

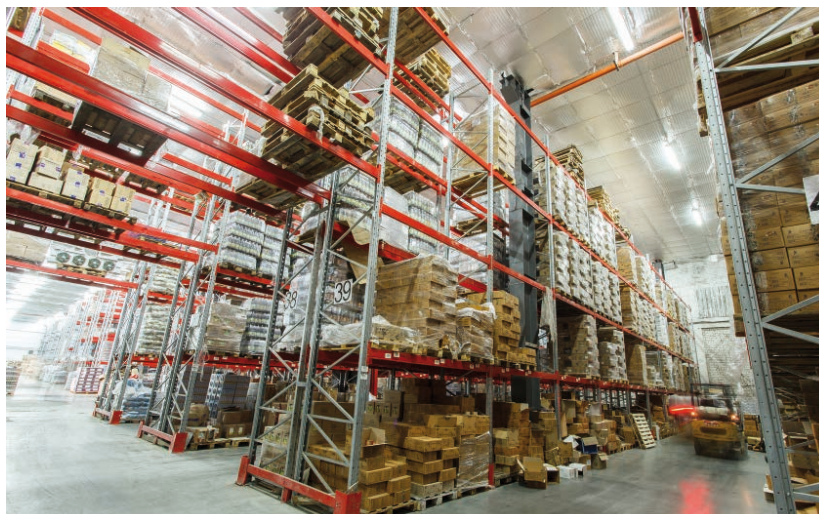
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Functional barriers against mineral oil from paper and cardboard packaging materials



Introduction

Mineral oil components from paper and cardboard packaging materials have moved more strongly into the focus of surveillance authorities in recent years. Attention centres on saturated and unsaturated hydrocarbons that are designated MOSH and MOAH. The unsaturated substances (MOAH) are appraised as having mutagenic and carcinogenic potential. The aim is to reduce migration of such substances from the packaging to the foods as far as possible. In response to the question of how the transfer of mineral oil components from cardboard packagings to foods can be minimised, the



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German Federal Institute for Risk Assessment (BfR) points out that the transfer of mineral oil components is influenced not only by their content level in the packaging material, but also by the storage conditions and the nature of the food. "It can be prevented by using virgin fibre-based board and printing inks free of mineral oils, as well as by integrating functional barriers in the packaging structure. Here not only the direct food packaging must be taken into account, but also the possibility of migration from secondary packagings" [1]. According to the third draft of the Mineral Oil Regulation, specific migration limits of 2 mg/kg for MOSH and 0.5 mg/kg for MOAH are planned [2].

Functional barriers are not all equally effective. Inner packagings made of paper or polyolefins delay migration (lag time), but do not prevent it. On the other hand aluminium, polyethylene terephthalate (PET) or polyamide (PA) barrier layers are considered to be migration-tight barriers that almost totally prevent the migration of the MOSH/MOAH [3, 4]. The ability to predict the extent of the mineral oil migration is essential for the selection of suitable packaging materials to minimise the mineral oil migration. Permeation measurements to test the functionality of barrier layers were proposed already in 2011 [3]. The Cantonal Laboratory of Zurich has also developed concepts for testing the functionality of barrier layers and adsorber materials [4].

Parameters influencing permeation through a functional barrier

The permeation of a substance through a functional barrier is influenced by a number of parameters. First of all the concentration of the permeant in the contaminated cardboard or in the gaseous phase is crucial. The higher this concentration, the higher the permeation rate of the permeant through the functional barrier. Furthermore, two distribution equilibria are critical. On the one hand the equilibrium between the gaseous phase across the cardboard and the functional barrier ($K_{g,b}$) and on the other hand the equilibrium between the barrier and the food ($K_{b/f}$). The equilibrium constant $K_{g,b}$ is a material constant for a given barrier/permeant pair at a specific temperature. $K_{g,b}$ is chiefly determined by the polarities of the polymer and the permeant. The equilibrium constant between barrier and food ($K_{b/f}$) plays hardly any role in good functional barriers, as the equilibrium between barrier and food is generally not reached within the storage period.

