SOME CONSIDERATIONS ON THE PERMEABILITY OF PLASTIC WRAPPINGS FOR PACKING FOOD

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In order to choose wrappings suitable for packing food on an up-to-date, namely on a scientific basis, the following factors influencing the efficiency of the packing have to be taken into consideration:

1. the dynamics of the packed product,
2. the ecological circumstances, and
3. the permeability of the packing material (plastic wrapping).

The requirements to be satisfied by the packing material in order to preserve the original quality of the food depend chiefly on the dynamics of the product to be packed. In our previous papers [1, 2] some examples have been described relating to these requirements, and at the same time it was emphasized that theoretical considerations were completely by experimental observations.

In addition to the dynamics of the packed products, the chemical composition of food and the particular structure of the packing material also cause an additional interaction. All these actions and interactions, that is, the ecological relations are generally followed even nowadays empirically i. e. only by experiments. The cause and explanation of this empirism is the fact that except for the mechanism of aqueous vapour permeation through plastic wrappings, the way of the penetration of gases, vapours etc. is not completely known in every case, and even the known facts are not consistently employed in the practice of packing. It is not known: e. g. the way and degree of penetration of essential or vegetable oils and fats, factors influencing the penetration, such as, dimensions, structure and distribution of occasional micropores, that is, the mechanism of penetration of these substances. Even in the most thoroughly-tested and theoretically-controlled cases, e. g. in case of dry gases, several contradictory data were obtained. However, it is quite obvious that the accurate and deliberate pre-planning of the protecting wrappings and the prediction of the permissible storage time of the packed food represent an interesting theoretical problem of the packing technique which, also from the practical point of view, requires an urgent answer.

To solve this problem it is indispensable to know the permeability of packing materials, at least of the most important materials; moreover an

unambiguous, easily performable and reproducible method for measuring
the permeability is needed. Namely, in our opinion, the incompleteness of the
methods for measuring gas-permeability, which several authors have com-
plained of, is due to the lack of suitably-constructed measuring instruments.
Although from this statement it cannot be spontaneously inferred that more
theoretical considerations lead automatically to the construction of a measur-
ing instrument, satisfactory in every respect, a more profound insight into
the nature of permeability and into the complex mechanism of permeation
is given by the examination of the different theoretical considerations.

From this very ramifying field of investigations, at present the method
and measurement of permeability of plastic wrappings for dry gases are
directly considered and dealt with. The principle for measuring the gas per-
meability of plastic wrappings consists in establishing a gradient of concentra-
tions or pressures across the wrapping, thus initiating the permeation of the gas.

According to the method for measuring the quantity of the permeating
gas, several measuring methods are known, from which only two possibilities
for measuring the absolute pressure difference follows: the volumetric and
the manometric methods. Although the ways of measurement with these
two methods are different, in both cases the interpretation of the temporal
course of gas-permeation is required which, taking into account up-to-date
knowledge [3], can be summarized as follows:

1. If the wrapping is considered as a sheet of thickness l which is per-
forated by small tubes, that is, by so-called ideal pores of diameter d [4],
then, there are two possibilities depending on the free mean path of the diffus-
ing gas. If the free mean path is smaller than the diameter of the pores and
if there is a pressure difference on the two sides of the wrapping, then a
POISEUILLE flow exists which is proportional to the difference of the squares
of the pressures existing at the two ends of the pore, and thus the quantity
of the transmitted gas can be expressed by the following equation:

$$V_d = \frac{k \cdot d^4 \cdot \pi (P_1^2 - P_2^2) t}{8 \cdot 16 \cdot \eta \cdot l \cdot R \cdot T}$$

where V_d = quantity of the gas passing through
     d = pore diameter
     l = thickness of wrapping
     R = gas constant
     T = gas temperature
     k = reducing factor
P_1, P_2 = pressures at the two ends (on the two sides) of the pore
            or wrapping
     η = viscosity
     t = time

If there is a concentration gradient then there is also diffusion and, according to FICK's law, the quantity of the gas passing through is proportional to the difference of the pressures:

$$V_d = \frac{k \cdot D \cdot d^2 \cdot \pi (P_1 - P_2) \, t}{l \cdot R \cdot T}$$

where D = diffusion constant.

If the free mean path is larger than the pore diameter then, in compliance with KNUDSEN, the quantity of the gas passing through is dependent on the pressure difference according to the following expression:

$$V_d = \frac{k \cdot d^3}{6} \cdot \sqrt{\frac{2 \cdot \pi \cdot g}{M \cdot R \cdot T}} \, \frac{(P_1 - P_2) \, t}{l}$$

where M = molecular weight.

It cannot be denied that these possibilities have very small probability, and even if they occur sporadically, they are of small importance. Namely, in case of FICK's diffusion, the gases having larger molecules ought to diffuse in a smaller quantity, because their diffusion constant is inversely proportional to their molecular weight. On the contrary, our mathematical-statistical investigations and estimations relating to the correlation between the molecular weights of several gases (CO_2, O_2, air, and N_2) and the gas permeabilities of some wrappings proved that the permeability of the transmitting wrappings increases with the molecular weight (Table 1).

