Combined Oxygen Scavenger and Oxygen Indicator – A Method for Monitoring the Integrity of Packages and the Functioning of Oxygen Absorbers

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Cold Chain Management 3rd International Workshop
June 2-3, 2008, Bonn, Germany

IVV

Fraunhofer Institut
Verfahrenstechnik
und Verpackung

Outline

1. **Motivation for the Employment of Combined Oxygen Scavenger and Oxygen Indicator**

2. **Developed Oxygen Scavengers**

3. **Developed Oxygen Indicators**

4. **Combination of Oxygen Scavenger and Oxygen Indicator**

5. **Testing of Filled Packages**

6. **Summary**

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1. Motivation for Use of Active and Intelligent Packaging

Trend towards:

- low-processed foodstuffs
- modified composition: highly sensitive components, e.g. natural food dyes
- consumers are increasingly critical towards food additives, e.g. antioxidants
- increasing use of transparent plastic packaging

Objective:

- food safety, information
- preserving nutrient-providing food components (vitamin, antioxidants)
- extension of shelf-life

1. Expedient Combinations of Active / Intelligent Packaging

Expedient Combinations:

- O_2-scavenger / O_2-indicator
- H_2O-scavenger / H_2O-indicator
- ethylene scavenger / ethylene indicator
- antimicrobial package / spoilage indicator

Combined Systems should:

- absorb oxygen
- monitor functionality of active system and
- monitor the integrity of the package

→ incorporation in packaging material

food	max. tolerable O_2-uptake (mg O_2 / kg)
beer	1 – 4
wine	3
milk	8
steril. vegetable	15
ketchup	15
fruit juice	20
roasted coffee	110
emmentaler cheese	500

Source: Heiss

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2. Oxygen Scavengers on the Market

Scavenger	Substrate	Catalysis / Activation
sachets	iron based	hygroscopic salts / moisture
		self working
	glucose	glucose oxidase / moisture
inlay	palladium (on fleece)	palladium / MAP with H_2
incorporated in polymers	iron based	different additives / moisture
	polyolefin based	photoinitiator+cobalt salts / UV-irradiation
	sulphite based	- / moisture
	Nylon-6	- / thermal irradiation
	PET-copolyester	cobalt / thermal irradiation




2. New developed Oxygen Scavengers

New developments in the area of oxygen scavengers

Fraunhofer worked on scavengers on the basis of:

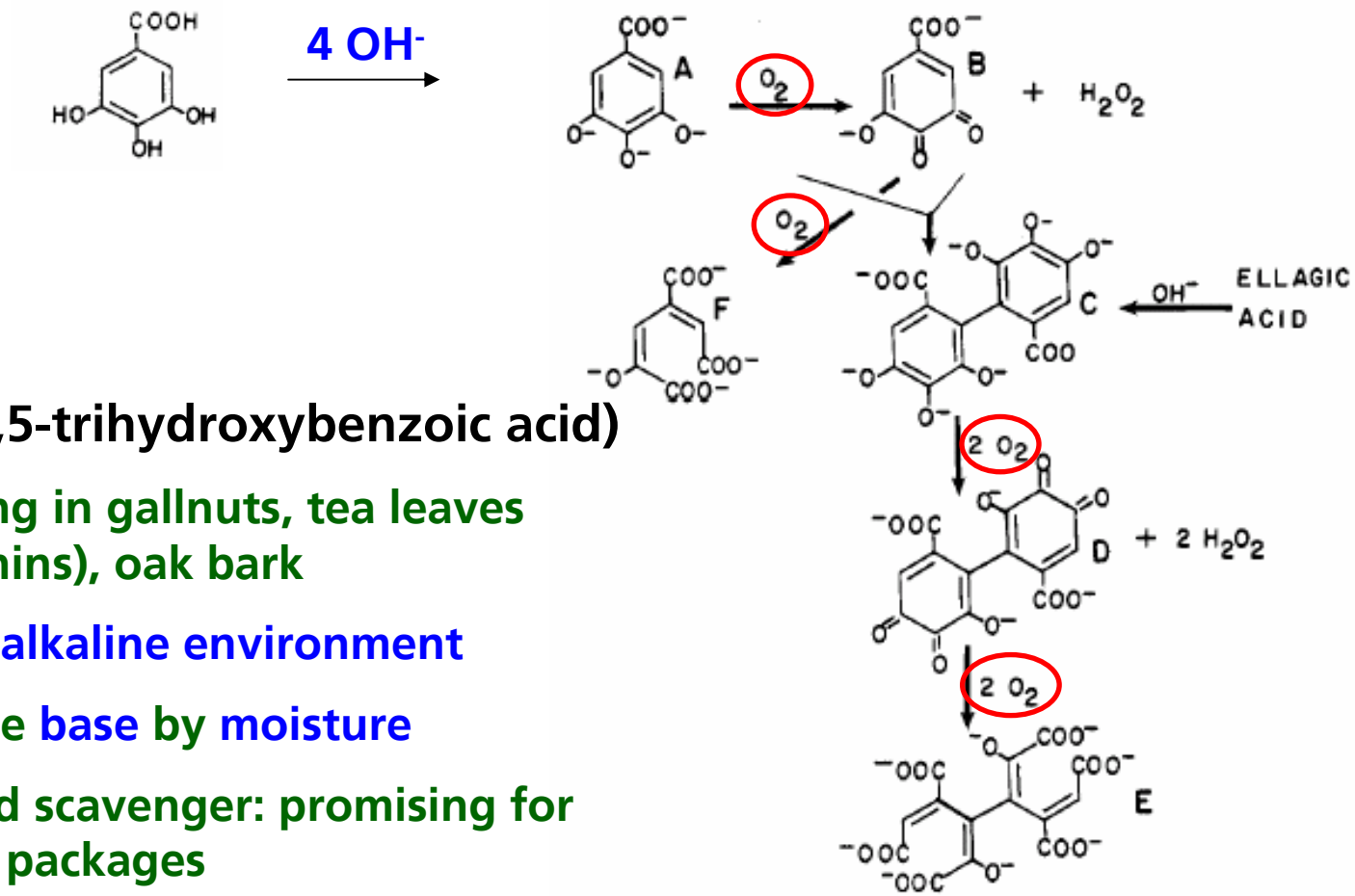
- **Gallic Acid (Fraunhofer IVV)**
- **Transparent Hybrid Polymers (Fraunhofer ISC)**