A further important parameter is the thickness (l) of the barrier layer. The greater the layer thickness, the longer the lag time of the permeant through the functional barrier. Not least the temperature exerts a great influence. The higher the temperature, the higher the permeation rate. The most important influencing parameter in the assessment of mineral oil barriers, however, is the diffusion coefficient (D_p) of the permeant in the barrier layer. The diffusion coefficient is also a material constant for a given pair of polymer and permeant at a specific temperature.

The permeation through a functional barrier is shown schematically in Figure 1. As MOSH and MOAH are substance mixtures, predicting the permeation is a complex operation. The substance transport into the food takes place primarily via transport in the gaseous phase and re-condensation on the food. Here it is limited to mineral oil components with a certain vapour pressure (hydrocarbons <C25). Depending on the nature of the packaging material and the food, however, in the case of direct contact between the packaging and the packaged material higher-boiling mineral oil components can also migrate into the food.

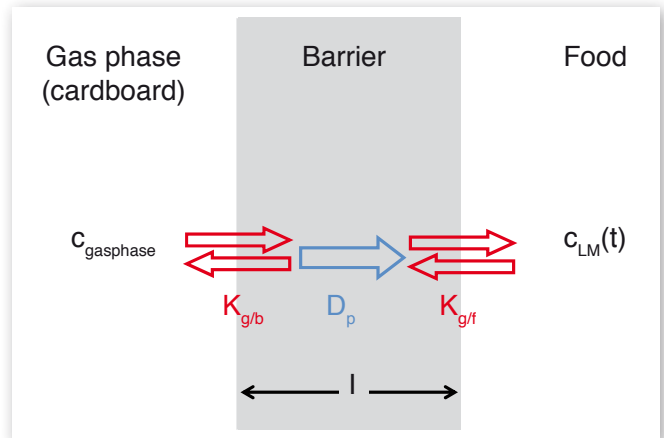


Figure 1: Diagram of the most important parameters influencing permeation through a functional barrier.

Methods for determining the properties of a functional barrier

The properties of a functional barrier can be determined via the following methods [5]:

- Migration tests
- Permeation tests with static acceptor
- Permeation tests with dynamic acceptor
- Lag-time experiments

The migration test

The migration test is the simplest experiment to determine the quality of a functional barrier. It is generally conducted with the real packaging. The migration test is carried out either with the real food or with a food simulant such as for example Tenax®. The migration experiment normally does not have any worst-case character and the concentrations of the contaminants in the cardboard are realistic. Storage is simply carried out at a higher temperature in order to shorten the test period. A migration test supplies a snapshot of a packaging with the food contained in it under the contact conditions applied. The result of a migration test is the quantity of contaminants that have migrated to the food per unit area of packaging (in mg per dm²). A typical example of such a migration test was recently published [6].

The permeation test

In a permeation test the property of a functional barrier is determined almost independently of the food. Generally elevated (“worst-case”) concentrations are used. In principle the cardboard can be dosed with either mineral oil [7] or model substances [3] that represent the mineral oil or other cardboard contaminants. However, the use of mineral oil has the crucial disadvantage that the mineral oil heap cannot be divided up analytically into individual substances. The functional barrier can therefore only be determined as a sum parameter. It is problematic here that small substances permeate distinctly faster than large molecules. That is why the mineral oil heap shifts in the course of time towards higher retention times, which makes quantitative determination more difficult. For permeation experiments it has therefore proved useful to use a series of model substances with sharp substance peaks that can be separated well by analysis instead of a mineral oil mixture. This also makes distinctly lower detection limits possible, which allows quantitative determination of the barrier properties of good barrier layers. The model substances are selected in such a way that they cover the entire relevant range of molecular weights (or volatilities). There are two different variants of a permeation test – with a static or dynamic acceptor. A disadvantage of both permeation tests is that the permeation depends on the concentration of the permeants. This means that the permeation measured depends on the experimental conditions. For example, if the concentration of the substances in the dosed cardboard is halved, then the permeation or the permeation rate are also halved. A further disadvantage is that the permeation starts already during application and heating of the permeation cells. Consequently the starting point of permeation is not defined and no lag time can be determined. However, the lag time is a critical parameter for assessing a functional barrier.

