The formation of dimethyldifluorosilane as described by Hofler et al may be caused by another reaction.


Guruviah’s conclusion that the process of corrosion in painted mild steel is governed by the diffusion of oxygen and not by the diffusion of water is not justified.


The explanation for the behaviour of picric acid in aqueous solutions, as given by Ives and Moseley, is based on an erroneous interpretation of the experimental results.


Yaseen and Ashton’s results with regard to the solvent retention in phenolic resin films can be interpreted in terms of plasticisation of the phenolic resin films by water.


The arguments of Matsuda et al that Cr\(^{\text{V}}\) is essential for the catalytic activity of Chromium oxide on silica-alumina are not conclusive.

VI
The data for the diffusion of ethyl p-aminobenzoate in silicon rubber membranes containing a silica filler are interpreted by Most in an unsatisfactorily manner.


VII
For the study of the kinetics of the oxidation of the bromide ion in an aqueous nitric acid Lonstaff used an unsuitable method.


VIII
The general and harmonious development of human society can only take place when the present nationalistic character of politics will disappear.

IX
In the past the introduction of industrial innovations have been made without adequate consideration of the social consequences.

X
At present the distinction between pure and applied science is not justified any more.
WATER TRANSPORT
IN PAINT FILMS

PROEFSCHRIFT
TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE
TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE
HOGESCHOOL DELFT, OP GEZAG VAN DE RECTOR
MAGNIFICUS IR. H. R. VAN NAUTA LEMKE, HOOG-
LERAAR IN DE AFDELING DER ELEKTROTECHNIEK,
VOOR EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN
OP WOENSDAG 8 SEPTEMBER 1971 TE 16.00 UUR

DOOR

DAN YOSEF PERERA
MASTER OF SCIENCE
GEBORNE TE BOEKAREST

MOUTON & CO. — 'S-GRAVENHAGE
Dit proefschrift is goedgekeurd door de promotor
PROF. DR. IR. P. M. HEERTJES.
To Henriette, Miriam and Judith
I hereby express my sincere thanks to all who helped me in preparing this thesis. I am particularly indebted to the personnel of the Verfinstituut TNO.
My special thanks are presented to Dr. R. Bult and Dr. P. Selier of the Verfinstituut TNO and Dr. D.T.F. Pals of the Central Laboratory TNO for their helpful and stimulating discussions during the course of the work. I am grateful to Mrs. Th. Albers for her co-operation in preparing the manuscript, and to Mr. B.H. van Nieuwenhoven, Mr. H. Vogt and Mr. F.I. van Bloois for technical help.
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The study of water transport in paint films is obviously of practical as well as of theoretical interest. Practically, it is of interest because paints are important protective materials, and theoretically because it involves the processes of permeation, sorption and diffusion in complex membranes. Water is generally recognized as a significant paint destroying agent. It may act per se or it may accelerate the action of other agents, e.g. ultraviolet radiation, temperature, oxygen, chemicals, micro-organisms, etc. In recent years there has been a renewed interest in water transport in paint films. Attention has been paid to such aspects as blister formation, correlation of water uptake-values with those of permeation, the interdependence between pigment-binder interaction and water absorption of paint films, liquid water permeation, and so on. Although a relatively large amount of work has been carried out a number of the conclusions appear to be contradictory and many problems remain unsolved. In most cases, these problems had to be treated qualitatively because of experimental and theoretical difficulties. The purpose of the present work is to elucidate the reason for some of the contradictions found in the literature and where possible to give a quantitative interpretation of the results. Four binders and two pigments, which were considered to be representative of a large range of materials used to-day in the paint industry, were used in this study. Two binders were hydrophilic namely an alkyd resin and an epoxy resin, and two were hydrophobic namely a chlorinated rubber with and without a plasticiser. The two pigments were a titanium dioxide and a red lead. The complexity of the problems as well as of the films, necessitated the division of the study into several aspects. In Chapter I, water sorption and water permeation measurements carried out with non-pigmented films under different experimental conditions, are described. The coefficients of permeability, solubility and diffusion are determined and their interdependence is discussed. In Chapter II the different dependencies of the diffusion coefficient on the water concentration are interpreted in the light of the 'clustering theory'.
In Chapter III the water transport process, under the influence of differences in osmotic pressure, is investigated.
In Chapter IV the experimental data obtained by means of differences in water vapour pressure and osmotic pressure are compared.
Chapter V is concerned with experiments carried out with pigmented films. Permeability, solubility and diffusion coefficients are calculated and expressed as a function of pigment volume fraction. A model for water permeation through pigmented films was developed.

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I. Permeation and sorption measurements with non-pigmented films

I-1. SUMMARY

Permeation and sorption of non-pigmented free paint films have been investigated. The variation of the permeability coefficient with the concentration is explained by the corresponding changes in the solubility and diffusion coefficient on which it depends. For hydrophilic materials the diffusion coefficients are obtained from an amended form of Fick’s law, by applying the principles of irreversible thermodynamics. The difference in the values of the diffusion coefficient determined from steady state and transient procedures are interpreted as a proof of the presence of immobile molecules of water in the film during the permeation process.

I-2. INTRODUCTION

The principal rôle of paint films is to protect the substrate from destructive agents. A premature deterioration of the paint films, by means of blistering, peeling, cracking, checking, etc., will accelerate destruction of the substrate.

In general, the paint films are permeable to water; it is usually accepted that water is totally or partially responsible for many forms of paint deterioration. The transport of water through paint films may occur via one or more processes. When these involve differences in vapour pressure, osmotic pressure, electrical potential, temperature and so on, the transport process is commonly referred to as permeation, osmosis, electro-osmosis, thermo-osmosis, respectively.

The rate of water transport can be a function of the nature of the paint components, experimental conditions, etc.

This Chapter is concerned with the mechanism of permeation and sorption of water in four non-pigmented films. The four binders are representative of some of the main materials used in the paint industry.
The permeability, solubility and diffusion coefficients are evaluated and their interdependence discussed. Some contradictions found in the literature are explained.

I-3. THEORETICAL

It can be seen from the literature that, for the most part two methods are used to investigate water transport through paint films, namely: permeation and sorption.

I-3.1. Permeation method
Permeation measurements are generally carried out under steady state conditions, in which the water flux through a film is determined under a constant pressure difference over the film. The mechanism of the permeation process can be considered as consisting of three steps:

- the transport to and the sorption of water at one boundary of the membrane, followed by
- the diffusion through the membrane under a concentration gradient, and
- the desorption of water at and the transport from the other boundary of the membrane.

As will be seen later, for all the materials investigated, the second step is by far the slowest of the three, and consequently it is also the rate controlling step of the whole process of permeation.

I-3.1.1. General case. A transport phenomenon can be treated in the general way by the application of the principles of irreversible thermodynamics. Thus, the equation that relates the flux \( q \) with the driving force \( X_R \) is expressed by relation\(^1\):

\[
q = \sum_{i=1}^{n} K_{ik} X_R \quad (I-1)
\]

where \( K_{ik} \) represents Onsager's coefficients. For the transport of a penetrant through a membrane as a result of a concentration gradient over the distance \( x \), Eq. (I-1) becomes\(^2,3,4\)

\[
q = -Kc \frac{d\mu}{dx} \quad (I-2)
\]

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$K$ is a proportionality factor, $\mu$ the chemical potential of the penetrant (water), and $c$ the overall concentration existing in the film. For a non-ideal system $\mu$ can be expressed as follows:

$$\mu = \mu^o + RT \ln a \quad \text{ (I-3)}$$

In Eq. (I-3), $a$ represents the activity of the penetrant in the membrane and $\mu^o$ the chemical potential of the pure penetrant (water).

