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vom Bruck, C.G., Eckert, W.R.. and
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PVC PACKS

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Damage to the health of workers who had spent many years in PVC-polymerisation plant, led to PVC gaining increasing publicity in respect of its use for packs. There is scarcely any doubt today that vinyl chloride can damage the health of people when it is breathed in with air over many years at high concentrations; in individual cases a particular form of liver cancer has also been observed.

Now toxicity is not a material property in itself. A toxic effect occurs only when a material with special properties is added to an organism in a certain concentration over a certain period. Only when a material can exert an effect for a sufficiently long period in a sufficiently high concentration, is the organism harmed. If this concentration is not reached within a specific period, there will be no damage. This is also true for VC.

As we know today, packs of PVC also contain monomer vinyl chloride, even if generally in only very small quantities. At normal pressure VC boils at -14°C . It was therefore assumed, earlier, that VC would completely escape at the high processing temperatures of PVC of $180^{\circ} - 220^{\circ}\text{C}$. However small quantities can be detected in the PVC with sufficiently sensitive methods. It was feared that these small quantities of VC might harm the consumer when they enter the foodstuff. Therefore we have tested the migration of VC from PVC and made a few theoretical observations on the mechanism of migration.

For the investigation of PVC- products a PVC sample is dissolved in dimethylacetamide in a closed container. According to H. Puschmann (1) the VC is determined by gas chromatography in gas samples which are removed from the headspace above the solution after 30 minutes at 50°C . Ether is used as an internal standard.

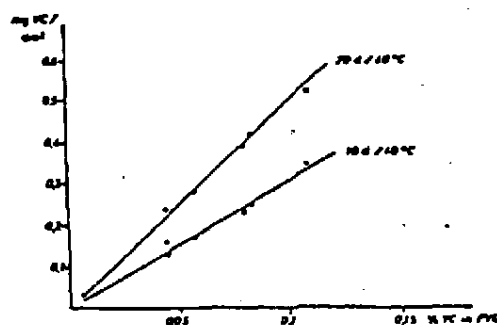
With this method it is possible to detect 0.00001% ($\Delta 0.1\text{mg/kg}$) VC in PVC and 0.000001% ($\Delta 0.01\text{mg/kg}$) VC in HB 307 test fat (this is supplied with constantly uniform composition by: NATEC-Gesellschaft für naturwissenschaftlich-technische Dienste mbH, Behringstr. 154, 2000 Hamburg 50) (2). For the following investigations the synthetic HB 307 test fat was used since it is particularly pure and therefore no troublesome substances need be anticipated in the course of the investigation.

In order to get some impression of the mobility of the VC in PVC, the emission of VC from deep-drawn PVC containers was first determined; these were hung up individually in the laboratory at room temperature (Table 1). After 35 days the VC-content of one PVC lid fell from 0.006% originally to 0.002%, in another from 0.0017% to 0.0006%. With individual storage, therefore, as much as one half to one third of the VC is lost in a period of about a month.

Table 1: VC losses of PVC deep-drawn products; individual storage at room temperature

	Wall thickness (μm)	VC content in %	
		Initially	after 35 days
Lid 1	150	0.006	0.002
Lid 2	150	0.0017	0.0006
Container 1	250 - 300	0.002	0.001
Container 2	250 - 200	0.004	0.002

In addition the migration of VC from PVC films with different VC contents was investigated. Figure 1 shows the migration of VC from PVC in the HB 307 test fat under standard conditions.



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It can be seen that, both after 10 and 20 days of storage there is a linear relationship between the initial VC content in the PVC and the migrated quantity of VC up to VC contents of somewhat more than 0.1%. This linearity is explained by the Fick diffusion theory. This argues that the structure of the PVC is not harmed by these small quantities of VC i.e. up to 0.1% VC does not have any plasticizing effect on PVC. On the other hand the migration must rise disproportionately with an increasing VC-content in the PVC. At present no data can be supplied about concentrations below 0.005% in PVC.

Table 2

Comparison of the migration of VC in triglyceride;
conditions: 40°C over 10 and 20 days respectively,
PVC with 0.035% VC initial value, thickness 160 μ m

Triglyceride	Migration after 10 days (mg/dm ²)	Migration after 20 days (mg/dm ²)	VC-content of the PVC after 20 days (%)
HB 307	0.15	0.17	0.020
Sunflower oil	0.14	0.17	0.021
Emulsion of 80% sunflower oil and 20% water	0.15	0.24	0.018

As Table 2 shows, the HB 307 test fat behaves in a manner similar to that of natural sunflower oil and an emulsion produced from such an oil of 20% water in 80% sunflower oil. After 10 days at 40°C approximately equal quantities of VC have migrated in all three contact media. After 20 days at 40°C the VC content of the emulsion is possibly somewhat higher; the difference has not, however, been proved statistically. Once again the VC content of the PVC has fallen significantly.