Permeation test with static acceptor

In this permeation test the functional barrier is located between a dosed reservoir and an acceptor material. The entire permeated quantity is caught on the acceptor material. A small quantity of the acceptor material is removed at regular intervals and examined for the permeant content. Based on the increase of the permeant over time, a permeation kinetic profile can be drawn up [3, 8, 9]. The actual measured value is the cumulative quantity of permeants per unit area packaging (in mg/dm^2). There are two distribution equilibria in the permeation test with a static acceptor, on the one hand between the dosed cardboard or the gaseous phase across it and the barrier material ($K_{g/b}$), and on the other hand between the barrier and the acceptor ($K_{b/r}$). The latter depends on the acceptor material (e.g. silicone paper, polyethylene film or simply a filter paper) and is not necessarily just as large as in the case of a food.

Permeation test with dynamic acceptor

In this permeation test a continuous gas flow replaces the acceptor material. The gas flow carries the permeated quantity along with it and catches this on a strongly cooled analytical trap. At short intervals the analytical trap is therefore desorbed quickly and injected directly into the gas chromatograph. The result supplied by this method is the permeation rate, in other words the permeated quantity per unit of time and area of packaging (in $\mu\text{g}/\text{d dm}^2$). By comparison with the method using a static acceptor, this method does not detect the cumulative quantity of permeants, but instead the quantity per measuring interval. The advantage of this is that it is possible to ascertain very simply when the stationary condition is reached. The permeated quantity per measuring interval (or the permeation rates) are then constant [3]. No equilibrium develops between the barrier material and the acceptor in the permeation test with dynamic acceptor. The partition coefficient between the barrier and the acceptor ($K_{b/r}$) can therefore be neglected.

The lag time experiment

The lag time experiment is a continuation of the permeation test with a dynamic acceptor. The apparatus design is almost the same, however it does not work with dosed cardboard but instead with a constant concentration in the gaseous phase. This means that the complete system can be built up and conditioned at the measuring temperature. At a pre-defined time the measurement is then started either by changing over to a dosed gas flow or by injecting the permeant through a septum. Consequently the starting point of permeation is established precisely and the lag time can be determined. Then the diffusion coefficient D_p can be determined from the lag time [10]. Furthermore, the partition coefficient $K_{g/b}$ can be determined from the rise of the permeation curve over time. As both D_p and $K_{g/b}$ are material constants that are no longer dependent on the concentration of the substances used, the concentration of the permeants can be set in an optimal concentration range. As in the permeation test with a dynamic acceptor, the value actually measured in the lag time experiment is the permeation rate.

Evaluation of the functional barrier

First of all it should be noted that neither the lag time determined nor the permeation rate determined possess any general informative value. A short lag time (high diffusion coefficient) combined with a very low permeation rate (favourable partition coefficient) supplies a passable barrier despite the fast breakthrough because ultimately the concentration in the food is critical. On the other hand, in the case of a long lag time (low diffusion coefficient) the boundary value for permeation can be exceeded despite this if the permeation rate (unfavourable partition coefficient) is correspondingly high after the breakthrough. For evaluation of a functional barrier, therefore, the diffusion coefficient (D_p) and the partition coefficient between the gaseous phase and the functional barrier ($K_{g/b}$) are crucial.