Table 1

Correlation between gas permeability of wrappings and molecular weight of gas

Wrapping	Number of gases examined	Correlation coefficient
Polyethylene	3	0.993
PVC	3	0.997
Sarane	3	0.998
Cellophane	3	0.772
Cellulose acetate	3	0.985
Ethyl cellulose	3	0.989
Polystyrol	4	0.997
Copolimer of acrylic nitrylstyrol	3	0.478

In case of POISEUILLE flow, at all temperatures the gas quantity passing through ought to be proportional to the viscosity of the gas:

$$V_d \sim 1/\eta$$

However, in case of the wrappings tested, the permeabilities for N_2, O_2, and CO_2 are quite different from the true ratio 1:0.88:1.22; namely, the differences are considerably larger. This ratio is e. g. 1:2.9—5:15.7—30.9.

Finally, in case of the KNUDSEN diffusion, at all temperatures the gas permeability ought to be proportional to the square root of the molecular weight that is

$$V_d \sim 1/\sqrt{M}$$

However, in practice the gases N_2, O_2, and CO_2, do not diffuse with the ratio 1:0.94:0.8 to be deduced from the above correlation, but the diffusion of these gases occurs just inversely and at a considerably higher degree.

All these facts show that the three theories of gas permeation described above in practice play an insignificant role from which it can be logically inferred that the tested wrappings have at most an ultramicroporous structure.

2. At small pressures, theoretically it can be assumed that the passing of the gases through the pore wall takes place by adsorption and subsequently by diffusion. For this so-called *surface diffusion* the following expression is valid:

$$V_d = 2r \cdot \pi \cdot D' \cdot \sigma^2 \cdot tp/P_1 - P_2)$$

where $D' =$ special diffusion constant

$\sigma =$ adsorption coefficient

and the σ adsorption coefficient is dependent on the gas pressure. Therefore, the amount of gas passing through is proportional not only to the pressure difference prevailing on the two sides of the wrapping but also to its own pressure. This theoretical supposition has not yet been justified by practical observations.

3. The best explanation for gas permeation also controlled in practice was elaborated by BARRER [5]. According to him, on the side of high pressure the gas is dissolved at first by the constituents of the wrapping, then, due to the concentration gradient, it diffuses through the wrapping, and finally it emerges from it on the side of low pressure. The equation serving to express this *dissolution diffusion* is similar to FICK's expression:

$$V_d = P^* F \frac{P_1 - P_2}{l} t$$

but the diffusion coefficient of this equation, the so-called permeation coefficient P^*, is the product of the diffusion coefficient and the solubility of the gas.

The permeation coefficient and its two factors depend exponentially on the temperature; consequently, the permeability can be doubled by a temperature-increase of $10°C$. During the measurements this fact has to be taken into account. Moreover, care has to be taken that the results of the measurements should not be influenced by the occasional moisture contents of the
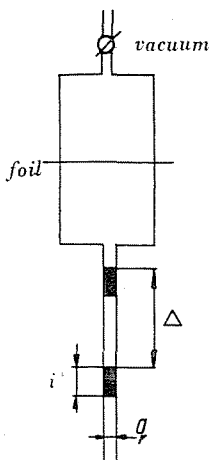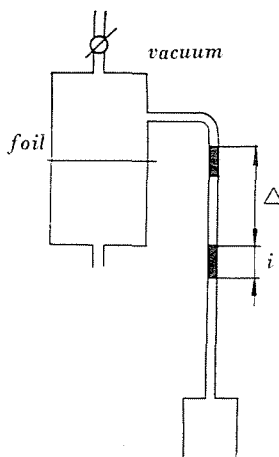

Fig. 1

Fig. 2

gases; therefore, in the following the experiences collected while measuring the permeability with dry gases are described.

To attain our experimental aims, four types of apparatuses could be devised which are illustrated by the following line diagrams:

1. volumetric measuring instrument: measurement on the side of high pressure (Fig. 1);
2. volumetric measuring instrument: measurement on the side of vacuum (Fig. 2);
3. manometric measuring instrument: measurement on the side of vacuum (Fig. 3);
4. manometric measuring instrument: measurement on the side of high pressure (Fig. 4).