- Application as lacquers or as adhesion layers

Successful production of prototypes or samples

Results were generated in the EU-project ACOSIC: www.acosic.com

2. Gallic Acid Based Scavenger: Reaction Mechanism

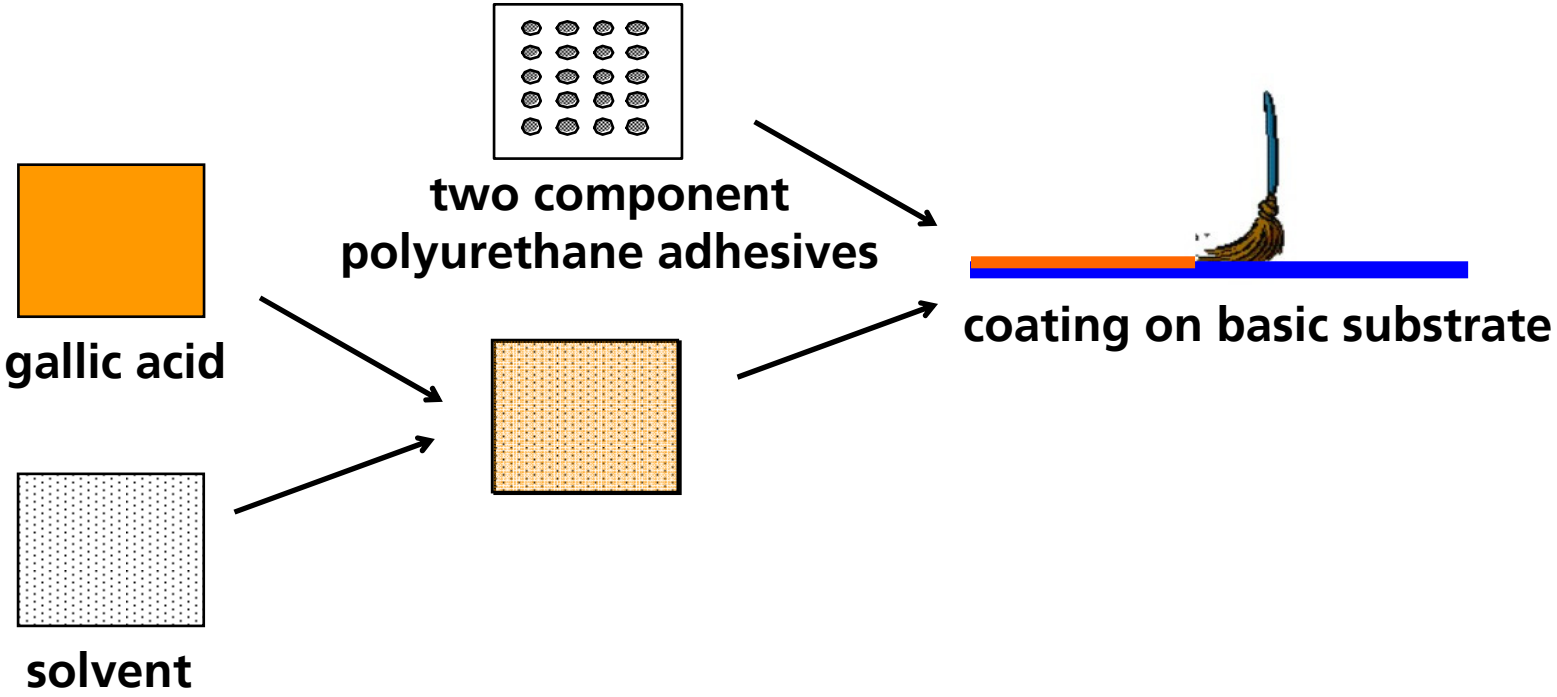


Gallic Acid (3,4,5-trihydroxybenzoic acid)

- natural occurring in gallnuts, tea leaves (in form of tannins), oak bark
