Development of a novel oxygen scavenger film and its potential application in food packaging

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Active Packaging

• Active Packaging: “...designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food”


Food Trends

• Increase in consumer demand* for
  ➢ natural high-quality foods less additives and without any preservatives
  ➢ No harsh preservation process (non-processed or minimally processed)
  ➢ fresh and convenient food products

• Acceptable shelf life and safe products
• Barrier properties reached their limits
• New packaging technologies
  ➢ Active packaging

Oxygen Scavengers

Oxidation

Discoloration and rancidity

Degraded appearance and nutritional value

Impaired sensory qualities

Lost freshness, unpleasant taste and aroma

Reduced Shelf life

Growth of aerobic microorganisms

Moulds and other spoilage organisms

O₂
Palladium Based Oxygen Scavenger

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \xrightarrow{\text{Pd}} \text{H}_2\text{O} \]

1. step
2. step
3. step
4. step

Palladium Based Oxygen Scavenger


Effect of Coating Substrate on the Oxygen Scavenging Activity

Reduction in oxygen concentration in the measurement cell with PET/\(\text{SiO}_x/\text{Pd}\), PET/\(\text{AlO}_x/\text{SiO}_x/\text{Pd}\), PLA/\(\text{SiO}_x/\text{Pd}\), LDPE/\(\text{SiO}_x/\text{Pd}\) and oPP/\(\text{SiO}_x/\text{Pd}\) films using a palladium deposition thickness of 1.1 nm and \(\text{SiO}_x\) pre-coating. Mean values ± standard deviation (n=3).

Best Substrates:
- PET
- PET/\(\text{AlO}_x\)
- PLA
- LDPE
- oPP

Effect of Palladium Deposition Thickness on the Oxygen Scavenging Activity

Reduction in oxygen concentration in the measurement cell with PET/SiOx/Pd films using Pd-deposition thicknesses of 0.3, 0.4, 0.7, 1.1 and 3.4 nm. Mean values ± standard deviation (n=3).

A case study: Use of palladium based oxygen scavenger to prevent discoloration of ham

Material & Methods

Packaging:
- Commercial cooked cured ham
- High barrier EVOH tray and film
- Gas: Modified atmosphere (MA): 2% O₂, 5% H₂, 93% N₂, normal atmosphere (NA)
- With and without scavenger (25 cm²)

Storage:
- 4±1°C, 21 days
- Illumination (1’000 lx): 24 h/d, 8 h/d or dark

Analyses:
- Colour: *a (redness), *L (lightness) (CR-410, Minolta)
- Headspace oxygen concentration (Fibox 4 trace, PreSens)
Changes in headspace oxygen concentrations

Modified atmosphere:
- Samples with scavenger stay $<0.05 \% \text{O}_2$
- Illuminated, without scavenger: decrease because of discoloration reaction

Normal atmosphere:
- Decrease starting after ~5 days, probably due to microbial growth
Discoloration of Ham

Changes in redness:

– No loss in redness for sample with scavenger, even though it was illuminated 24 h/d
– Even slight increase in redness, compared to dark stored samples
– Illuminated samples show pronounced discoloration, significant after 2 h
Discoloration of Ham

after 1 day of storage

after 21 days of storage
### Discoloration of Ham

<table>
<thead>
<tr>
<th></th>
<th>0 h</th>
<th>4 h</th>
<th>7 d</th>
<th>21 d</th>
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<tr>
<td>MAP light</td>
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<td><img src="image15" alt="Image" /></td>
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A case study:
Use of palladium based oxygen scavenger to prevent mould growth of bakery product

Rüegg N, Blum T., Ebenreth M., Yildirim S. Use of palladium based oxygen scavenger to prevent mould growth of bakery product. Manuscript in preperation
Experimental Set-up

Par-baked bread   Toast bread   Gluten free bread

Normal atmosphere (NA)

Modified atmosphere (MAP)
(93 vol. % N₂, 2 vol. % O₂, 5 vol. % H₂)

MAP + Scavenger
(MAP + Active Label)

No inoculation, Stress test
*Aspergillus niger* (9.7 x 10³ KBE)

Storage
25 °C, 50 % RH
Experimental Set-up

Par-baked bread  Toast bread  Gluten free bread

Normal atmosphere (NA)  Modified atmosphere (MAP)

(93 vol. % N₂, 2 vol. % O₂, 5 vol. % H₂)  (93 vol. % N₂, 2 vol. % O₂, 5 vol. % H₂)

+ Scavenger

(MAP + Active Label)

No inoculation, Stress test

Aspergillus niger (9.7 x 10³ KBE)

Storage

25 °C, 50 % RH
Par-backed bread, NA
Par-backed bread, NA
Par-backed bread, MAP

![Graph showing oxygen concentration and mouldy samples over time.

- **O$_2$-MAP**
- **O$_2$-NA**
- Mould growth - MAP + Active Label

Axes:
- **Y-axis**: Oxygen concentration [vol. %]
- **X-axis**: Time [d]

Graph indicates a sharp decline in oxygen concentration over time, showing the effectiveness of MAP in maintaining low oxygen levels to prevent mould growth.]
Par-backed bread, MAP
Par-backed bread, MAP + Active Label
Par-backed bread, MAP + Active Label
Toast Bread
Scientific Opinion on the safety assessment of the active substances, palladium metal and hydrogen gas, for use in active food contact materials

EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF)

European Food Safety Authority (EFSA), Parma, Italy

This scientific opinion of EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids deals with the safety assessment of the active substances palladium metal (CAS No 7440-05-3, FCM No 993) and hydrogen gas (CAS No 1333-74-0, FCM No 1038), which are intended to be used as an oxygen scavenger in packages of foods and beverages at room temperature or below. The active article is designed as a gas permeable but liquid impermeable laminated pad, which is placed within a cap or closure or as an adhesive label on tray lids. The palladium metal is not in direct contact with the food being separated from it by different layers of passive materials. The specific migration of palladium metal into conventional food simulants was not detected at the limit of quantification of 0.6 \( \mu g/kg \). Palladium was considered to be non-genotoxic and of no toxicological concern under a low exposure level resulting from a concentration up to 50 \( \mu g/kg \) food in a previous evaluation (EFSA CEF Panel, 2012). Based on these previously drawn conclusions and given the intended conditions of use leading to non-detectable migration, the CEF Panel concluded that the active substances palladium and hydrogen do not raise a safety concern for the consumer when used as an oxygen scavenger in packages for foods and beverages at room temperatures or below. Palladium should not be in direct contact with food and should be incorporated in a passive structure impermeable to liquids which prevents the migration at detectable levels.
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