Substituting Eq. (I-3) in Eq. (I-2), it follows that:

$$q = -Kc \frac{d(\mu^o + RT \ln a)}{dx} \quad \text{ (I-4)}$$

Since at constant temperature and pressure, $\mu^o$ is a constant, by differentiation, Eq. (I-4) becomes:

$$q = -KRTc \frac{d \ln a}{dx} \quad \text{ (I-5)}$$

Assuming that all the penetrant molecules have the same mobility in the membrane, the product $KRT$ can be substituted by a coefficient $D$, which is called the diffusion coefficient.

$$q = -Dc \frac{d \ln a}{dx} \quad \text{ (I-6)}$$

or:

$$q \, dx = -D \frac{c}{a} \, da \quad \text{ (I-7)}$$

Since at the steady state the flux ($q$) is the same through each section of the membrane, the left hand side of Eq. (I-7) can easily be integrated.

$$q \int_q^L \, dx = q \, L = -\int_{a_1}^{a_2} D \frac{c}{a} \, da \quad \text{ (I-8)}$$

The right hand side of Eq. (I-8) can be integrated, if it is assumed that $D$ is independent of the concentration.

For those materials where $D$ is dependent on the concentration, the $D$-values calculated in such a manner are only ‘mean values’.

$$qL = -\int_{a_1}^{a_2} D \frac{c}{a} \, da = D \int_{a_1}^{a_2} \frac{c}{a} \, da \quad \text{ (I-9)}$$

The integral can be solved since the interdependence between $c$ and $a$ can be obtained from separate measurements of sorption. This procedure is
justified, because the chemical potentials of water at boundaries separating the film \( \mu_f \) and the water phase \( \mu_w \), at equilibrium, are equal, namely:

\[
\mu_f = \mu_w \quad \text{or:} \\
\mu_f^0 + RT \ln a_f = \mu_w^0 + RT \ln a_w.
\]

Since the standard chemical potentials \( \mu_f^0 \) and \( \mu_w^0 \) are taken as equal, it follows that

\[ a_f = a_w. \]

In order to be able to express activities numerically, it is convenient to choose as standard state, the solvent in the pure state (of vapour pressure \( p_o \)), for which the activity is arbitrarily taken as unity. It follows, therefore, that the activity \( a \) of a solvent of vapour pressure \( p \) at the same conditions of temperature and pressure is given by

\[ a = \frac{p}{p_o}. \]

If it is difficult to obtain a numerical expression for \( c = f(a) \), graphical integration can be used. By plotting in a graph \( c/a \) against \( a \), the surface between the limits of each system can be determined and a 'mean diffusion coefficient' \( \bar{D} \), can be calculated.

\[
\bar{D} = \frac{qL}{\int_{a_1}^{a_2} \frac{c}{a} \, da} \quad \text{(I-10)}
\]

By a similar procedure a 'mean concentration' of water in the film \( \bar{c} \), can also be determined, but in this case from a graph representing \( c \) versus \( a \):

\[
\bar{c} = \frac{\int_{a_1}^{a_2} c \, da}{a_1 - a_2} \quad \text{(I-11)}
\]

I-3.1.2. Ideal case. It is instructive to note that, from the expression derived from thermodynamic considerations, for a transport phenomenon, namely:

\[
q = -D \bar{c} \frac{d \ln a}{dx} \quad \text{(I-6)}
\]

all the relations of permeability, solubility, and diffusivity known for ideal cases can be deduced.
Thus, by writing Eq. (I-6) as
\[
q = -Dc \frac{d \ln a}{dx} = -D \frac{d \ln a}{d \ln c} \cdot \frac{dc}{dx} \tag{I-6}
\]
and assuming that the concentration changes linearly with the activity:
\[
\frac{d \ln a}{d \ln c} = 1,
\]
Eq. (I-6) becomes:
\[
q = -D \frac{dc}{dx} \tag{I-12}
\]
The equation (I-12) is mathematically analogous with Fourier's relationship of heat by conduction, and it is commonly referred to as Fick's first law of diffusion.

For a stationary state, integration gives:
\[
q \int_{c_1}^{c_2} dc = -D \int_{c_1}^{c_2} dc = \overline{D} \Delta c \quad \text{or:}
\]
\[
\overline{D} = \frac{qL}{\Delta c} \tag{I-13}
\]
Eq. (I-13) is the same as Eq. (I-10) if a linear dependence of the concentration on the activity exists.

By replacing \(a\) by \(p/p_o\), in Eq. (I-6), the well known expression of the permeability coefficient \((P)\) can also be derived:
\[
q = -D \frac{c}{p} \frac{dp}{dx} \tag{I-14}
\]
According to Henry's law:
\[
\frac{c}{p} = S \tag{I-15}
\]
where \(S\) is the solubility coefficient.

By substituting Eq. (I-15) in Eq. (I-14):
\[
q = -DS \frac{dp}{dx} \tag{I-16}
\]
The product of \(D\) and \(S\) is called the permeability coefficient \((P)\):
\[
P = DS \tag{I-17}
\]
Then Eq. (I-16), can be written as:

\[ q = -P \frac{dp}{dx} \]

which, under stationary conditions may be integrated:

\[ q \int_{0}^{L} dx = -P \int_{p_1}^{p_2} dp = P \Delta p \]

or:

\[ P = DS = \frac{qL}{\Delta p} \]  \hspace{1cm} (I-18)

It has already been demonstrated\textsuperscript{5,6,7} that these equations are valid only if complete inertia exists between the film and the penetrant. Previous investigations on water permeation through polar polymers showed that in this case \( P, S \) and \( D \) are not constant at all but are a function of the water concentration.

Similar behaviour for the hydrophilic binders investigated was expected. Thus, a complete investigation calls for the determination of concentration-dependence of all three factors.

For the sake of simplicity, the treatment is limited to the isothermal case (temperature constant) and to a steady state (flux constant). Then \( P, D \) and \( S \) are independent of the temperature and the time.

I-3.2. \textit{Sorption method}

The sorption technique used for the determination of diffusion coefficients is a non-steady procedure in which the mass of penetrant gained or lost by the film, when exposed to different but constant activity is followed gravimetrically.

