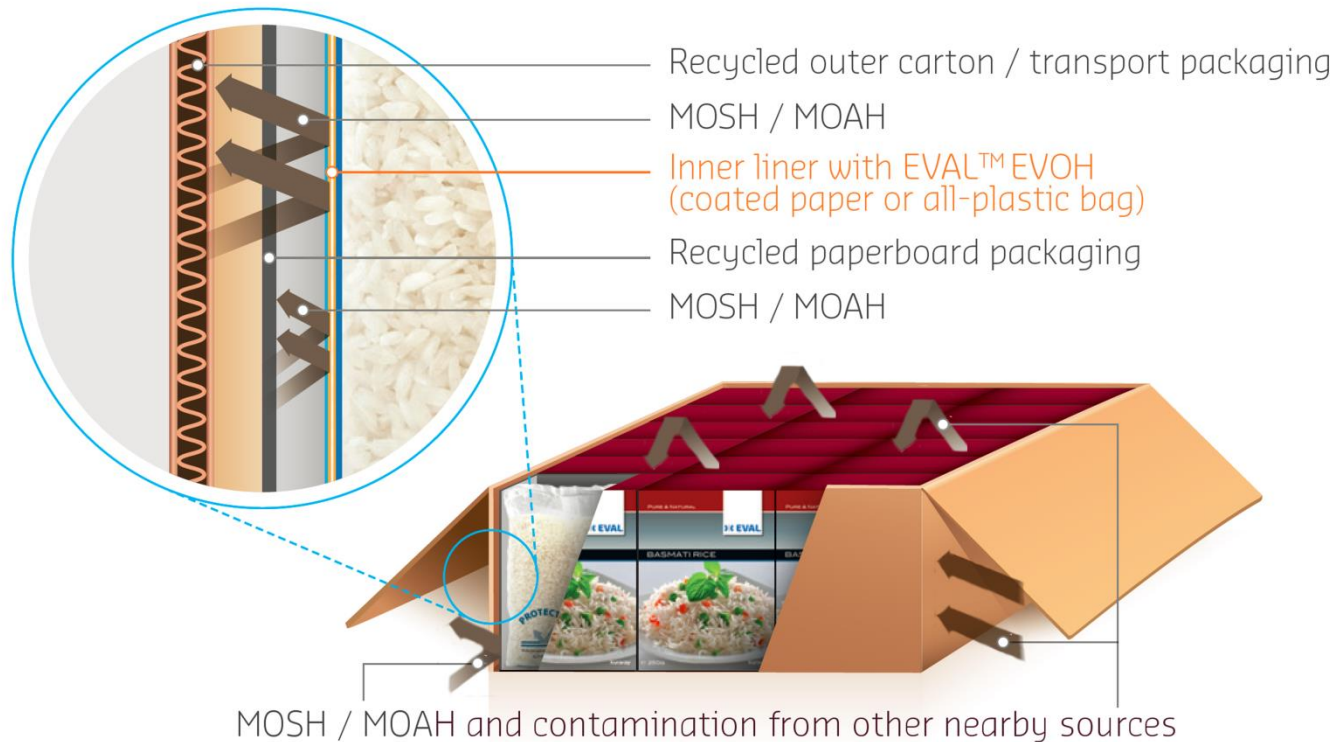
- Waiting for results *Commission Recommendation (EU) 2017/84*
  - Monitor presence of MOH in food during 2017-2018 & investigate possible source(s)
  - Results expected by 28 February 2019
- Some countries already have own regulation/recommendation
  - Austria → Recommendation: “Foods packed into recycled paperboard should be protected by a **functional barrier**.”
  - Switzerland → “*Bedarfsgegenständeverordnung*”: Recycled paper- & cardboard not in contact with food unless appropriate measures are taken.  
For instance by means of a **barrier layer**.
  - Germany → 4<sup>th</sup> Draft Ordinance: Functional barrier mandatory for recycled paper- & cardboard. Focus only on **MOAH: SML ≤ 0,5 mg/kg food**