- is oxidised in a alkaline environment
- activation of the base by moisture
- gallic acid based scavenger: promising for biodegradable packages

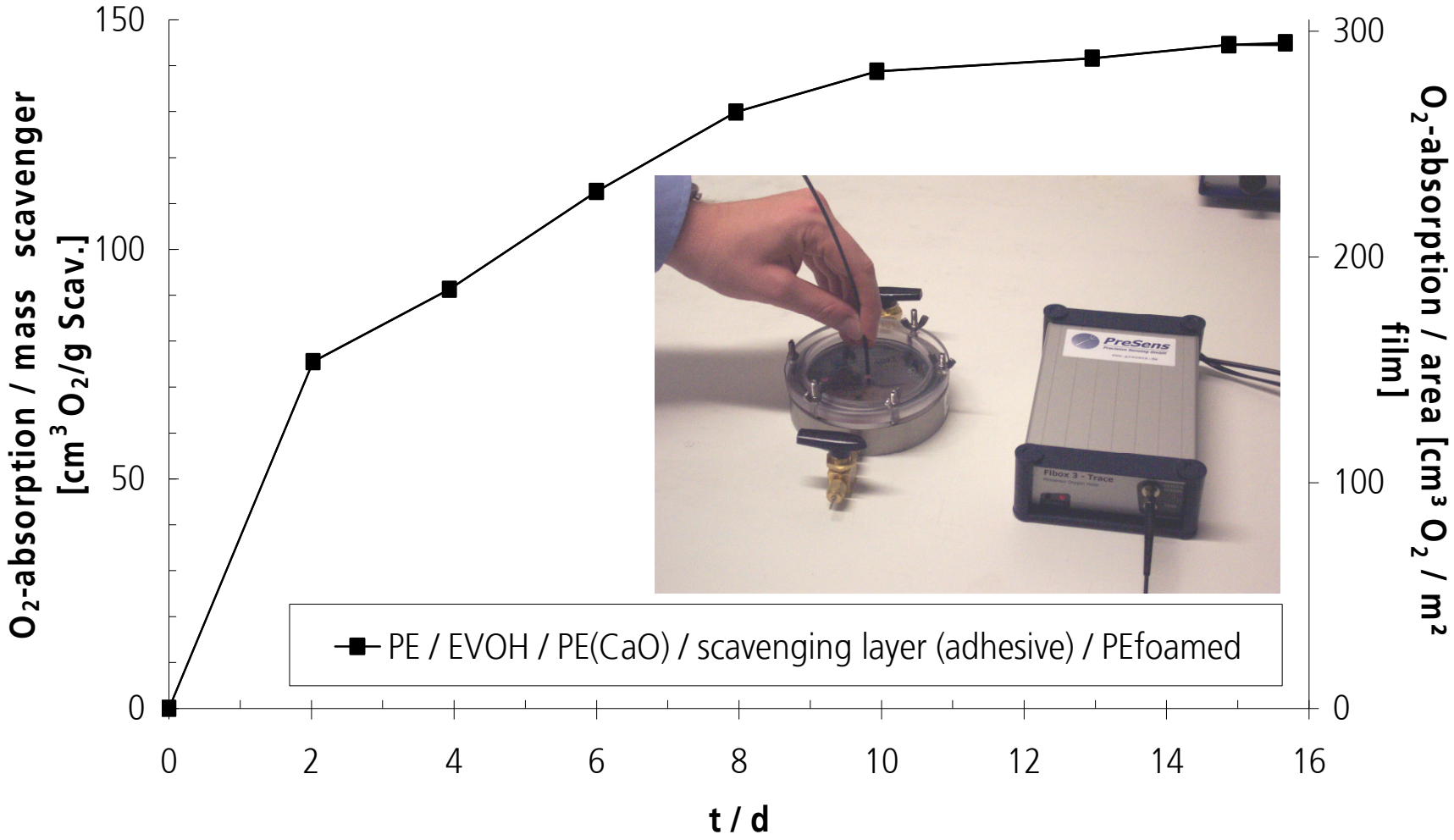
Source: Tulyathan V. et al.: Oxygen Uptake by Gallic Acid as a Model of Similar Reactions in Wines, J. Agric. Food Chem., 37, 1989, 844-849