This situation is described by the following expression:

\[ \frac{dc}{dt} = D \frac{d^2c}{dx^2} \]  \hspace{1cm} (I-19)

which in the literature is usually called Fick’s second law of diffusion. For the boundary conditions corresponding to the present experimental situations, Crank\textsuperscript{8} and Park found the following solution for Eq. (I-19):

\[ \frac{Mt}{Me} = 1 - \left( \frac{8}{\pi^2} \right) \sum_{m=0}^{\infty} \left\{ \frac{1}{(2m+1)^2} \right\} \exp \left\{ -\left( \frac{2m+1}{\pi} \right)^2 \frac{D \pi^2}{L^2} \right\} \]  \hspace{1cm} (I-20),

where \( D \) is the diffusion constant, \( L \) the film thickness; \( m = 0, 1, 2, \ldots \).
$M_t$ is the weight change (sorption or desorption) at time $t$; and $M_e$ is the equilibrium weight change. By representing $M_t/M_e$ versus $t^2/L$ graphically, the so-called 'reduced sorption curves'\textsuperscript{8,9} can be obtained. Equation (I-20) can be simplified if the linear portion of the 'reduced sorption curve' extends to the time $M_t/M_e = \frac{1}{3}$. Then, the value $t/L^2$ for which $M_t/M_e = \frac{1}{3}$, conventionally written as $(t/L^2)_\frac{1}{3}$, is given by:

\[
(t/L^2)_{\frac{1}{3}} = -\frac{1}{\pi^2 D} \ln \left\{ \frac{\pi^2}{16} - \frac{1}{9} \left( \frac{\pi^2}{16} \right)^9 \right\};
\]

or with an error of 0.001% it can be written:

\[
D = \frac{0.0494}{(t/L^2)_{\frac{1}{3}}}
\]

Unfortunately Eq. (I-21) cannot be applied for sorption which does not give initial linear 'reduced sorption curves'. It could be applied to hydrophobic materials, but only for a limited number of cases for hydrophilic ones. Once $D$ is determined, $P$ may be calculated from: $P = D \times S$.

I-4. EXPERIMENTAL

I-4.1. Materials

The following binders were investigated:

1. An air drying medium length oil alkyd synthesized in the laboratory from linseed oil fatty acids, glycerol and phthalic anhydride (35%).
2. An epoxy resin (Epikote 1001), cured with diethylene triamine (ratio = 25/1 by weight).
4. Chlorinated rubber with plasticiser (chlorinated diphenyl) (ratio = 2.7/1 by weight).

I-4.2. Film preparation

Tin foils were laid on wet glass plates and pressed with a rubber roll until a perfect flat surface was obtained. The binder solutions were cast on the tin foils with a doctor blade of the desired thickness, and the system was dried in a room at constant temperature (20°C + 1) and relative humidity (65% ± 2), for a period of 30 days. Films of the desired area were removed from the tin foils by amalgamating the tin with mercury. Before use the films were cleaned and immersed in continuously stirred...
distilled water for 48 hours, in order to free them from solvent and other water soluble substances. The films were dried again, for 48 hours in a vacuum stove at 30°C.

For the test only films with a maximum deviation of ± 1 μm in thickness per dry film were used. Attempts were also made to obtain films on other substrates such as glass, mercury, photographic paper and Teflon. With some binders good results were obtained.

To avoid the substrate having any possible influence on the water transport measurements it was decided to prepare all the films on the same substrate, i.e. tin foil.

I-4.3. Permeation measurements

The flux at steady state was determined with the cup-method, by measuring the loss of weight at various time intervals. As soon as the stationary states were reached, the measurements were discontinued.

Two systems were investigated.

<table>
<thead>
<tr>
<th>System</th>
<th>Cups</th>
<th>Desiccator</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>different RH</td>
<td>RH = 0 (P₂O₅)</td>
</tr>
<tr>
<td>II</td>
<td>RH = 100%</td>
<td>different RH</td>
</tr>
</tbody>
</table>

In system I, the water transfer occurs from various RHs acting in the cup to RH = 0 in the desiccator. In system II the water transfer occurs from RH = 100% in the cup to various RHs in the desiccator. Using these two systems almost the whole range of RHs was investigated, and not only two or three situations as demanded by ASTM-E-96-66.

Saturated solutions of lithium chloride, calcium chloride, calcium nitrate, sodium chloride, potassium bisulphate and zinc sulphate, all at 20°C, were used to obtain a water activity of 0.15, 0.32, 0.55, 0.75, 0.86 and 0.90, respectively.

After the cups were filled about half full with the desired solution and the films were tightly secured between the cups and waxed aluminium rings, in such a way that any possible leakage was avoided, the cups were placed in desiccators. The desiccators and balance were kept in a room at constant temperature (20°C ± 1) and RH (65% ± 2).

Preliminary experiments were performed to assess the validity of the cup method.

Two series of experiments were carried out: In the first series, the amount (or level) of water in the cup was varied. No change in water transfer at the steady state was found. Identical results were obtained when the films were in direct contact with the liquid water.
In the second series of experiments an equal number of cups were placed in two desiccators, one of them being equipped with a ventilator. From the equal results obtained with different speeds of ventilation and without ventilation it was concluded that, for a small number of cups (i.e. three) placed in sufficiently large desiccators (i.e. about 5 litres), ventilation was not necessary. This result is also in agreement with the fact that the evaporation rate at the lower concentration side of the film ($\sim 10^{-2} - 10^{-1}$ g/cm$^2$.h) greatly exceeds the transfer rates ($\sim 10^{-5}$ g/cm$^2$.h) under equivalent test conditions.

By these means it was established that, for all the systems and the materials investigated, every resistance which might affect the permeation process, except the resistance of the film itself, was negligible.

The experimental error varied from 7% to 9%. Each data was measured in triplicate.

To avoid any possible influence of the film thickness on $P$, $S$ and $D$-values, 'identical' thicknesses (with a maximum deviation of $\pm 2 \mu$m, between different films of the same binder) were used.

Fig. I-1. Schematic diagram of quartz spring balance.
I–4.4. Sorption measurements

The sorption (desorption) isotherms were determined with a quartz spring balance\(^{14}\), known as the McBain or isoteniscop method, at 20°C. A schematic description of the apparatus used is given in Fig. I–1.

A complete sorption cycle (absorption-desorption) of a film was made first, exposing it to vacuum (0.01 mmHg), then exposing it to the desired water activity, and finally exposing it to vacuum again.

The gradual increase (for absorption) or decrease (for desorption) in the weight of the film was recorded as a function of time. A cathetometer was used for readings. In this way the absorption-desorption measurements were successively carried out over a range of water activities, namely 0.1; 0.2; 0.3; 0.4; 0.6; 0.9. The different water activities were obtained using a water reservoir, connected to a cooling/heating system. The quartz spring balance extended 1 cm for each 40 mg, and the accuracy of the reading with the cathetometer used was 0.002 cm. It follows that, for the films investigated, with a weight between 200 mg and 300 mg, the experimental error was about 0.05%.

Water uptake measurements at \( a = 1 \) (liquid water) were done separately. Films of known weight and size were immersed in continuously stirred distilled water, at 20°C, for different lengths of time. The films were then removed from the water, blotted free of superficial water and weighed immediately. They were then placed in a desiccator and weighed weekly until a constant weight was obtained.

I–5. RESULTS

The sorption isotherms, as presented in Fig. I–2 and Table I–1 show that the four binders have dissimilar sorption behaviour.

The hydrophilic epoxy and alkyd resins have typical S-form sorption curves, characteristic of polymers with strong hydrogen bonding sites\(^{15}\) and belonging to the group II (multilayer absorption) in the B.E.T.\(^{14,16}\) (Brunauer, Emmet and Teller)-classification. For such materials water uptake is relatively high at very low water activity (see the rise of the curve at very low \( a \)), and at high \( a \) it increases again strongly. The two effects are pronounced at low activity for the epoxy resin, and at a high activity for the alkyd resin.