# How can we prevent migration of mineral oils?

Migration into food over time



# Integrate functional barrier into the primary packaging

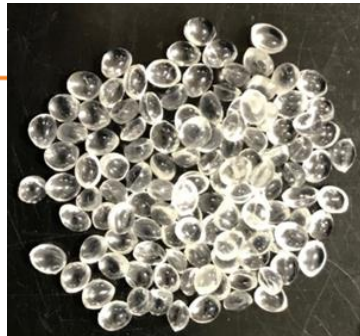
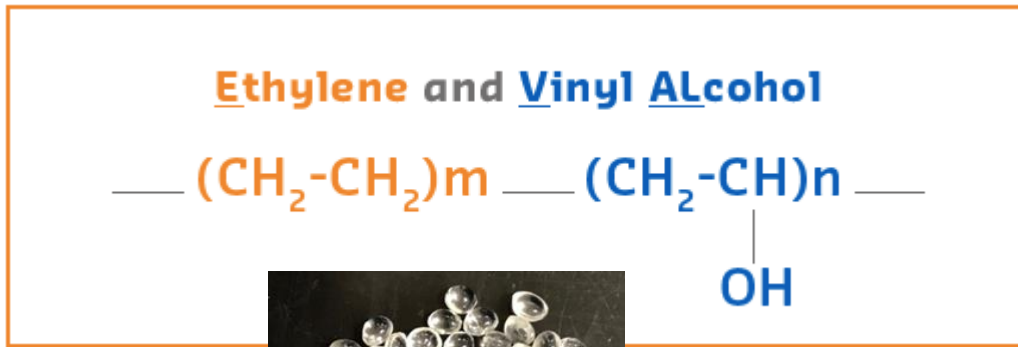




# EVAL™ EVOH is a functional barrier

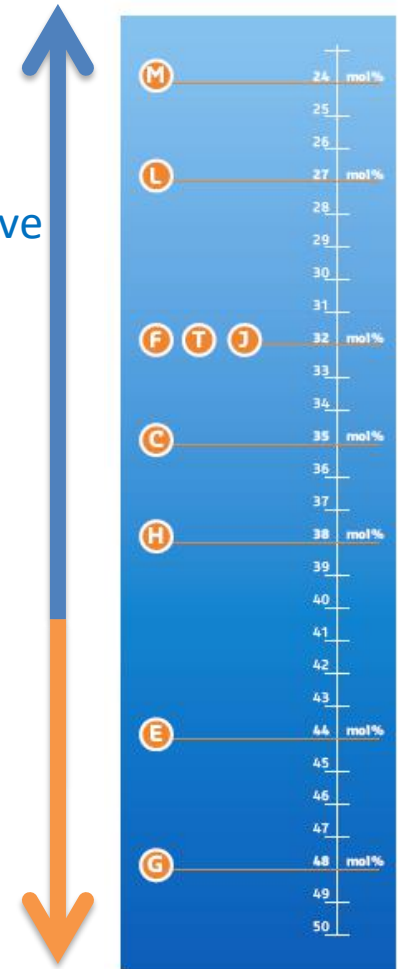
Random copolymer, combining the strengths of **E**thylene and **V**inyl **A**lcohol

- less ethylene
- higher barrier
- more RH sensitive



- more ethylene
- thermoplastic
- hydrophobic
- flexible

EVAL™ is very resistant to micro-crack and pinhole formation during folding, processing and transport.