A further problem in evaluating a functional barrier is that mineral oil contaminants represent complex mixtures that cannot be divided up into individual substances in experiments. Therefore in principle it is not possible to determine the permeation rates or the diffusion or partition coefficients. One possible solution here lies in segmenting the mineral oil heap. For this the mineral oil heap is overlaid by individual model substances, for example alkanes, and their permeation rates, diffusion coefficients or partition coefficients are determined in each case. The diffusion data determined experimentally for the respective previous model substance are used for the sum of the following undissolved mineral oil substances (Figure

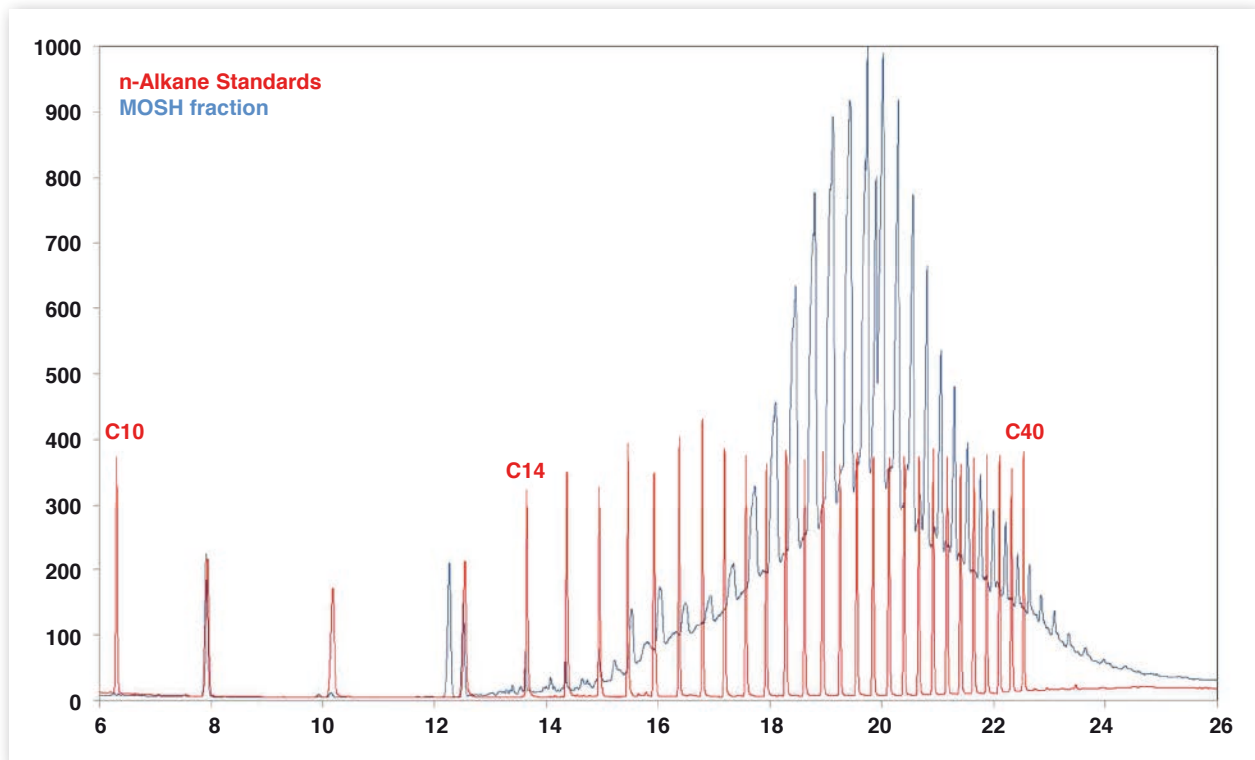


Figure 2: Example of the segmentation of the MOSH mineral oil heap measured (blue) by means of model substances (red, alkanes C10-C40)

2). With the help of this segmentation it is possible to produce a description of the permeation behaviour of a complex substance mixture.