From the two types of permeation systems investigated it can be seen that for the same absolute difference in activity (\( \Delta a \)), different values of \( P \) are obtained (see Fig. I–3A and Table I–2). The values are always higher for system II where, on both sides of the film, \( a \) is higher than zero. This indicates that \( P \) is concentration-dependent.
Table I-1. Water concentration at different activities

<table>
<thead>
<tr>
<th>a</th>
<th>Alkyd resin</th>
<th>Epoxy resin</th>
<th>Chlorinated rubber</th>
<th>Chlorinated rubber with plasticiser</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2.90</td>
<td>3.30</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.2</td>
<td>4.40</td>
<td>5.40</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.3</td>
<td>—</td>
<td>6.60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.4</td>
<td>10.90</td>
<td>8.10</td>
<td>0.69</td>
<td>0.35</td>
</tr>
<tr>
<td>0.6</td>
<td>18.00</td>
<td>10.80</td>
<td>0.92</td>
<td>0.71</td>
</tr>
<tr>
<td>0.9</td>
<td>35.00</td>
<td>15.91</td>
<td>1.38</td>
<td>4.97</td>
</tr>
<tr>
<td>1</td>
<td>42.40</td>
<td>17.80</td>
<td>1.58</td>
<td>19.25</td>
</tr>
</tbody>
</table>

Fig. I-2. Concentration c (in g/cm³) vs. activity (a).

The increase of $P$ with the water concentration ($\varepsilon$) (see Fig. I-3B) in the film can be explained only if $\bar{D}$ and/or $S$ depend on the water concentration.
Fig. I-3A. Permeability coefficient \( P \) (in g/cm.h.mmHg) as a function of difference in activity (\( \Delta a \)).

- system I (in cup: various \( a \); in desiccator: \( a = 0 \))
- system II (in cup: \( a = 1 \); in desiccator: various \( a \))

Fig. I-3B. Permeability coefficient \( P \) (in g/cm.h.mmHg) as a function of mean water concentration \( \bar{c} \) (in g/cm²).
Table I-2. $\bar{c}$ (g/cm$^3$), $P$ (g/cm.h.mmHg), $S$ (g/cm$^3$.mmHg) and $D$ (cm$^2$/h) under different experimental conditions

**System I**

<table>
<thead>
<tr>
<th>$a_1-a_2$</th>
<th>Alkyd resin</th>
<th>Epoxy resin</th>
<th>Chlorinated rubber</th>
<th>Chl. rubber with plasticiser</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{c} \times 10^3$</td>
<td>$P \times 10^9$</td>
<td>$S \times 10^3$</td>
<td>$D \times 10^6$</td>
</tr>
<tr>
<td>0.15</td>
<td>2.50</td>
<td>9.61</td>
<td>1.55</td>
<td>6.20</td>
</tr>
<tr>
<td>0.32</td>
<td>4.10</td>
<td>14.20</td>
<td>1.48</td>
<td>9.63</td>
</tr>
<tr>
<td>0.55</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.75</td>
<td>10.30</td>
<td>17.60</td>
<td>1.65</td>
<td>10.70</td>
</tr>
<tr>
<td>0.86</td>
<td>13.30</td>
<td>19.85</td>
<td>1.74</td>
<td>11.40</td>
</tr>
<tr>
<td>0.90</td>
<td>14.20</td>
<td>21.61</td>
<td>1.79</td>
<td>12.07</td>
</tr>
<tr>
<td>1</td>
<td>17.00</td>
<td>28.00</td>
<td>1.85</td>
<td>15.10</td>
</tr>
</tbody>
</table>

**System II**

<table>
<thead>
<tr>
<th>$a_1-a_2$</th>
<th>Alkyd resin</th>
<th>Epoxy resin</th>
<th>Chlorinated rubber</th>
<th>Chl. rubber with plasticiser</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{c} \times 10^3$</td>
<td>$P \times 10^9$</td>
<td>$S \times 10^3$</td>
<td>$D \times 10^6$</td>
</tr>
<tr>
<td>1</td>
<td>19.80</td>
<td>28.50</td>
<td>1.87</td>
<td>15.40</td>
</tr>
<tr>
<td>1.04</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1.05</td>
<td>28.20</td>
<td>36.33</td>
<td>2.00</td>
<td>18.20</td>
</tr>
<tr>
<td>1.07</td>
<td>33.85</td>
<td>47.60</td>
<td>2.15</td>
<td>22.20</td>
</tr>
<tr>
<td>1.08</td>
<td>37.50</td>
<td>55.30</td>
<td>2.22</td>
<td>25.00</td>
</tr>
<tr>
<td>1.09</td>
<td>38.80</td>
<td>63.52</td>
<td>2.36</td>
<td>27.00</td>
</tr>
</tbody>
</table>
For the hydrophobic materials, any pronounced change in $P$, $D$ and $S$ with $a$ or $c$ is not to be expected, since the polar groups are absent. In spite of the fact that both chlorinated rubber and its plasticiser are hydrophobic, the presence of the plasticiser considerably changes the properties of this binder. For chlorinated rubber, and chlorinated rubber with plasticiser, $P$ is independent of $\Delta a$. For the chlorinated rubber with plasticiser, this is true in spite of the fact that the solubility is strongly dependent on activity. At high $a$ the clear, transparent appearance of the plasticised chlorinated rubber changes to a milky one; the strong turbidity being accompanied by a remarkable increase in water uptake.

I-5.1. The determination of $\bar{D}$ from permeation measurements

The mean diffusion coefficients ($\bar{D}$) were calculated from Eq. (I-10), and are shown in Fig. I-4 and Table I-2 as a function of the mean water concentration ($\bar{c}$) obtained from Eq. (I-11). Equations (I-10) and (I-11) can be solved by graphical integration. If the functionality $c=f(a)$ is easily available from the graph $c$ against $a$, the numerical integration is possible and is to be preferred for its ease and accuracy. The numerical expressions of $c=f(a)$ for alkyd and epoxy resins were determined by using the method of ‘least squares’. Different polynomials were tried until the mean square deviation ($MSD$) fell within the limits of the experimental error. In the present cases the equations could be limited to polynomials with three adjustable coefficients:

*Alkyd resin*: $c \times 10^3 = 1.63 + 8.94a + 31.8a^2; (MSD = 0.36.10^{-3})$ (I-22)

*Epoxy resin*: $c \times 10^3 = 2.24 + 13.64a + 1.79a^2; (MSD = 0.24.10^{-3})$ (I-23)

I-5.2. The determination of $\bar{D}$ from sorption measurements

When ‘reduced sorption’ curves show an initial linear dependence, $\bar{D}$ can also be calculated from Eq. (I-21). This seems to be the case for epoxy resin only at intermediate activities (Fig. I-5). The values of $\bar{D}$ obtained from Eq. (I-10) $- \bar{D}_p$, and Eq. (I-21) $- \bar{D}_s$ are represented in Fig. I-6. It can be seen that, in spite of their similar shape, $\bar{D}_s$ has higher values than $\bar{D}_p$. This difference may be explained on the basis that, a certain amount of water sorbed ($C_w$) is strongly ‘bound’ to the polar groups. This is confirmed by the relatively high amount of water sorbed instantaneously, and by the relatively long time needed for a complete desorption, as well as by the results of other investigators which proved the existence in polar polymers of two or three states of
Fig. 1-4. Mean diffusion coefficient $D$ (in cm$^2$/h) as a function of mean water concentration $\bar{c}$ (in g/cm$^3$).