2. Gallic Acid Based Scavenger: Film Coating



The system is suitable for coating and printing.

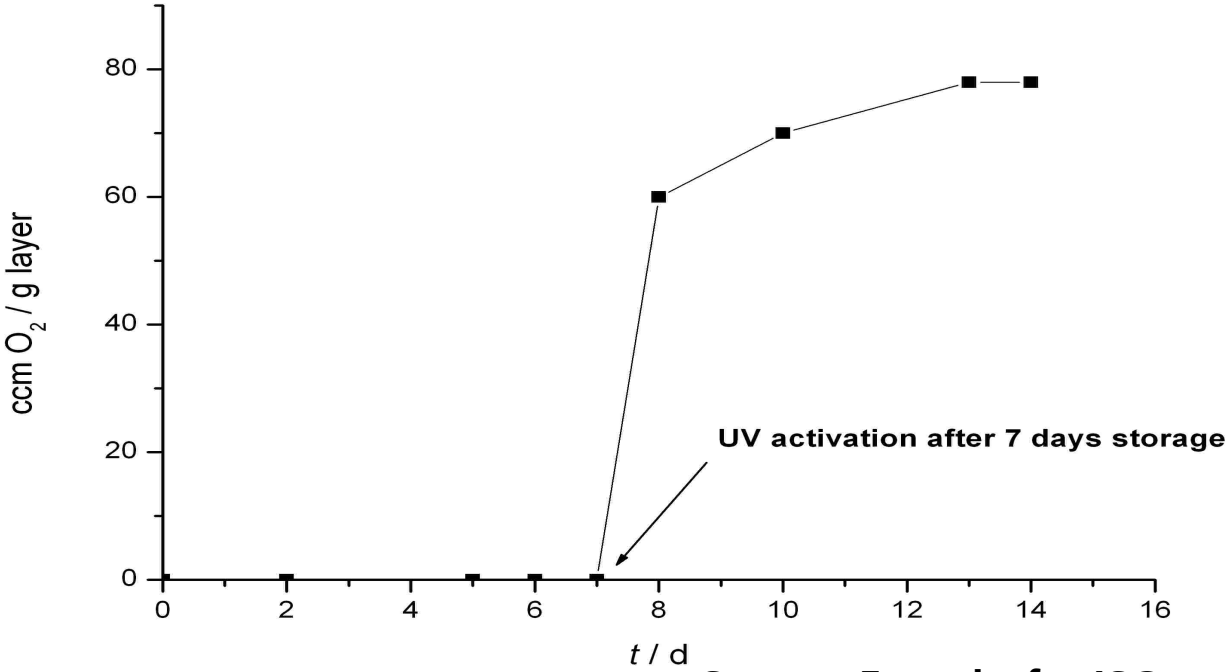
2. Gallic Acid Based Scavenger: Functional Characterisation



2. Hybrid Polymer Based Scavenger: Functional Characteris.

Composition: Silicate-backbone, catalyst, photoinitiator, antioxidant

Chemical reaction: Photo-initiated, metal catalyzed oxidation of oxidisable substance bonded chemically to a silicate backbone.



Source: Fraunhofer ISC

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3. Oxygen Indicators on the Market, Working Groups

Task of an oxygen indicator:

- Indication of exceeding an oxygen threshold, e.g. caused by a damage of the package.

