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

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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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6. Summary
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

<table>
<thead>
<tr>
<th>food</th>
<th>max. tolerable $O_2$-uptake (mg $O_2$ / kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>beer</td>
<td>1 – 4</td>
</tr>
<tr>
<td>wine</td>
<td>3</td>
</tr>
<tr>
<td>milk</td>
<td>8</td>
</tr>
<tr>
<td>steril. vegetable</td>
<td>15</td>
</tr>
<tr>
<td>ketchup</td>
<td>15</td>
</tr>
<tr>
<td>fruit juice</td>
<td>20</td>
</tr>
<tr>
<td>roasted coffee</td>
<td>110</td>
</tr>
<tr>
<td>emmentaler cheese</td>
<td>500</td>
</tr>
</tbody>
</table>

Source: Heiss
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## 2. Oxygen Scavengers on the Market

<table>
<thead>
<tr>
<th>Scavenger</th>
<th>Substrate</th>
<th>Catalysis / Activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>sachets</td>
<td>iron based</td>
<td>hygroscopic salts / moisture self working glucose oxidase / moisture</td>
</tr>
<tr>
<td></td>
<td>glucose</td>
<td></td>
</tr>
<tr>
<td>inlay</td>
<td>palladium (on fleece)</td>
<td>palladium / MAP with H₂</td>
</tr>
<tr>
<td>incorporated in polymers</td>
<td>iron based polyolefin based sulphite based Nylon-6 PET-copolyester</td>
<td>different additives / moisture photoinitiator+cobalt salts / UV-irradiation - / moisture - / thermal irradiation cobalt / thermal irradiation</td>
</tr>
</tbody>
</table>
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)
- naturally occurring in gallnuts, tea leaves (in form of tannins), oak bark
- is oxidised in an alkaline environment
- activation of the base by moisture
- gallic acid based scavenger: promising for biodegradable packages

2. Gallic Acid Based Scavenger: Film Coating

The system is suitable for coating and printing.
2. Gallic Acid Based Scavenger: Functional Characterisation

![Graph showing the absorption of O₂ over time for different materials.](image)

**Graph Description:**
- The graph plots the absorption of O₂ over time (t/d) for a scavenger.
- The x-axis represents time in days (t/d), ranging from 0 to 16.
- The y-axis represents O₂ absorption in mass scavenger [cm³ O₂/g Scav.], ranging from 0 to 150.
- The data points show the absorption rate over time for different materials.

**Materials Tested:**
- PE / EVOH / PE(CaO) / scavenging layer (adhesive) / PEfoamed

**Notes:**
- The project is supported by the European Commission.
- ACOSIC - A project supported by the European Commission.
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.

![Graph showing cm³ O₂ per g layer over time](image)

**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 O₂-indicator: Ageless-Eye®

- 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)

Oxygen can change the food quality
nutritional value, taste, odour, colour

Oxygen free Pack is OK
Oxygen inside Pack is not OK

design proposal for an oxygen indicator

ACOSIC - A project supported by the European Commission.
3. New Developed Oxygen Indicators: Methylene Blue Based

Manufacturing process Methylene Blue Based Indicator:

adding indicator + additives → coating film

lacquer

inclose film under oxygen free atmosphere

O₂ recolouring

no O₂ discolouring

O₂

Source: Fraunhofer ISC

ACOSIC - A project supported by the European Commission.
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 $O_2$

<table>
<thead>
<tr>
<th>![Image before reaction]</th>
<th>![Image after reaction]</th>
</tr>
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</table>

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

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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

Cheese and meat sausage – oxygen absorption
Adaptation of scavenger characteristic and oxygen consumption of food.
→ $O_2$-scavenger must absorb oxygen faster than food.

Weight: (40 .. 50) g
headspace: 100 cm³
temperature: 5 °C

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5. Filled Packages

**Cheese – effect of the O₂-scavenger in MAP package**

→ lid with novel O₂-scavenger on the basis of gallic acid

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Weight cheese: 100 g  
headspace: 40 cm³  
temperature: 5 °C

Effect of O₂-scavenger to reduce residual oxygen.

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Fraunhofer  
Institut Verfahrenstechnik und Verpackung  

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- 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.