Fig. 1-5. Reduced sorption curves of epoxy resin at different water activities ($a = 0.2$ (△), 0.3 (○), 0.4 (□)).

Meaning of the symbols see text, Eq. 21.
Mean diffusion coefficients calculated from sorption ($D_s$) and permeation ($D_p$) methods as a function of mean water concentration ($c$).

water namely firmly bound, and/or loosely bound and free water.$^3,17,18,19$

The participation of 'bound' water ($C_o$) in the permeation process is restricted by its very low mobility, but is automatically registered in sorption measurements. In Eq. (I-10) it is assumed that all molecules of water present in the film ($c$) would participate equally in the diffusion process. In reality only free water ($c-C_o$) molecules do so entirely ($C_o$ molecules can be practically regarded as immobilized by the polar groups); this would explain the lower values of $D_p$. Taking this effect into account, Eq. (I-10) can be modified to:

$$D_p = \frac{qL}{\int_{c_1}^{c_2} \frac{(c-C_o)}{a} da} \quad (I-10')$$

where an approximate value for $C_o$ can be found by assuming that

$$\lim_{a \to 0} c = C_o$$

For the alkyd resin and the epoxy resin the calculated amount of 'bound' water is, respectively, $(1.63 \pm 0.36) \cdot 10^{-3}$ and $(2.24 \pm 0.24) \cdot 10^{-3}$. The results before and after the correction are given in Fig. I-6. Eq. (I-21) cannot be applied to alkyd resin and plasticised chlorinated rubber, because their 'reduced sorption curves' are initially not linear.$^9$

The results for chlorinated rubber are shown in Table I-3. They must
be regarded with some caution, since water absorption is low and close to the experimental error.

**TABLE I-3. Chlorinated rubber**

<table>
<thead>
<tr>
<th></th>
<th>Permeation measurements (Eq. I-10)</th>
<th>Sorption measurements (Eq. I-21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D (cm²/h)</td>
<td>(110 ± 10) × 10⁻⁶</td>
<td>(101 ± 10) × 10⁻⁶</td>
</tr>
<tr>
<td>S (g/cm³.mmHg)</td>
<td>(0.087 ± 0.002) × 10⁻³</td>
<td>(0.087 ± 0.002) × 10⁻³</td>
</tr>
<tr>
<td>P (g/cm.h.mmHg)</td>
<td>(9.5 ± 1) × 10⁻⁹</td>
<td>(8.8 ± 1) × 10⁻⁹</td>
</tr>
</tbody>
</table>

I-5.3. *The determination of S from sorption measurements*

Solubility coefficients (S) were obtained from the following relationship

\[
S = \int_{p_2}^{p_1} \frac{c}{p} dp (g_{H_2O}/cm^3.mmHg) \tag{I-24}
\]

**Fig. I-7.** Solubility coefficient S (in g/cm³.mmHg) vs. mean water concentration c (in g/cm³).
If the dependence of $c/a$ on $a$ is already known (see Eq. (1-22) and (1-23)), $S$ can also be calculated by numerical or graphical integration from

$$S = \int_{a_2}^{a_1} \frac{c}{a} \, da \quad \text{at } 20^\circ \text{C}$$

since, $a = p/p_o = p/17.535$ at 20°C and $c$ depends on $p$ in a similar way to $a$. The results are represented in Fig. I-7 and Table I-2. It can be seen that, whilst $S$-values of chlorinated rubber are concentration independent, the other materials show two different characteristics: relatively high values at low concentrations (presumably caused by the strong water sorption by polar groups), and a large increase at high concentrations (presumably caused by cluster formation).

The first effect obviously applies with epoxy resin, whilst the latter is pronounced with plasticised chlorinated rubber. The alkyd resin has intermediate properties. The relation mentioned above (Eq. (I-24) or Eq. (I-25)), gives an overall value of $S$, representing all molecules of water present in the film, independent of their mobility and participation in the permeation process.

I-6. DISCUSSION AND CONCLUSIONS

Analysing the results obtained for the coefficients of permeability, solubility and diffusion as a function of concentration, it can be concluded that:

a. For the 'Epoxy Resin', the decrease in $S$ is compensated by a higher increase in $D$. As a result $P$ increases (see Fig. I-8)

b. For the 'Air Drying Medium Length Oil Alkyd', the dependence of $P$ on concentration is due to the dependence of both $S$ and $D$ on concentration. In the range of low concentration $S$ at first decreases, but shows an increase at higher concentration (see Fig. I-9).

c. For the hydrophobic 'Chlorinated Rubber', $D$ and $S$ appear to be independent of the concentration; as a consequence $P$ is constant (see Fig. I-10).

d. 'Chlorinated Rubber' with 'Chlorinated Diphenyl'. The presence of the (hydrophobic) plasticiser in chlorinated rubber changes the properties of the binder, particularly at high activity, where a strong cluster formation takes place. The film changes its appearance, becoming milky. This, however, does not affect the permeability coeffi-
Fig. I-8. Epoxy resin.
Variation of $P$, $S$ and $D$ with mean water concentration ($C$).

Fig. I-9. Alkyd resin.
Variation of $P$, $S$ and $D$ with mean water concentration ($C$).
The present experiments show that the ASTM-E-96-66 method for the determination of water permeation through paint films correctly estimates the behaviour in the ideal cases where, the coefficients of permeability, solubility and diffusion are concentration independent (Fick’s and Henry’s
laws are obeyed). For hydrophilic, and in some cases also for hydrophobic materials, the method is too limited to allow conclusions to be drawn about the whole process of permeation, because it measures only two or three of the whole range of situations.

In the light of the above, it is not surprising that in some earlier investigations\textsuperscript{20,21,22} a good correlation between water sorption and permeation was not always found. Whilst $P$, determined from the permeation measurements, includes both $D$ and $S$, the sorption measurements reflect only the latter property. $D$ and $S$ may act either in the same or in opposite directions.

Equation (I–10) is a useful relationship for the determination of permeability, diffusion, and solubility coefficients, which will give a general picture of the water transport process through paint films. Compared to the sorption method for calculation of $D$, Eq. (I–21), it has the great advantage that it is applicable to all systems, with Fickian as well as non-Fickian behaviour.

For the epoxy resin the differences between the values of diffusion coefficient calculated from sorption [Eq. (I–21)] and permeation [Eq. (I–10)] data were explained on the basis of the presence in the film of a certain amount of water molecules firmly attached to specific sites. The presence of immobilized water molecules by cluster formation, as well as their influence on the diffusion process, will be considered in the subsequent Chapter.

The differential values of the diffusion coefficient will be treated in Chapter IV.

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II. Water transport and cluster formation

II-1. SUMMARY

In the previous Chapter the mean water diffusion coefficients of four non-pigmented paint films were calculated from permeation measurements. It was found that in some cases the diffusion coefficient was dependent on the water concentration. This phenomenon can be satisfactorily explained by Zimm and Lundberg’s cluster theory. The clustering function was obtained from isothermal sorption measurements.