Evaluation criterion 1 % breakthrough

One simple evaluation criterion is the percentage quantity that permeates through a functional barrier [4]. Here the permeation in per cent of the available (dosed) quantity in the cardboard is stated. A maximum transfer of 1% of the available quantity of mineral oil in the cardboard was fixed as maximum permeation. The storage period at which a breakthrough of 1% of the dosed quantity of the contaminants occurs is accordingly determined with the experimental tests. When fixing this criterion, it is assumed that the typical mass ratio between cardboard and food is about 1: 10. The total quantity of a (model) contaminant is transferred into the food. If a concentration of $10 \mu\text{g}$ of a permeant per kg in the food is accepted as uncritical, then there can thus be a maximum of 0.1 mg/kg mineral oil in the cardboard. If a functional barrier now only allows 1% of the total quantity of contaminants through under the given storage conditions, the maximum concentration in the cardboard can now be 10 mg/kg. The advantage of this evaluation method is that the concentration in the cardboard can be used as monitoring parameter. The goal is therefore to keep the concentration of contaminants below 10 mg/kg. Here, though, the evaluation only applies for the test conditions applied. The results can however be converted to other temperatures with the help of the Arrhenius equation.

Evaluation of the permeation rate neglecting the lag time

A further simple evaluation method is based on experimentally determined permeation rates [11] and uses the specific migration limit levels, for example 2 mg/kg MOSH or 0.5 mg/kg MOAH [2]. In this evaluation method it is assumed that the permeation takes place from the first minute onwards at a constant permeation rate (no lag time). This results in over-estimation of the permeation. If the permeation rate for a permeant and a barrier is known, the time up to reaching the specific migration limit level t_{SML} can be calculated in accordance with the following equation. However, here too the evaluation is only valid for the test conditions applied.

Compound	Model component for	b.p. [°C]	Permeation rate [$\mu\text{g/d dm}^2$]					
			BOPP 20 μm	BOPP 20 μm metallised	EVOH 20 μm	Acrylic 31 μm	PVDC/Acrylic 25 μm	BOPET 12 μm
Dodecane	MOSH	216	4900	1640	0.02	1.43	1.51	0.010
Naphthalene	MOAH	218	693	395	0.009	0.44	0.39	0.010
1-Methylnaphthalene	MOAH	243	1590	808	<0.006	0.98	0.79	<0.006
Tetradecane	MOSH	254	1390	1250	0.014	3.90	4.05	0.008
1-Ethyl-naphthalene	MOAH	260	1000	690	<0.006	1.90	1.57	<0.006
2,7-Diiso-propylnaphthalene	MOAH	279	88.0	79.5	<0.006	1.30	1.45	<0.006
TXIB	Photoinitiators	280	244	103	<0.009	0.25	0.26	0.015
Hexadecane	MOSH	287	238	275	0.008	3.85	6.14	<0.006
Benzophenone	Photoinitiators	305	68.0	76.5	0.008	0.21	0.26	<0.007
Octadecane	MOSH	317	33.0	31.5	0.010	2.61	4.02	0.009
4-Methylbenzophenone	Photoinitiators	326	22.0	22.5	0.017	1.27	0.59	0.017
Phenanthrene	MOAH	336	32.0	31.5	<0.006	1.37	1.00	<0.006
Eicosane	MOSH	343	5.51	4.95	<0.006	0.76	1.17	<0.006
Docosane	MOSH	369	1.02	0.90	<0.007	0.11	0.11	<0.007
Tetracosane	MOSH	391	<0.03	<0.03	<0.007	<0.007	<0.007	<0.007

Table 1: Experimentally determined permeation rates at 40 °C [11]

$$\text{Equation 1: } t_{\text{SML}} = \frac{\text{SML } m_{\text{LM}}}{P A}$$

- t_{SML} : Time up to reaching SML (in days)
 SML: Specific migration limit (in $\mu\text{g/kg}$ food)
 m_{LM} : Weight of the food (in kg)
 P: Permeation rate (determined by experiment in $\mu\text{g/d dm}^2$)
 A: Contact area of the packaging material (in dm^2)

Evaluation via diffusion and partition coefficient

The permeation of a contaminant into a food can be calculated directly from experimentally determined diffusion coefficients and partition coefficients. As both the diffusion coefficient and the partition coefficient represent material constants at a given temperature, these parameters can be determined once for a barrier polymer. After this, the permeation can be calculated for all possible barrier thicknesses and packaging geometries. The more precisely the diffusion and partition coefficients were determined, the more precisely a prediction can be made. As no worst case scenario is applied for this system, an additional safety factor should be included in the calculation. Shorter storage periods (minimum shelf life) than those calculated can be applied, or the diffusion coefficient can be increased slightly for the calculation. Diffusion coefficients can be estimated from the molecular volume in the case of substances that can no longer be captured by measurement [10].