Tablet with O_2-indicator: Ageless-Eye®

before reaction with O_2

after reaction with O_2

Working groups:

- VTT Finland: "Ink composition and oxygen indicator" – redox dye, printable indicator
- University of Strathclyde: redox dye methylene blue; UV-activated
- University of Ottawa: zeolite fixed indicator; UV-activated
- Fraunhofer IGB (Project ACOSIC): enzyme-catalysed system

3. New Developed Oxygen Indicators

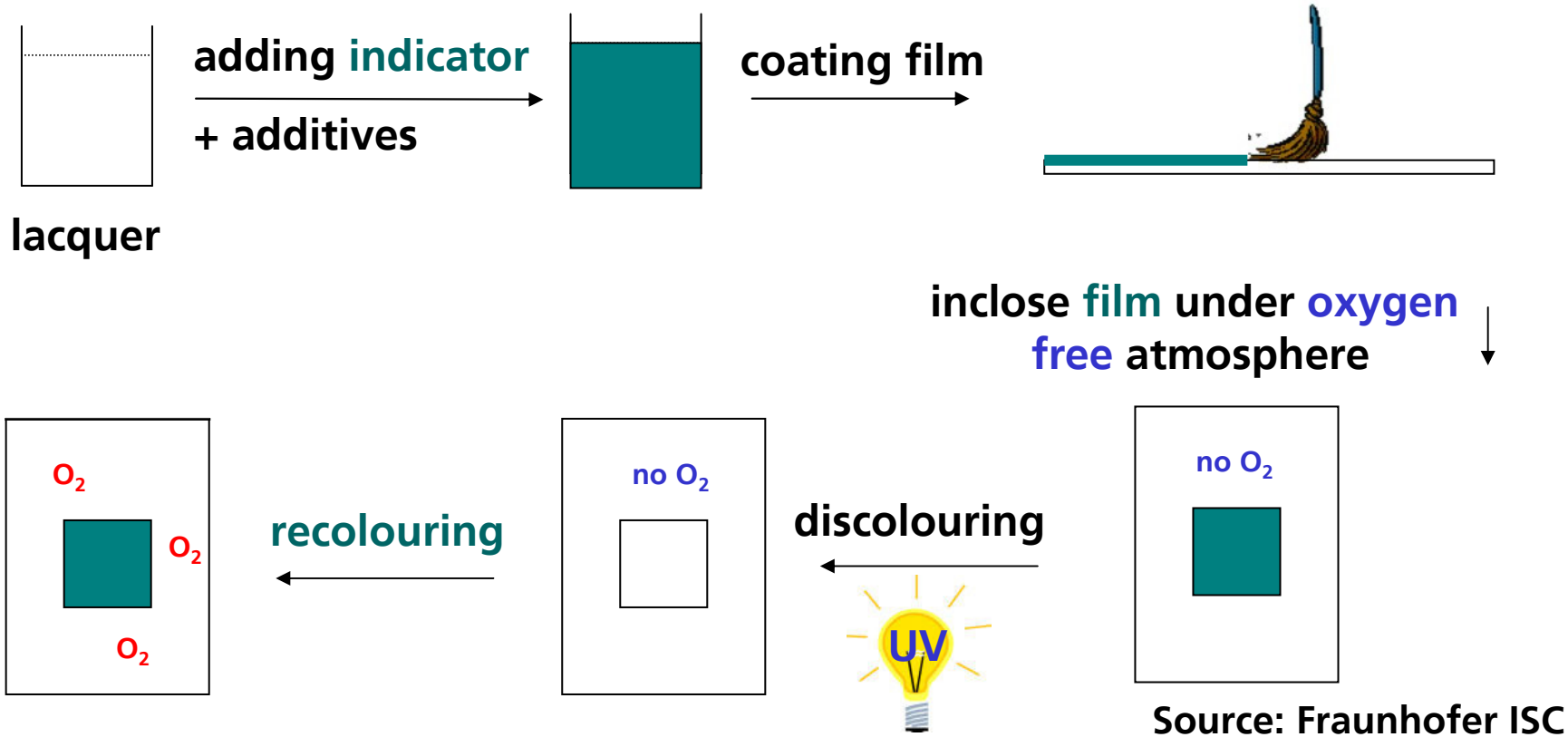
Fraunhofer worked on indicators on the basis of:

- **Methylene Blue (Fraunhofer ISC)**
- **Gallic Acid (Fraunhofer IVV)**

design proposal for an oxygen indicator

3. New Developed Oxygen Indicators: Methylene Blue Based

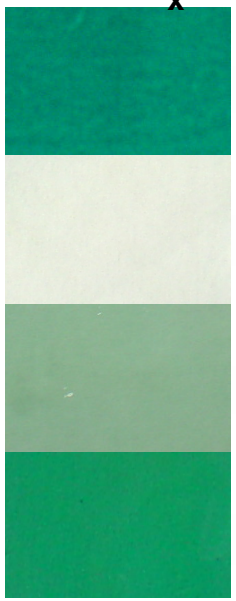
Manufacturing process Methylene Blue Based Indicator:



Source: Fraunhofer ISC

3. New Developed Oxygen Indicators: Methylene Blue Based

PET/SiO_x/ Indicator (lab scale):