II-2. INTRODUCTION

In the previous Chapter, the water transport through four binders, commonly used in paint manufacture was investigated. It was found that different permeation characteristics do exist; the diffusion and solubility coefficients either increased, decreased or were constant with increase of the water concentration, dependent on material affinity to water. Such behaviour has previously been described in the literature for other materials, e.g. polymer films. For most of the hydrophilic materials (such as wool, cellulose, polyvinyl alcohol, nylon) the diffusion coefficient, $D$, increases with the water concentration, while for less hydrophilic materials (such as polyethylene\(^1\), rubber hydrochloride\(^2,3\), ethylcellulose\(^4\), polymethylmethacrylate\(^5\), polyurethane elastomers\(^6\)) $D$ decreases with the water concentration. For hydrophobic materials (such as polyolefines) $D$ is independent of the water concentration.

The clustering theory developed by Zimm\(^7\) from statistical mechanics in 1953, and applied by Zimm and Lundberg\(^8\) in 1956 to ‘sorption of vapours by high polymers’, was subsequently used to explain the different aspects of water transport mechanism through polymer films\(^2,6,9\). In the light of this theory the water transport process through an air drying medium long oil alkyd, an epoxy resin, a chlorinated rubber with and without plasticiser, will be explained.
II-3. THEORETICAL

Zimm arrived at the clustering function by defining a ‘molecular pair distribution function’ $F_2(i,j)$ in such a way that $(1/V^2) F_2(i,j) d(i) d(j)$ is the probability that molecules $i$ and $j$ are each at the position specified by the coordinates $(i,j)$ in the range $d(i)$ and $d(j)$. $V$ represents the total volume of the system. Then the ‘cluster integral’ $G_{11}$ is defined as:

$$G_{11} = \frac{1}{V} \int \int \{F_2(i,j) - 1\} d(i) d(j);$$

where $i$ and $j$ represent the molecules of component 1 of a binary mixture. Further, using Mayer and McMillan’s power series, Zimm found a relation between the penetrant activity ($a_1$), the volume fraction ($\phi_1$) and $G_{11}$:

$$\frac{G_{11}}{V_1} = -\phi_2 \left\{ \frac{\partial (a_1/\phi_1)}{\partial a_1} \right\}_P - 1 = -(1 - \phi_1) \left\{ \frac{\partial (a_1/\phi_1)}{\partial a_1} \right\}_P P_1 T - 1 \quad (II-1)$$

In Zimm’s terms, $V_1$ represents the partial molecular volume of the penetrant, $G_{11}/V_1$ the tendency of the penetrant molecules to cluster, and $\phi_1 G_{11}/V_1$, the excess of the penetrant molecules over the mean concentration found in the close vicinity of a given penetrant molecule. The theory is limited to systems of negligible compressibility, and does not show what is the state of water in the cluster, i.e., if it is present in one or more phases. It also assumes additivity of volumes in calculating volume fractions, which may cause error in the clustering function calculation.

II–3.1. The three limiting cases of the clustering function

A detailed analysis of the clustering function shows that the magnitude of the function $G_{11}/V_1$ (see Eq. II–1) can be:

a. $G_{11}/V_1 = -1$

b. $G_{11}/V_1 > -1$

c. $G_{11}/V_1 < -1$

a. When $a_1/\phi_1$ does not vary with the activity ($a_1$), the function $G_{11}/V_1 = -1$, which is the ideal case. This means that a penetrant molecule can be replaced by another without disturbing their distribution.

b. When $a_1/\phi_1$ decreases with increase of the concentration, the tangent $\partial (a_1/\phi_1)/\partial a$ has negative values, and $G_{11}/V_1$ becomes larger than $-1$ and rapidly reaches positive values. This shows that the penetrant concentration is higher than expected in the
close vicinity of a given penetrant molecule; in other words 'cluster formation' takes place.
c. When the values of $G_{11}/V_1 < -1$, there is a tendency for penetrant molecules to segregate one from another. This is generally interpreted\textsuperscript{10,11} in terms of localized sorption of penetrant molecules on specific polymer sites.

II-3.2. The correspondence between the clustering function and the diffusivity

The three cases described above must correspond to three different types of diffusivity:
a. For the materials for which $G_{11}/V_1$ is constant and equal to $-1$ through the whole range of the concentration, the diffusion coefficient must also be independent of the concentration.
b. High positive values for $G_{11}/V_1$ indicate strong cluster formation. Cluster formation may occur if the water-water interaction is stronger than the water-polymer interaction, and/or sufficient centres for initiating cluster formation or some form of capillary condensation are present in the material. As a consequence of the interaction of the water molecules resulting in cluster formation, the amount of mobile single water molecules decreases when the total concentration increases, and $D$ must decrease.
c. Negative values for $G_{11}/V_1$ show that clusters are not formed in the film. This is the case for hydrophilic materials, where the interaction between water and polar groups is stronger than that of the water-water interaction. Therefore no cluster formation will occur. In this case $D$ increases with the increase of the water concentration.

In addition to these clearly defined cases, more complex ones may exist, when competitive processes of clustering and specific interactions occur. Then $D$ is the resultant of opposite processes, and unpredictable results are obtained.

Another difficulty in the interpretation of the relation between the clustering function and the diffusivity may be caused by the enlargement of interstitial spaces, if swelling processes of the polymer network takes place. The possibility might also exist that some type of cluster such as dimers or trimers may contribute to the transport process. The clustering function does not give any information about the state of water in the cluster.
II-4. RESULTS AND CONCLUSIONS

For the four binders investigated, the mean diffusion coefficients as determined in Chapter I, from the permeation measurements, showed a different dependence on the water concentration (see Fig. I-4). An attempt has been made to explain the diffusion behaviour in terms of Zimm's theory.

The clustering function \( \frac{G_{11}}{V_1} \) was calculated from equation II-1, using the water sorption measurements data (Fig. I-2 and Table I-1).

II-4.1. Chlorinated rubber

The results obtained for \( \frac{G_{11}}{V_1} \) are represented in Fig. II-1. It can be seen that \( G_{11}/V_1 \) is \(-1\) for the whole range of \( \phi_1 \) (which in this case is very small). \( D \) is also independent of the water concentration (Fig. I-4), which is in accordance with the interpretation given previously. The chlorinated rubber-water system behaves as an ideal system.

II-4.2. Chlorinated rubber with Chlorinated diphenyl as plasticiser

With increase of the water concentration the appearance of the film changes from clear to milky. This has to be attributed to the formation of clusters in the material. The effect can be seen visually as well as with a phase contrast microscope. The high positive values found for \( G_{11}/V_1 \) (Fig. II-1) and the decrease of \( D \) with the water concentration (Fig. I-4) agree well with the assumption of cluster formation in the film. Although the exact reason for cluster formation in the film is not yet known, its existence cannot be doubted.

II-4.3. Epoxy resin

The hydrophilic epoxy resin is an example of a material, in which interaction between water and polar groups in the film takes place. The clustering function \( G_{11}/V_1 \) has negative values reaching \(-1\) only at a high water concentration (Fig. II-2). The strong interaction between water and the material prevents cluster formation, and explains the increase of \( D \) with the water concentration (Fig. I-4).

II-4.4. Alkyd resin

The alkyd resin used is characterised by its dual behaviour, since the interaction between the material and water, as well as the water-water interaction, may occur. The first interaction already takes place at a low water concentration, and the latter at higher concentrations. The two
Fig. II-1. Clustering function \( \frac{G_{11}}{V_1} \) vs. volume fraction \( \Phi_1 \).