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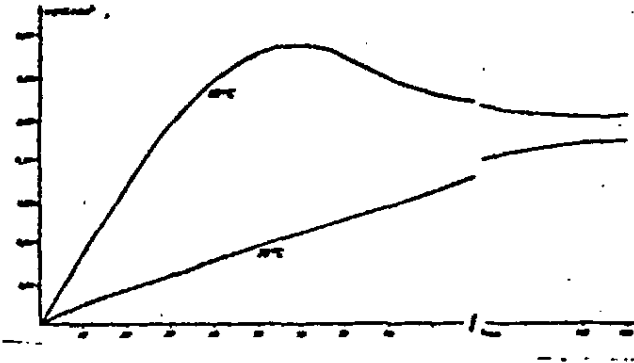


Figure 2: Migration of VC in HB 307 (Initial value: 0.006% VC in PVC)

In addition the progression in time of the migration of VC from PVC into HB 307 (Figure 2) was extensively investigated. The experiment ran for 160 days at temperatures of 40°C and 20°C respectively. A temperature of 40°C was chosen in order to accelerate migration, one of 20°C to simulate, approximately, behaviour at room temperature. At 20°C there is, up to about 100 days, a linear increase of the VC in HB 307; at 160 days the increase has been significantly reduced. The result at 40°C is more interesting. Here a clear maximum is reached after about 50 to 60 days; subsequently the VC-content of the HB 307 falls slowly which is also to be anticipated in accordance with the theory discussed in the following. After 160 days at 40°C the VC-content of the PVC fell from 0.006% originally to below 0.0001%. The appearance of a maximum means that VC must have migrated back from the HB 307 through the PVC into the outer atmosphere. Because of its volatility the VC thus represents an interesting special case of migration from packs into their contents.

By means of the Fick formulation of the diffusion theory the distribution of the VC in PVC and in fat was calculated as a function of the depth of penetration and the time. As simplest approximation it was assumed that the PVC is in contact with air on both sides (Figure 3, left-hand side - see, for example, J. Crank, The Mathematics of diffusion, Oxford University Press, London, 1967). The ordinate gives the VC concentration, the abscissa the distance from the film surface. At the start one obtains, in theory, an exact rectangular curve since the initial

concentration was assumed to be constant. As more VC is lost, the curves become flatter and flatter. The basis of the calculation is the well-known diffusion equation:

$$D_{PVC} \frac{\partial^2 c}{\partial x^2} - \frac{\partial c}{\partial t} = 0$$

which describes the concentration c of the VC in the PVC as a function of location x and time t : D_{PVC} is the coefficient of diffusion of the VC in PVC, which changes with the experimental temperature.

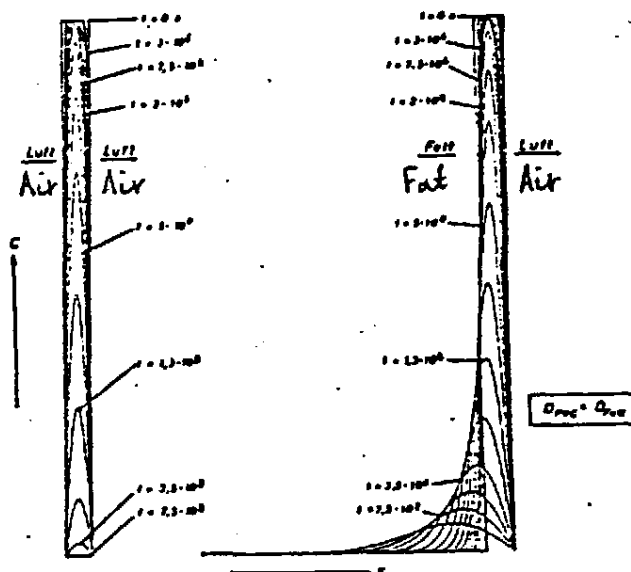


Figure 3: Dependence of the VC concentration c on the depth of penetration x at different periods t .

Conditions become somewhat more complicated when there is air on one side of the film but HB 307 test fat of specific thickness on the other side (Figure 3, right-hand side). It is assumed that on the one side of the air the VC-concentration is practically always kept at zero. On the other side the concentration

of VC in the fat increases gradually. It was assumed here that the coefficients of diffusion in HB 307 and PVC are of the same magnitude which at least gives the anticipated VC-concentration in the fat. Figure 4 shows the spatial progression of the VC-concentration under the other extreme, the assumption of an infinitely large coefficient of diffusion of the VC in the fat. In the case of liquid fat, for example, this case occurs with convection. It can clearly be seen that, after a certain period, there will be rediffusion of the VC from the HB 307 into the PVC and subsequently outwards.