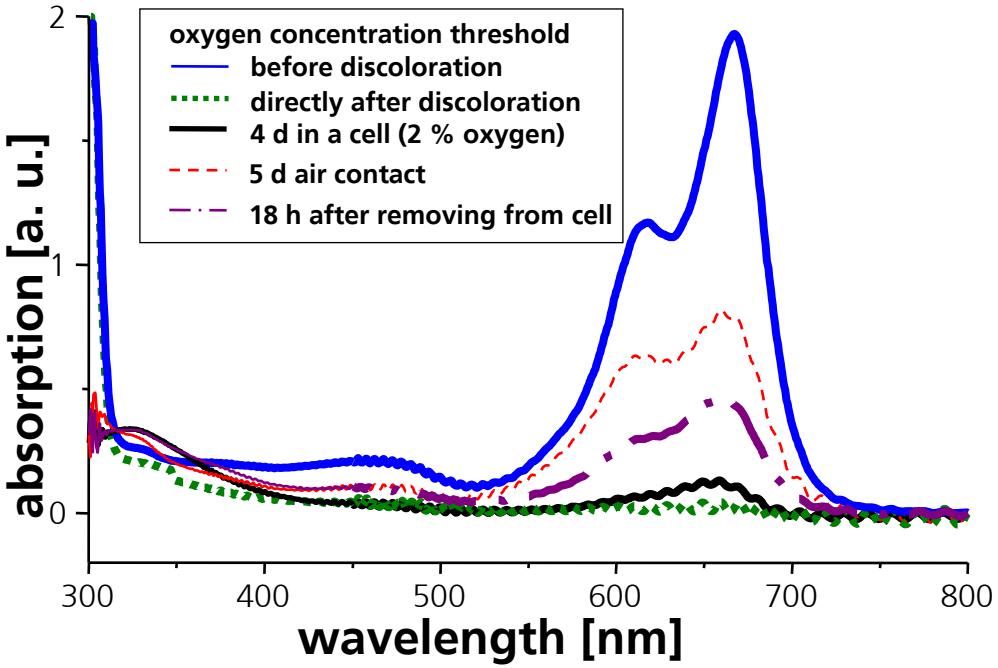


before discoloration

directly after discoloration

4 d in a cell (2 % oxygen)

18 h after removing from cell



Source: Fraunhofer ISC

3. New Developed Oxygen Indicators: Gallic Acid Based

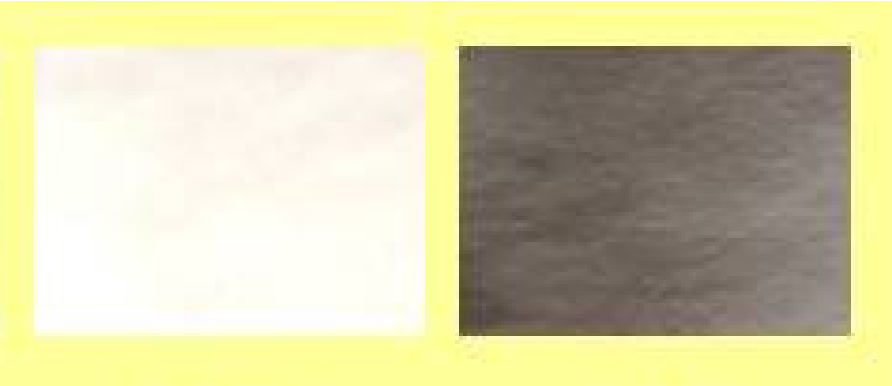
Manufacturing:

- **Incorporation of gallic acid in lacquers**
- **Printing of lacquer with gallic acid**

Initialisation: humidity + alkaline additives

Printed oxygen indicator based on gallic acid:

before reaction with O_2



after reaction with O_2

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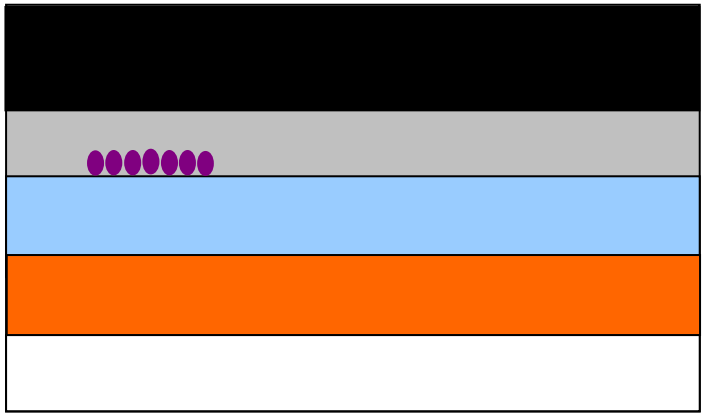
4. Combination of Oxygen Scavenger and Indicator, Demands