From the relations theoretically deduced above according to the law of solution diffusion the validity of which has been proved in practice, the amount of gas passing through during unit of time is proportional to the

difference of pressures or partial pressures and the wrapping surface. Using this relation and the ideal gas law, equations describing the course in time of gas-permeation, and characteristic for the individual types of apparatus have been elaborated. By the calculations separable differential equations of the first order were obtained which could be solved even for the special case of the different types of apparatus. The equations are as follows:

In general for a volumetric apparatus:

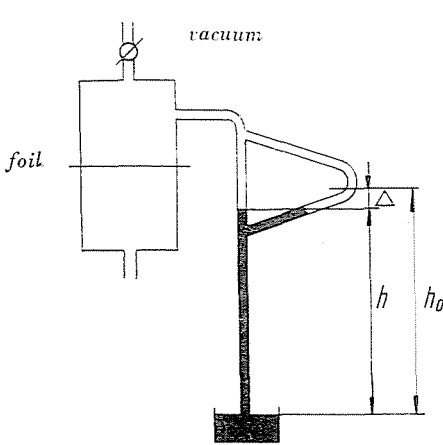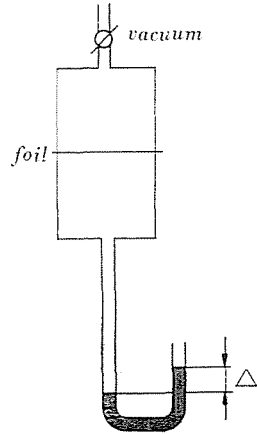$$dv = \frac{\lambda \cdot F \cdot R \cdot T}{\pi} (P - p)dt$$

Fig. 3

Fig. 4

In general for manometric instruments:

$$d\pi = \frac{\lambda \cdot F \cdot R \cdot T}{v} (P - p)dt$$

where v = volume (in general)

λ = permeation coefficient/1
F = surface
R = gas constant
T = gas temperature
p = pressure on vacuum-side
P = pressure on high pressure-side
π = pressure (in general)
t = time

moreover Δ = difference of mercury levels
v = volume on vacuum-side
q = cross-section of a capillary
P_0 = external atmospheric pressure
V = volume on high pressure-side
l = foil thickness

From the two general equations, the following equations were deduced for the special types of apparatus:

1. Volumetric instrument; measurement on the side of high pressure:

$$\Delta = \frac{v}{q}\,\frac{P - p_0}{P}\,\Bigl(1 - e^{-\frac{\lambda FRT}{v}t}\Bigr).$$

2. Volumetric instrument; measurement on the side under vacuum: There are two special possibilities. If

   a) P = constant (there is a gas stream or free air on the side of high pressure, that is the change of pressure can be neglected) then:

$$\Delta = \frac{\lambda F \cdot R \cdot T}{q}\,\Bigl(\frac{P}{p} - 1\Bigr)t$$

   b) $P \neq$ constant (there is a stationary gas of fixed volume on the side of high pressure) then:

$$\Delta = \frac{(P_0 - p)\,V}{pq}\,\Bigl(1 - e^{-\frac{\lambda FRT}{V}t}\Bigr).$$

3. Manometric instrument: measurement on the side under vacuum: Again two special cases can be imagined. If

   c) P = constant (there is a gas stream or free air on the side of high pressure, that is the change of pressure can be neglected) then:

$$\Delta = (P - p_0)\Bigl(1 - e^{-\frac{\lambda FRT}{v}t}\Bigr),$$

   d) $P \neq$ constant (there is a stationary gas of fixed volume on the side of high pressure) then:

$$\Delta = \frac{P - p_0}{\varepsilon}\,\Bigl(1 - e^{-\frac{\varepsilon\lambda FRT}{v}t}\Bigr) \text{ and } \varepsilon = 1 + \frac{v}{V}.$$

4. Manometric instrument, measurement on the side of high pressure:

$$\Delta = (P_0 - p)\Bigl(1 - e^{-\frac{\lambda FRT}{V}t}\Bigr).$$

The type of apparatus which is the most suitable for practical requirements was chosen on the basis of investigating and analyzing the circumstances and results of measurements built on these theoretical considerations. In case of wrapping thickness of 25 μ, the permeability of the plurality of the wrappings tested, ranged from 1.2×10^{-3} ml/days. dm^2.atm to 50 ml/day. dm^2.atm at 20°C. Generally the instruments were provided with a millimeter scale; therefore, for the sake of quick comparison, the times necessary for the shift of the mercury filament which could be well observed in the individual types of instruments, that is the times necessary for a shift of one mm, are summarized in Table 2, omitting the calculations. It can be stated that the volumetric estimation *under vacuum* and the instrument constructed on the basis of this principle is the method and the instrument, respectively, which is outstanding in every respect, quick, reliable and sensitive.

Table 2

Comparison of measuring apparati

Type of apparatus	Time necessary for a shift of 1 mm Hg: hours
Volumetric instruments	
1. Volumetry on the high pressure side	12.85
2. Volumetry on the vacuum side	
a) $P =$ constant	0.17
b) $P \neq$ constant	0.17
Manometric instruments	
3. Manometry on the high pressure side	13.5
4. Manometry on the vacuum side	
a) $P =$ constant	1.35
b) $P \neq$ constant	1.35

Summary

Based on theoretical considerations and by means of mathematical-statistical methods, investigations were carried out in order to elucidate the mechanism of gas-permeation through plastic wrappings. It could be stated that — of the various possibilities — the volumetric estimation of the gas on the vacuum side is that method which best satisfies the theoretical requirements of permeability measurements.

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