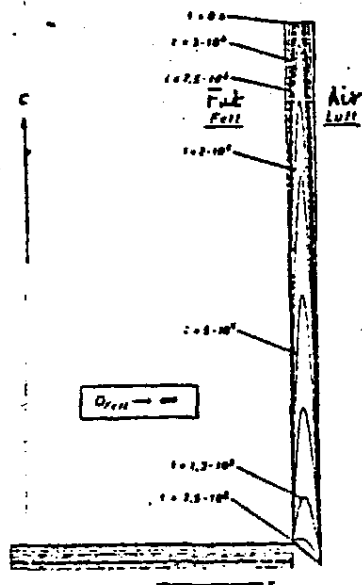


Figure 4: Dependence of the VC concentration c on the depth of penetration x at different periods t .

The true conditions are reproduced by a state which lies between the data on Figure 3 on the left and Figure 4.

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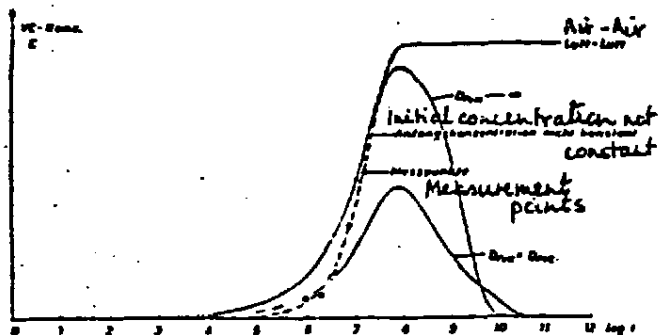


Figure 5: Mean VC-concentration in the HB 307 test fat as a function of time (20°C)

If the progression over time of the mean concentration of the VC in the HB 307 test fat is calculated in accordance with these models, the results are curves like those shown in Figure 5 (unbroken curves), time being plotted in a logarithmic scale. The measured values of Figure 2 are also plotted in this graph. As can be seen, the VC-concentration in the fat rises too early according to this theory: in addition the curve is too flat. The situation is correctly reproduced, however, when it is remembered that the film was stored for some period before the experiment. This means that, at the beginning of the experiment, there was no rectangular distribution but a concentration gradient of the VC in the film. If such a concentration gradient in the PVC is borne in mind, the measured values can be closely approximated by the theoretical curve (Figure 5 dotted curve). The coefficients of diffusion of VC in PVC, the storage period before the start of the experiment and the initial VC-concentration during film production can be calculated for both experimental temperatures.

The coefficients of diffusion thus calculated (2.3×10^{-12} at 20°C and 1.5×10^{-11} at 40°C) are in satisfactory agreement with the literature values (7.7×10^{-13} at 20°C and 4.48×10^{-12} at 40°C) when it is remembered that the latter was measured on PVC-powders; on the other hand the former were obtained by measurement on PVC which, as a result of processing, contains a few percent of additives which disturb the PVC structure and thus lead to greater coefficients of diffusion. The calculated storage

periods are $1 \cdot 10^7$ s at 20°C and $2.5 \cdot 10^6$ s at 40°C .

Finally a few practical consequences will be discussed. As a result of the linear dependence between VC-concentration in the contents and the initial concentration in PVC under identical conditions (quantity, geometry, contact medium) the concentrations in the contents after specific periods can be calculated from the VC-concentrations in the pack.

In Figure 2 0.03mg VC/dm^2 was found as a migration value with 0.006% VC as an initial value in PVC at 20°C after 84 days = 12 weeks. On the assumption of a ratio of 6 dm^2 packaging material per kg of contents a concentration of $0.00002\% = 0.2\text{mg VC/kg}$ contents is then calculated. This is one fifth of the concentration currently regarded as tolerable in Germany.

On average about 1kg of foodstuffs are eaten by an adult per day. If it is also borne in mind that only a fraction of these foodstuffs are packaged in PVC, it can be seen that danger to the consumer is actually very much smaller, even with PVC with 0.006% VC.

Finally your attention is drawn to the fact that, of course, one can demand that the VC content of packs be reduced. However one should be clear that this is associated with additional costs as is shown by the following information supplied by PVC manufacturers and processors. Additional measures to produce PVC packs with a VC-content of $<0.0005\%$ VC, increase the price by about 3%; the costs of waste air cleaning have not yet been included.

English PVC-producers alone (without processors) reckon with an investment of DM 80 million (for 410,000 tonnes PVC/year) to keep below a VC concentration below 25 ppm in the room air. According to information supplied by F.D. Snell (3), U.S. Dept. of Labour, the costs of 1 kg of PVC rise by 4 pf if a maximum permitted room air concentration of 50 ppm is fixed, 15 pf. with < 25 ppm and 44 pf/kg PVC with < 10 ppm VC in the room air i.e. about 30%.

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References

1. H. Puschmann, The analytical determination of the residual monomer content in PVC and simulating foodstuffs, paper given at the PVC discussion day, Darmstadt, 26 and 27 September 1974.
2. W. R. Eckert, Fette-Seifen-Anstrichmittel, 77, 319 (1957)
3. F.D. Snell, Modern Plastics Inc., October 1974, p. 40.