Oxygen Absorbers. The barriers of plastic bottles, in oxygen-sensitive device covers and sterilizable packaging can be improved by oxygen absorbers. In order to utilize these substances efficiently, their effectiveness has to be tuned to the application at hand.

Typical applications of oxygen scavengers include beverage packaging, food covers and plastic compound films

Active Packaging Functions

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Since the mid-1970's, conventional packaging tasks, such as transportation, protection or communication have come to include active properties. By "active packaging" or "active packing" we generally mean a packaging technology that has an active and sustained influence on packaging properties. The first active packaging components were introduced in Japan in 1977 and added to the packaging in the form of small cushions, so-called sachets. These cushions still consist of a permeable membrane containing O_2 absorbers [1]. O_2 absorbers, however, are not the only cases of application for "active packaging". The packaging atmosphere can also be influenced by moisture absorbers and regulators as well as by CO_2 or ethylene absorbers and/or CO_2 or ethanol emitters. A further interesting area of use is the addition of antimicrobial materials [2]. A special type of active packing is so-called intelligent packaging where an internal or external indicator documents product quality or the life history of the contents from bottler to customer. Examples of this are time, temperature, moisture, CO_2 or O_2 indicators [3, 4]. Of the numerous active systems developed in recent years, only a few are commercially significant: These include oxygen scavengers (oxygen absorbers), moisture absorbers and anti-microbially effective plastics.

How Oxygen Absorbers Work

Sachets are, of course, very effective O_2 scavengers and have high O_2 absorption capacity, but also have the disadvantage of being unsuited for direct contact with fluids. Nor are they acceptable in Europe. Their active material is thus preferably incorporated in the polymer matrix of the packaging material [1, 5]. The reaction speed of scavengers bound in the polymer matrix is generally slower than that of the iron-base materials found in sachets [6]. Theoretically, any substance that reacts with O_2 can serve as an O_2 scavenger. But if the scavenger is used in connection with food packaging, it has to have additional properties: It must be easily handled and must not produce any

$4\,Fe(OH)_2 + O_2 + 2\,H_2O$	→	$4\,Fe(OH)_3$
$2\,Na_2SO_3 + O_2$	→	$2\,Na_2SO_4$
Ascorbic acid + ½O_2	→	Dehydro ascorbic acid +H_2O
Glucose + O_2	⇄ Glucose oxidase	Glucono lactone + H_2O_2
H_2O_2	→ Catalase	H_2O + ½O_2
Polyamide + O_2	→ Cobalt	Oxidized polymer
Pigment	→ Light	Pigment* (activated)
Pigment* (activated) + O_2	→	Pigment + O_2^* (activated)
O_2^* (activated) + acceptor	→	Acceptor-oxide

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Fig. 1. Reaction mechanisms of commercially applied O_2 scavengers [8]

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toxic products or substances with an undesirable smell or taste. It also must not be too expensive, has to have a defined O_2 absorption capacity and high reaction speed. Thus the number of available chemicals is limited [7].

The O_2 absorbent can be either a polymer or a reagent dissolved or dispersed in the polymer. Among the materials with O_2 absorbent properties in use until now are metal-sulfite compounds, ascorbic acid or iron. An additional possible combination involves the two enzymes glucose oxidase and catalase **(Fig. 1)**.

Important parameters for describing the properties of an O_2 scavenger include

- O_2 absorption capacity,
- O_2 reaction kinetics,
- duration of activation,
- activation moisture and
- temperature dependence.

Some typical applications for oxygen scavengers are beverage packaging (especially caps and plastic bottles), food covers and plastic composite films **(Title photo)**.

	Oxygen absorption by permeation	
Type of bottle	**[cm³(STP)/(bottle d bar)]**	**[mg/(l ³/₄ year)]**
Cap – passive barrier	0.01 – 0.05	0.8 – 4
Cap – active barrier	<0.001 – 0.01	<0.1 – 0.8
PET monolayer without barrier	0.3 – 0.4	24 – 32
PET monolayer barrier blend	0.05 – 0.3	4 – 24
PET monolayer with active barrier	0.02 – 0.2	1.6 – 16
PET monolayer with inside coating	0.015 – 0.05	1.2 – 4
PEN monolayer	0.04 – 0.08	3.2 – 6.4
PET multilayer with passive barrier	0.03 – 0.2	2.4 – 16
PET multilayer with active barrier	0.01 – 0.1	0.8 – 8

Table 1. Oxygen uptake of beverages through bottle (1-l plastic bottles) and closure (assumption: bottle weight 35 to 45 g) [9]

Application Case: Beverage Packaging

Cap manufacturers currently offer various crown caps and plastic screw-on caps with O_2 scavengers. However, what is important for practical use is the possibility of closing the bottles in conventional closing machines, as well as for caps that are not too expensive. That is why systems with the scavenger integrated into the sealing cap are used almost exclusively by commercial applications. Their rate of O_2 consumption depends on scavenger reactivity and concentration, as well as the permeability and surface of the compound. Mostly sulfate-base scavengers are used in the cap area. Depending on the scavenger formula, the oxygen permeability of plastics screw-on caps can be lowered to values of <0.001 to 0.01 cm^3 (STP)/(closure day bar). Caps with exclusively passive barriers exhibit values of 0.01 to 0.05 cm^3 (STP)/(closure day bar).