Fig. II-2. Clustering function \( \frac{G_{11}}{V_1} \) vs. volume fraction \( \Phi_1 \).
- ○ Alkyd resin
- ○ Epoxy resin
effects influence the diffusion coefficient (Fig. I–4) and the clustering function (Fig. II–2). The strong increase of $D$ with the water concentration, characteristic for hydrophilic polymers, is counteracted by cluster formation. The values of the clustering function prove the presence of the clusters in the film. This is confirmed by a microscopic examination of the alkyd film previously soaked in water, which shows a light turbidity. Once again the importance of a complete series of measurements including both sorption and permeation measurements must be stressed. From the permeation measurements only the amount of water which actually participates in the transport process will be found, whereas in the sorption measurements all the water taken up by the film independent of the mobility of the water molecules will be measured.

The recognition of the fact that the immobility of water is caused by specific interaction with the polar groups at low regains, or by cluster formation at high regains will give a more complete picture of the process of water transport.

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III. Osmotic flow through non-pigmented films

III-1. SUMMARY

The water transport process, under the influence of differences in osmotic pressure through four non-pigmented paint films, has been investigated. It was found that, for sodium chloride solutions as well as for sucrose solutions, the films behave virtually as semipermeable membranes. For the hydrophobic materials used the diffusion coefficient appeared to be independent of the water concentration within the film. For the hydrophilic materials the diffusion coefficient was a function of the concentration and increased with the water concentration within the film. These results are qualitatively in accordance with the diffusion coefficients as determined by means of water vapour permeation measurements. However, it must be mentioned that for the hydrophilic epoxy resin, in some cases, the differences found were very large. The explanation will be given later on.

III-2. INTRODUCTION

It has been found that paint systems are more susceptible to blistering under conditions of immersion in distilled water than in sea water or sodium chloride solutions. Without actual proof, some authors attributed blister formation to the phenomenon of osmosis. Others stated that blistering is caused by water sorption and swelling, electro-endosmosis, thermosmosis, formation of atomic hydrogen by corrosion, and even by hydrolysis when ester groups are present.

Obviously, blistering is a result of complex phenomena, due to a series of physico-chemical processes. One or more causes may predominate as a function of the conditions, the kind of paint and the adhesion on substrate. There is however no doubt that osmosis plays an important rôle in paint deterioration. In spite of this, only a few studies on the osmotic flow process have appeared, and even then the observations given were of a qualitative and speculative nature.
In Chapter I, the water uptake and water permeation by means of differences in water vapour pressure through four non-pigmented paint films were investigated. The objective of the present work is to study the water transport through the same four materials, under the influence of differences in osmotic pressure.

In the subsequent Chapter an attempt will be made to correlate the results obtained by means of differences in osmotic pressure with those obtained by means of differences in water vapour pressure.

III-3. THEORETICAL

The osmotic phenomenon can be defined as 'the spontaneous flow of a solvent into a solution, or from a more dilute to a more concentrated solution, when the two liquids are separated by a semipermeable membrane". By semipermeability is meant that property of the membrane which allows free passage to the solvent, but not to the solute.

Numerous attempts have been made to explain the osmotic mechanism. It was found that, as a function of the nature of the penetrant and/or membrane, osmosis can occur by more than one mechanism. Whatever the mechanism, on thermodynamic grounds the solvent transport through a semipermeable membrane has to be explained by the difference in the chemical potential of the solvent in the boundaries of the membrane.

Under equal conditions of temperature and pressure, the solvent in a solution is at a lower chemical potential than in its pure state; as a result the solvent has a tendency to pass through the membrane into the solution, until equilibrium is reached.

In such a way the osmotic pressure of a solution (\( \pi \)) relative to its pure solvent, is defined as the difference in chemical potential (\( \Delta \mu \)) of solvent on both sides of the membrane.

\[
\pi = -\frac{\Delta \mu}{\bar{V}_1} \quad (\text{III-1})
\]

where \( \bar{V}_1 \) is the partial molar volume of the solvent in the solution.

For non-ideal solutions, Eq. (III-1) can be rearranged to give

\[
\pi = -\frac{RT}{\bar{V}_1} \ln a \quad (\text{III-2})
\]

where \( R \) is the gas constant, \( T \) the temperature (°K), and \( a \) the activity of the solvent in the solution.
As has already been shown in Chapter I, a relationship exists for the
transport of a penetrant through a membrane under steady state condi­
tions, namely:

\[ \int_{a_1}^{a_2} D \cdot c \cdot d \ln a \]

(III-3)

where \( q \) is the flux (g/h.cm²), \( L \) the film thickness (cm), \( D \) the diffusion
coefficient (cm²/h), \( c \) the penetrant concentration inside the membrane
(g/cm³), and \( a \) the activity of the penetrant.

For a solution of solvent activity \( a_1 \) and its pure solvent (for which the
activity is taken as unity) separated by a semipermeable membrane,
Eq. (III-3) can be rewritten as follows:

\[ \int_{a_1}^{1} D \cdot c \cdot d \ln a \]

(III-4)

where \( a \) is the activity of the solvent (in our case water) in the membrane.

In order to be able to integrate the right hand side of Eq. (III-4), it was
assumed that, at the film boundaries, the solvent activity in the film is
equal to the solvent activity in the solution.

For those membranes where \( D \) is concentration-dependent, \( D \)-values cal­
culated in such a manner are only mean values \( \langle D \rangle \) as indicated in Eq.
(III-5).

\[ \int_{a_1}^{1} D \cdot c \cdot d \ln a = \langle D \rangle \int_{a_1}^{1} \frac{c}{a} \cdot da \]

(III-5)

In Eq. (III-5), \( q \) and \( L \) are known from the measurements; the integral is
solved by graphical or numerical integration from the dependence of \( c \)
on \( a \) (obtained from sorption measurements where \( a \) is taken as the
activity of water in equilibrium with the film of the concentration \( c \)).
\( \langle D \rangle \) is then calculated from the rearranged equation (III-5):

\[ \langle D \rangle = \frac{qL}{\int_{a_1}^{1} \frac{c}{a} \cdot da} \]

(III-6)

It will now be shown that, Eq. (III-6) is in fact equivalent to one found
by Laidler and Lonsdale\textsuperscript{11}, by applying the kinetic laws to an osmotic
process. They found that, when two solutions of the same solvent, but of
different concentrations, are separated by a membrane, the diffusion
coefficient of the solvent is given by the following equation:
In Eq. (III-7) \( q \) represents the flux of solvent (g/cm\(^2\).unit of time), \( \bar{D} \) the diffusion coefficient (cm\(^2\)/unit of time), \( L \) (cm) the thickness of the membrane, \( RT \) the product of the gas constant and the temperature, \( \bar{V}_1 \) the partial molar volume of the solvent (cm\(^3\)/mole), \( \Delta \pi \) the difference between osmotic pressure of the two solutions, \( P \) the hydrostatic pressure, and \( C_t \) the total concentration of all species present in the membrane (g/cm\(^3\)). When a solution \( \beta \) and its pure solvent \( \alpha \) are separated by a semipermeable membrane, it means that no solute is present in the membrane, and that the osmotic pressure of the pure solvent is zero. These considerations lead to the following equations:

\[
\Delta \pi = \pi_\beta - \pi_\alpha = \pi_\beta - 0 = \pi \quad (III-8)
\]

\[
C_t = c \quad (III-9)
\]

where \( c \) represents the solvent concentration in the membrane (g/cm\(^3\)). Substituting Eq. (III-8) and Eq. (III-9), in Eq. (III-7) and restricting the treatment to small values of \( P \), such that \( P \) is negligible in comparison to \( \pi \), it follows that:

\[
q = \frac{\bar{D} c \bar{V}_1 \Delta \pi}{L RT} \quad (III-10)
\]