Barrier layer:
- oxygen scavenger is not a substitution for a barrier layer

Contact layer:
- high oxygen permeability,
- a high water vapour transmission rate is needed, if the system is activated by moisture,
- migration of decomposition products must be avoided

UV-activated system:
- high UV-transmission rate of the layers



barrier layer (outside)

adhesion layer: two component polyurethane adhesive **oxygen indicator dot**

intermediate layer with **alkaline substance**

oxygen scavenging layer (gallic acid based) and adhesion layer

contact layer / sealing layer (inside)

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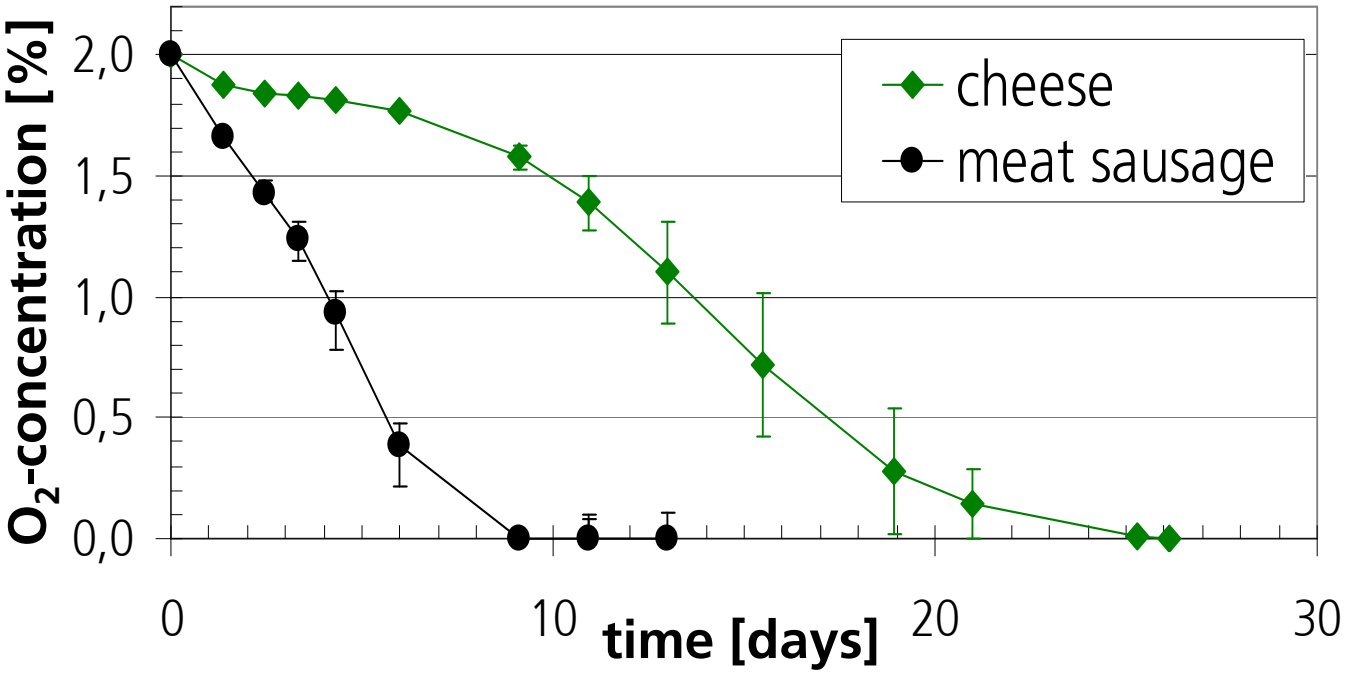
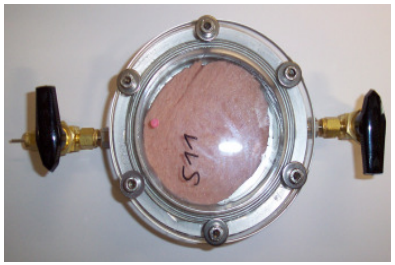
5. Oxygen Consumption of Food