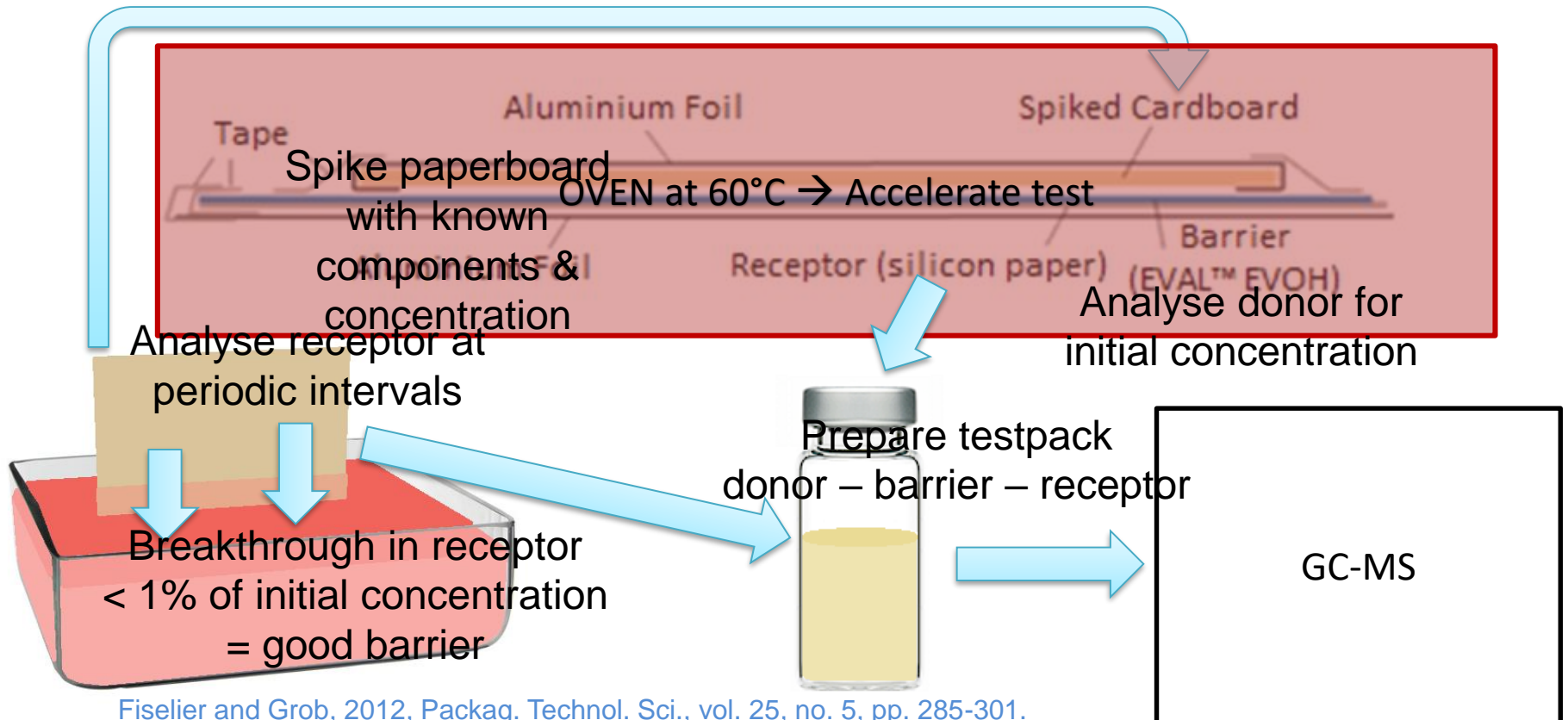
# EVAL™ EVOH is a functional barrier

- Already widely used for paper based and full plastic consumer packaging
  - oxygen barrier (extended shelf life)
  - aroma barrier
  - grease barrier
  - resistance to flex-crack and pinholes in folding, processing and transport



# Evaluation of mineral oil barriers

## Method



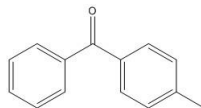
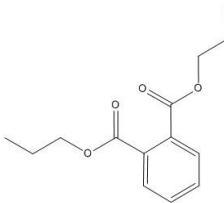

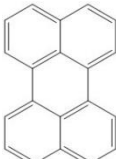
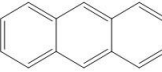
Fiselier and Grob, 2012, Packag. Technol. Sci., vol. 25, no. 5, pp. 285-301.

Biedermann-Brem, Biedermann and Grob, 2017, Packag. Technol. Sci., vol. 30, no. 3, pp. 91-102.

“Schweizerisches Verpackungsinstitut SVI Guideline 01.2015\_Internal bags”

# Evaluation of mineral oil barriers

## Surrogate components

Name	Abbrev.	Structure	Simulant for
4-methyl benzophenone (1)	MBP		Photo-initiator
di- <i>n</i> -propyl phthalate (1)	DPP		Plasticiser
<i>n</i> -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

# Evaluation of mineral oil barriers

## Samples

Barrier	mol% ethylene	Average layer distribution LDPE/tie/ <b>Barrier</b> /tie/LDPE [μm]	O <sub>2</sub> GTR @ 20°C, 65% RH [cm <sup>3</sup> /(m <sup>2</sup> .day.atm)]
EVAL™ L171B	27	22/5/ <b>3</b> /5/21	<b>0.7</b>
EVAL™ F171B	32	21/5/ <b>3</b> /5/20	<b>1.7</b>
EVAL™ F171B	32	21/4/ <b>5</b> /5/20	<b>0.7</b>
PA6/6.6	/	20/5/ <b>3</b> /4/18	<b>479</b>
PET	/	<b>12</b>	<b>91</b>