PET bottles are being used more and more often for oxygen sensitive beverages such as beer and fruit juices. Monolayer PET bottles have proven unsuitable for bottling oxygen sensitive beverages. Assuming, for example, a bottle weight of 35 g to 45 g for a 1 l juice bottle, the oxygen permeability of a monolayer PET bottle is on the order of approx. 0.3 to 0.4 cm^3 (STP) /(bottle day bar). Given a shelf life of nine months, oxygen permeation through the bottle wall would add up to around 24 to 32 mg/l (ppm). By using active or passive barrier materials, as summarized in **Table 1**, permeability can be reduced by approximately one order of magnitude.

In **Table 1** we see that, both for passive as well as active barrier materials, the band width of achieved barrier values varies strongly even within a single category. For example, a 10 % admixture of PEN to PET in a PET/PEN blend bottle improves barrier quality by only 5 to 10 %. When MXD6 is used for the blend, the achievable barrier value is directly dependent on the MXD6 content. An MXD6 content of 6 % in PET reduces oxygen permeability by approx. 50 %, 12 % MXD6 by some 70 to 75 %.

For PET bottles with active barriers, the consideration of oxygen permeability is even more complex: In addition to the passive barrier, activation, kinetics, capacity and duration of scavenger activation then have to be taken into consideration. That is why the values even within the group of PET bottles with active barriers vary by a whole order of magnitude. The efficiency of active systems has to be monitored in each individual case.

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Application Case: Meal Trays

When instant meals are sterilized in plastic packaging (with ethylene vinyl alcohol copolymer (EVOH) as the barrier layer), sterilization (typically for a few minutes at 121°C) temporarily weakens the oxygen barrier. This behavior, known as retort shock, has an unfavorable effect on product shelf life. The solution may lie in integrating oxygen scavengers in the packaging material to protect the packaged food against oxygen **(Fig. 2)**.

The packaging for frozen meals with long shelf lives requires a high oxygen barrier. Since the packing material has to be deep drawn, multilayer compounds with EVOH (PP/EVOH/PP) as the oxygen barrier are utilized in the great majority of cases. To be sure, other barrier materials, such as SiOx, do not exhibit retort shock, but these materials cannot be deep drawn.

The oxygen barrier of EVOH clearly worsens with high relative humidity. Assuming that EVOH with 32 % ethylene content at 50 % relative humidity has an O_2 permeation coefficient of 0.05 cm^3 (STP) 100 µm/(m^2 day bar), its O_2 permeation coefficient increases 20 fold at 90 % relative humidity (approx. 1 cm^3 (STP) 100 µm/(m^2 day bar)) **(Fig. 3)**. And that is exactly what happens during sterilization.

When damp heat treatment is used for sterilizing, the water vapor permeability of PP is increased by 3 to 4 orders of magnitude. That is why the EVOH layer absorbs large quantities of water during the approx. 0.5-hour sterilization phase. Due to this immense water absorption, there is a rapid increase in oxygen permeability in the EVOH barrier layer. Following sterilization, the packaging is cooled off again. This causes the water permeability in the PP to fall again, so that water is trapped in the EVOH layer, so to speak. It takes several weeks for the water to escape from the EVOH layer. In this phase, the oxygen barrier in the EVOH layer does →

Fig. 2. Oxygen scavengers incorporated into meal covers protect packaged food against oxygen

not function and cannot protect the packed goods. **Figure 4** shows the effect of retort shock on the oxygen absorption of food packaging. The sterilized packaging absorbs approx. 1.5 mg oxygen during the first 14 days after sterilization. In unsterilized packaging, the amount is only 0.015 mg, or a hundred times less.

This is where the oxygen scavenger steps in. The oxygen-base scavenger typically used is activated by damp heat and provides precisely the oxygen barrier required in the post-sterilization phase while the EVOH is still wet. Curve three in **Figure 4** shows this so-called scavenger effect by which oxygen absorption can be reduced by a factor of 6 in the first 14 days following sterilization.

Application Case: Flexible Packaging

Whereas the clear advantage of longer shelf lives has been proven for oxygen scavengers in the above mentioned cases, i.e., for beverage packaging and sterilizable food covers, they have been applied only to a very small extent in the area of flexible packaging, even though there may be meaningful areas of application. Potential applications include packaging for oxygen-sensitive sausages, nuts or convenience products.