Weight: (40 .. 50) g

headspace: 100 cm³

temperature: 5 °C



Cheese and meat sausage – oxygen absorption

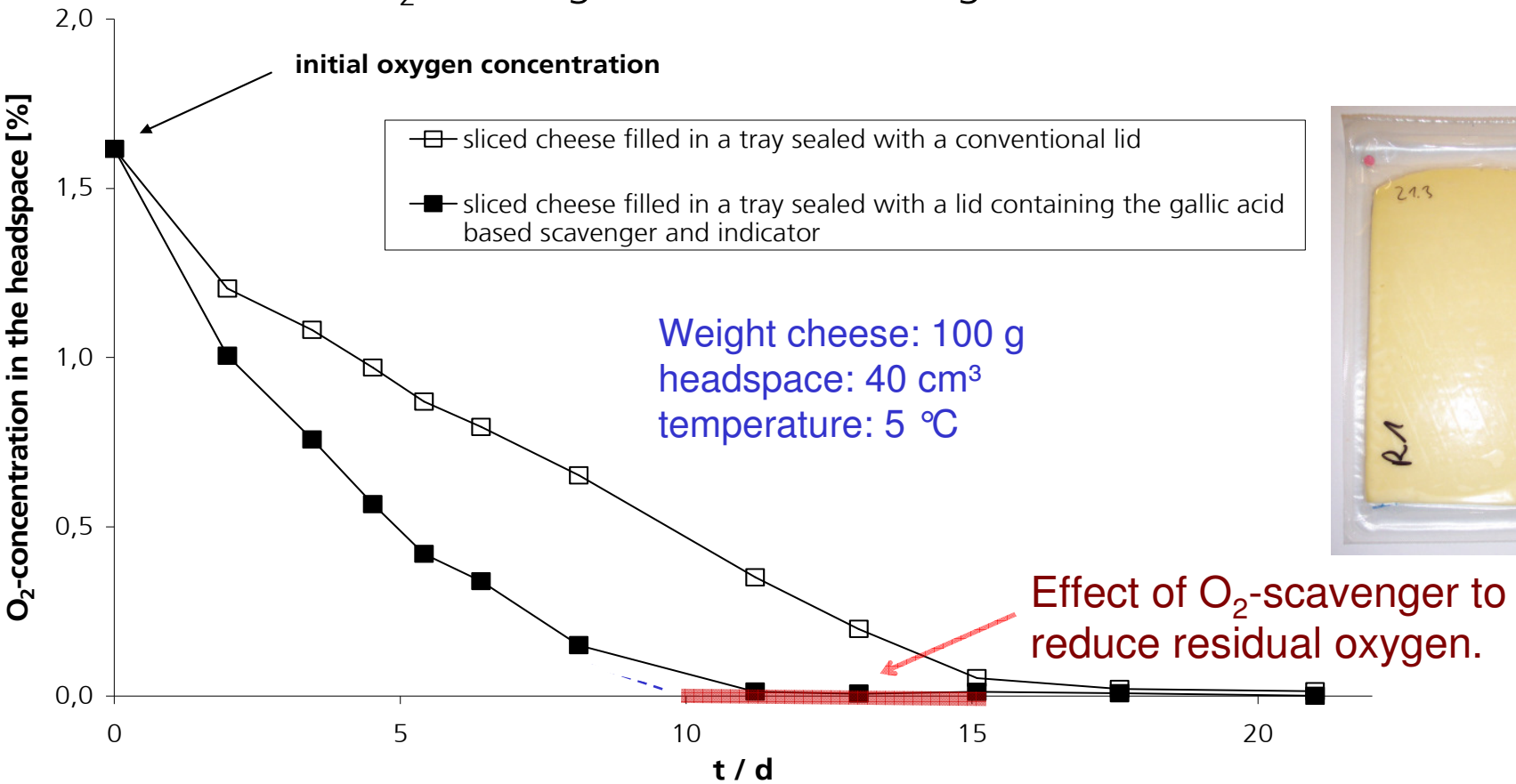
Adaptation of scavenger characteristic and oxygen consumption of food.

→ O_2-scavenger must absorb oxygen faster than food.

5. Filled Packages

Cheese – effect of the O_2-scavenger in MAP package

→ lid with novel O_2-scavenger on the basis of gallic acid



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6. Summary

- The combination of O_2-scavenger and O_2-indicator is reasonable to scavenge oxygen and to simultaneously monitor the functioning of the O_2-scavenger and the integrity of the package.
- During the project ACOSIC prototypes of new O_2-scavengers – lacquers and adhesives – and new O_2-indicators were developed and combined.
- The O_2-scavenger and O_2-indicator has to be adapted to the food – the O_2-scavenger should absorb the oxygen faster than the food.
- Further application areas for other combined systems like humidity absorber and humidity indicator or antimicrobial package and spoilage indicator are beneficial.


Thank you for your attention.