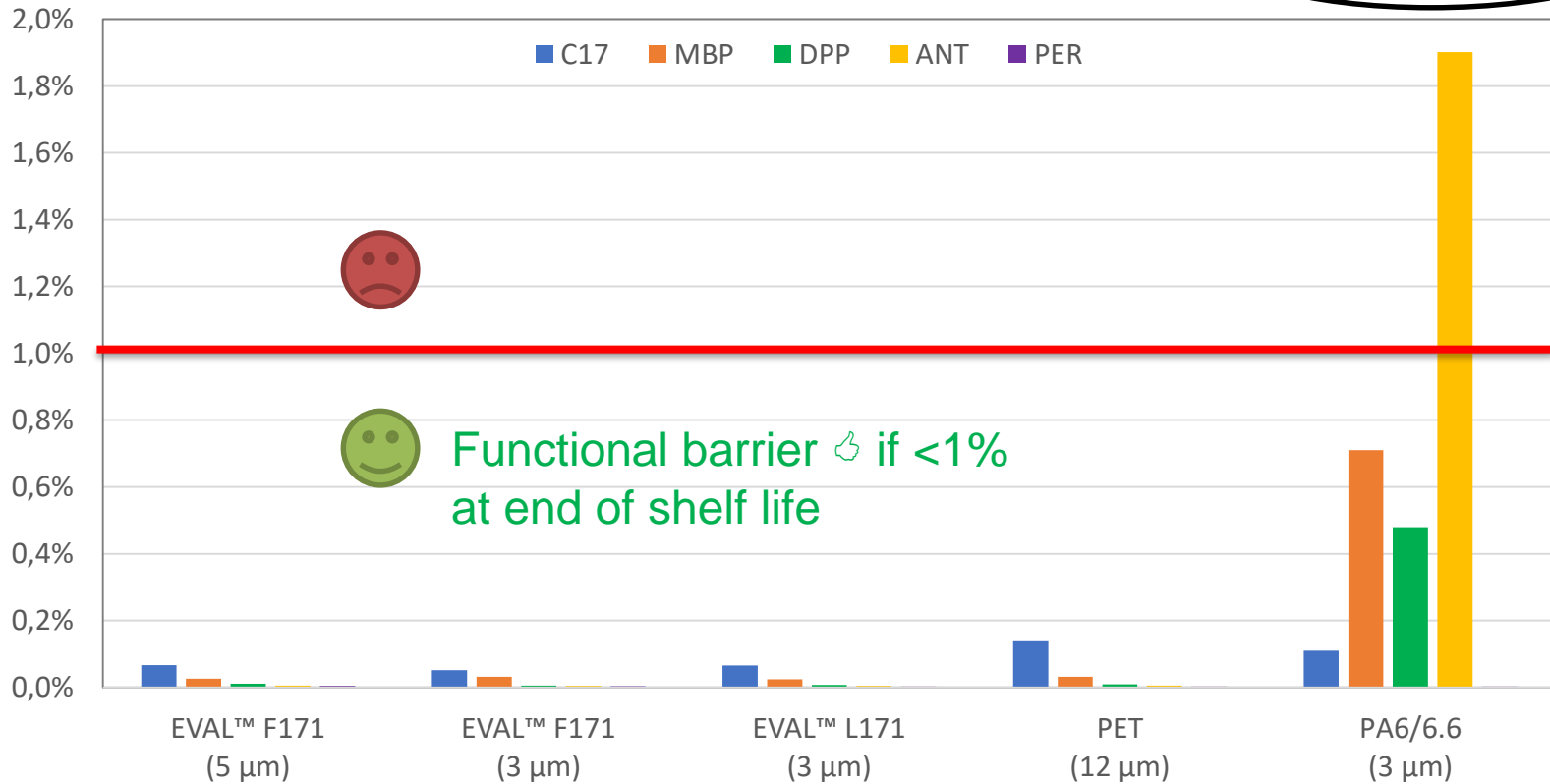
- Films extruded on Dr. Collin 5-layer blown film pilot line
- Layer distribution determined by microscopic analysis
- O<sub>2</sub>GTR determined on MOCON OXTRAN® 2/21 (ASTM F1927)