Series of Articles

This is the first of two articles in a series to provide an overview of active packaging systems. The current state of research will be outlined. The first part treats the areas for application of the most widely used oxygen scavengers. The second part, which appears in our February issue, will concentrate on additional active working principles, such as moisture regulating and anti-microbial films as well as their manufacturing methods.

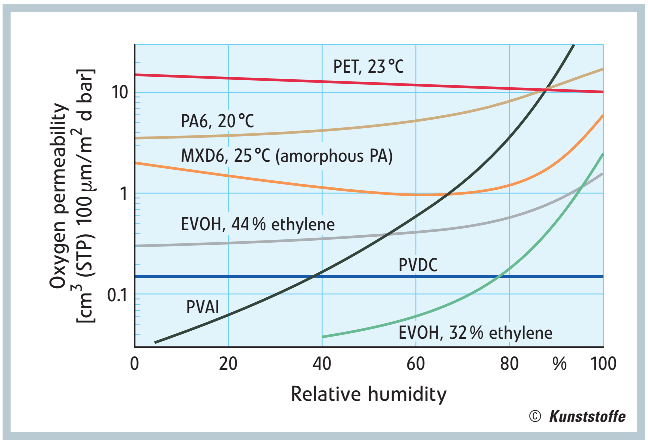


Fig. 3. Oxygen permeability of various polymers as a function of moisture (source: EVAL Europe)

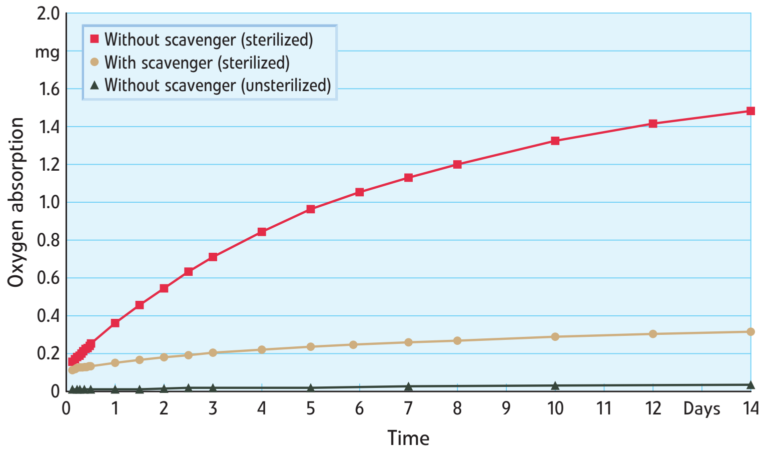
Sausages packed in transparent materials are subject to photosensitized oxidation processes in consequence of which they gray due to the combined influence of light and oxygen. This graying can be avoided if any influence from either light or oxygen can be entirely eliminated. The oxygen influence is the one to be avoided, since the customer would like to look at the packaged goods in the store, i.e., the exclusion of light would not be understood. Several approaches have been tried for protecting sausages with oxygen scavengers, however, previously available commercial scavengers have failed to provide the necessary reaction kinetics. Oxygen scavengers with increased reaction kinetics are currently in the development phase.

It would be theoretically possible to use oxygen scavengers for food with long or very long shelf lives. They could contribute to improved quality maintenance or additional safety: Due to the packing process, partial damage to the passive barrier layer occasionally occurs, or permeability increases at the seal seams. Oxygen scavengers are capable of closing barrier gaps to a certain extent. Of course, oxygen permeability due to larger effects cannot be compensated by oxygen scavengers. The limit to which the barrier gap can be closed is determined by the absorption kinetics and/or economic aspects, and is currently being verified at the Fraunhofer Institute for Processing Technology and Packaging, IVV, in Freising, Germany.

Conclusion

Oxygen scavengers have mainly been used previously to improve the barriers in plastic bottles and caps for oxygen-sensitive beverages as well as to avoid so-called retort shock in sterilizable packaging. There are additional, meaningful approaches that would use them to protect food packaged in flexible packing materials. However, their wide-scale commercial use has been delayed. The use of oxygen scavengers is not just limited to food packaging. Particularly in the area of high-barrier films, e.g., for technical applications, they could also be used to enable further barrier improvement.

For all scavenger systems, however, the general rule is: In order to utilize scavengers efficiently, their effect has to be tuned to the particular application. To this end, scavenging capacity, scavenging kinetics as well as the type and duration of activation must be known. These parameters can be determined in the testing center especially equipped for oxygen



scavenging packaging at the Fraunhofer IVV. The testing and development center is a part of the competence center for "Active and Intelligent Packaging" installed at the Fraunhofer IVV. The institute is also capable of equipping films with active components in commercial manufacturing and refining processes.

The potential for equipping films with active function capabilities and other interesting active systems, such as moisture regulating and anti-microbial systems will be treated in Part 2 of this series of articles. ■

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