Conclusions

Predicting the extent of the mineral oil permeation through a functional barrier is essential for selecting appropriate packaging materials. However, migration and permeation experiments can only be used for generally valid assessment of the properties of a barrier to a limited extent, because the results depend on the framework conditions applied (concentration of the model substances, temperature, packaging area). This limits the informative value of the evaluation of functional barriers and makes comparisons between the results obtained by different laboratories difficult. On the other hand the material constants – diffusion and partition coefficients – obtained through the lag time experiment make it possible, to describe the properties of a functional barrier extensively via a mathematical evaluation. For real packaging scenarios the contamination limit level of foods with mineral oil components following a certain time can be predicted on the basis of the

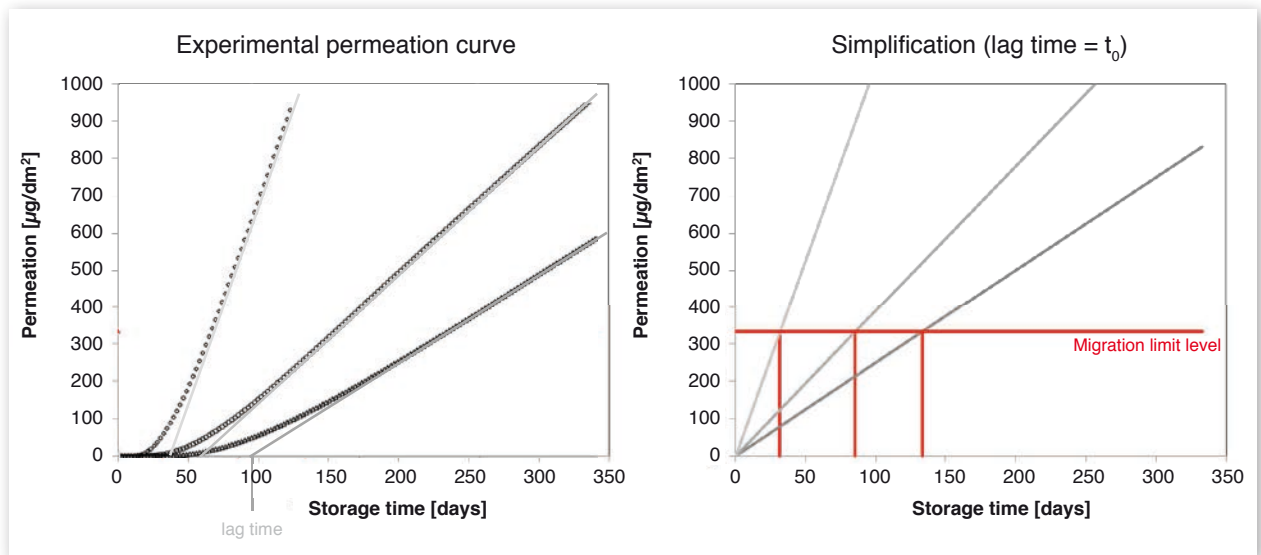


Figure 3: Simplified evaluation. Left: experimental data and lag time. Right: worst-case Simplification with uniform permeation rate as of t_0 , without consideration of the lag time.

starting conditions, such as for example the starting contamination of the packaging, the nature of the packaging, storage time and temperatures.

The ideal barrier against mineral oil components is a polar polymer (favourable partition coefficient) with high density (low coating weight) and low diffusion coefficients (long lag time). In practice this ideal mineral oil barrier cannot always be realised either technically or economically.

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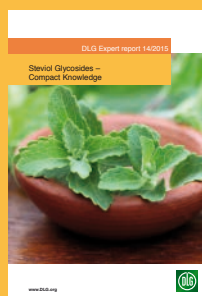
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