# Evaluation of mineral oil barriers

## Results

Breakthrough after 25 days at 60°C

Shelf life of 2 years at 25°C



# Evaluation of mineral oil barriers

## Neutral dataset confirms results

- Independent lab SQTS - Swiss quality testing services
  - Performed experiments on EVAL™ F171B (5µm)
    - 50°C for 60 days and 60°C for 25 days  
= 2 years at 25°C
    - Same components as experiment at UHasselt
    - Breakthrough values < 1%

➔ EVAL™ F171B (5 µm) = a good mineral oil barrier

- Previous results published in “Schweizerisches Verpackungsinstitut SVI Guideline 01.2015\_ Internal bags”
  - HDPE (50 µm) ➔ breakthrough > 1% after less than a week!
  - BOPP (35 µm) metalized by vapour ➔ breakthrough > 1% after a week!

# Evaluation of mineral oil barriers

## Migration modelling of functional barriers

„Migration modeling is recognized by the European Union as a compliance tool for specific migration with Regulation (EU) No. 10/2011 (formerly Directive 2001/62/EC, repealed by Directive 2002/72/EC, repealed by Regulation EU 10/2011)“

*EU Commission Modeling Taskforce*

- Kuraray has established **polymer constants specifically for EVAL™ EVOH**

Polymer specific constant  $A_p'$  (realistic) &  $A_p'^*$  (worst case)

Partitioning coefficient  $K_{PE/EVOH}$

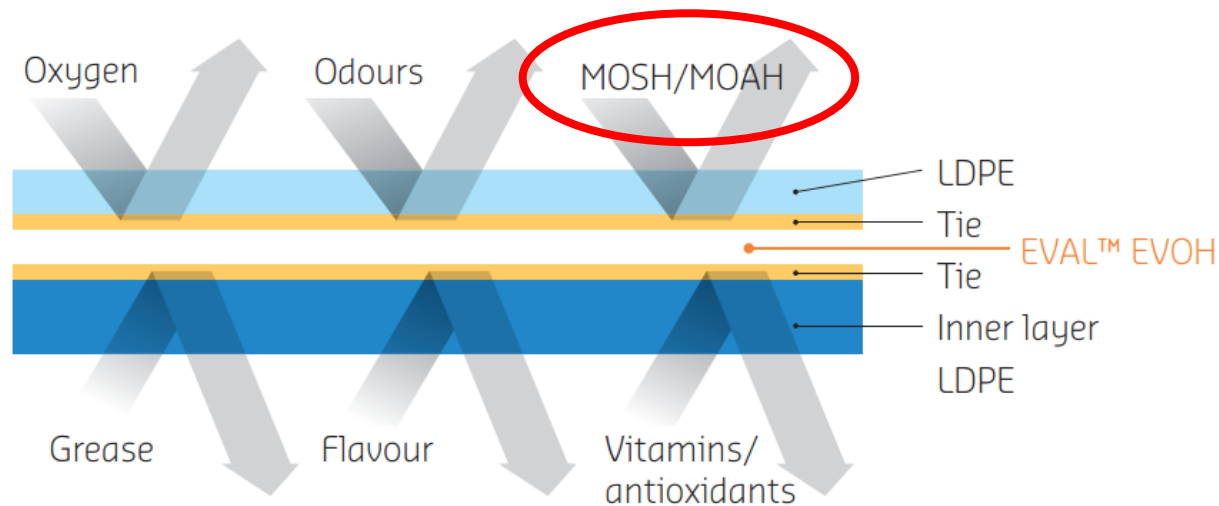
- These polymer constants can be used with migration simulation software to **simulate the amount of migration** for a certain packaging material structure. The outcome can be compared to current regulations in order to determine compliance.



# Conclusions

## EVAL™ = Multifunctional solution

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



And this study also proves

**EVAL™ = a good mineral oil barrier**

# And ...

- EVAL™ is a versatile and robust solution
  - Avoids contamination from secondary packaging or the environment
  - Not susceptible to damage during manufacture and handling
  - Minimized thickness
  - Immediately implementable; already commercially used for paper based and full plastic packaging



**Full plastic**



**Coated paperboard**



**PLASTIC inner liner**



**Coated PAPER inner liner**





**Thank you for your attention!**

**Questions?**



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More information: [www.evalevoh.com](http://www.evalevoh.com)