According to thermodynamics, at constant temperature and composition:

\[
\frac{d \ln a}{dP} = \frac{\bar{V}_1}{RT} \quad (III-11)
\]

For dilute solutions, the partial molar volume (\( \bar{V}_1 \)) is practically independent of the pressure, and Eq. (III-11) becomes:

\[
\int_{a_1}^{1} d \ln a = \int_{0}^{\pi} \frac{\bar{V}_1}{RT} dP = \frac{\bar{V}_1}{RT} \cdot \pi \quad (III-12)
\]

Substituting Eq. (III-12) in Eq. (III-10):

\[
q = \frac{\bar{D} c}{L} \int_{a_1}^{1} d \ln a \quad (III-13)
\]

or:

\[
\bar{D} = \frac{q L}{c \int_{a_1}^{1} d \ln a} \quad (III-14)
\]
Since $c$ is activity-dependent, Eq. (III–14) rearranges to Eq. (III–6).

$$\bar{D} = qL \int_{a_1}^{a} c \, d \ln a$$

This means, therefore, that Eq. (III–6) and Eq. (III–7) are equivalent, and that the diffusion coefficient of a solvent through a semipermeable membrane separating a pure solvent and a dilute solution can be determined from either Eq. (III–6) or Eq. (III–10).

In applying the above relations to the non-pigmented paint films investigated, the assumption is tacitly made that the films are semipermeable and that the solutions used are dilute solutions.

III–4. MATERIALS

The properties and preparation of three of the four materials investigated (air drying medium length oil alkyd, epoxy resin, chlorinated rubber) were described in Chapter I. The fourth material is chlorinated rubber plasticised with chlorinated paraffin (cereclor 42) in a proportion of 2/1 by weight.

This material replaces chlorinated rubber with chlorinated diphenyl used earlier because this last material was found to be too brittle for the present experimental purposes.

III–5. APPARATUS AND METHOD

The experiments were carried out with osmometers developed by the Central Laboratory TNO. A schematic description of the osmometer is given in Fig. III–1.

Each osmometer was assembled in the following manner: two films (f) of the same thickness and area were placed between the two faces of a well polished glass ring (a) and two perforated stainless-steel supporters (b). The cell so formed was tightly held together with the help of three screws. The osmometer was filled with the desired solution, using suitable syringe needles, before inserting the capillary. The junction between capillary (c) and cell was sealed with mercury (d), in order to avoid possible leakage. For the same reason the contacts between films and their supports, were covered with a silicon grease insoluble in water. The osmometer was then
inserted in a glass container (e) with distilled water, and the whole was placed in a thermostat. The capillary diameter was 1 mm. To avoid correction for the capillary rise, a reference capillary (r) of the same bore (1 mm) was placed in distilled water.

The difference in level compared with that in the reference capillary was measured as a function of the time. The duration of the experiments depended on the water permeability of the films investigated. A cathetometer was used to measure the levels. Most measurements were carried out at 25°C, except for a few carried out at 20°C, using water solutions of sodium chloride and sucrose of concentrations equivalent to osmotic pressures of $3.6 \times 10^3$, $7.6 \times 10^3$ and $17.4 \times 10^3$ cmHg. These osmotic pressures correspond to concentrations of sodium chloride solutions of $1N$, $2N$ and $4N$. In calculating the concentrations and the osmotic pressure Kimura and Sourirajan’s15 tables were used. For all the materials, no difference in water transfer rates could be detected at the two different temperatures chosen. The error introduced in the calculation by assuming that the partial molar volume of water in the solution is equal to the molar volume of the water is approximately 0.3% for a $4N$ sodium chloride solution in water. This error is insignificant in comparison with the calculated experimental error (6%–8%).

Fig. III-1. Schematic diagram of osmometer.
The solute permeation through the films investigated was determined in the following way: at the end of each experiment the water of container (e) was evaporated until a residue of 1 ml remained. This was analysed with a solution of 0.1 N silver nitrate\textsuperscript{19}, or a Feigl reagent\textsuperscript{20} for the presence of chloride or sucrose, respectively. These tests gave negative results for most of the experiments. Those tests which give positive results were due to a leakage of the osmometer. In such case the measurements were not taken into consideration. The limits of identification are about $10^{-7}$ g for chloride and about $10^{-6}$ g for sucrose. These data, when compared with the amount of water transferred through the films (about $10^{-3}$ g/10 days), show that the films may be considered to be virtually semipermeable. Each measurement was made in triplicate. Similar results which also show low solute diffusion through the paint films have already been reported in the literature\textsuperscript{12,13}.

III-6. CALCULATIONS

The water transfer ($T$) and the water transfer rate ($W$) were calculated from:

$$T = \frac{AL}{s} \quad \text{(III-15)}$$

$$W = \frac{AL}{st} \quad \text{(III-16)}$$

where $A$ is the amount of water transferred through the film (g), $L$ (cm) and $s$ (7.06 cm$^2$) the thickness and the area of the film, respectively and $t$ the time (hours).

Because the densities of the solutions and water at 25°C are almost the same and approach unity, the amount of water ($A$) was taken to be equal to its volume. The error introduced in this way is much smaller than the experimental error.

Now:

$$A = \pi r^2 l = 3.14 \times (0.05)^2 \times l = 7.85 \times 10^{-3} \times l \quad \text{(III-17)}$$

where $l$ (cm) represents the difference in water level between the capillary and the reference capillary. Combining Eq. (III-17) with Eq. (III-15) and Eq. (III-16), respectively and taking into consideration the fact that
in the osmometer there are two films of the same thickness and area it follows that

\[ T = 0.55 \times 10^{-3} \cdot L \cdot l \ (g/cm) \]  
(III–18)

\[ W = 0.55 \times 10^{-3} \cdot L \cdot l/t \ (g/h.cm) \]  
(III–19)

The water activity \((a)\) of sodium chloride solutions of 1\(N\), 2\(N\) and 4\(N\), at 20°C and 25°C was determined from data published in the literature\(^{16,17,18}\).

The following relationships were used in the calculations:

1. Robinson\(^{16}\) and Stokes’ equation:

   \[ \log a = \log p/p_o = 0.00782 \nu m \phi \]
   
   where \(\nu\) represents the number of ions from one molecule of salt, \(m\) the molality and \(\phi\) the osmotic coefficient.

2. Long’s\(^{17}\) expression relating the water activity to the water potential (\(\psi\)):

   \[ \ln a = \ln p/p_o = \psi \cdot 18.016/1000 RT, \text{ and} \]

3. an equation describing the lowering of the water vapour pressure by salt\(^{18}\):

   \[ 100 R = 100 \cdot (p_o - p)/mp_o. \]

The three references give tables representing the variation of \(\phi\)\(^{16}\), \(\psi\)\(^{17}\), and \(100 R\)\(^{18}\) with the concentration (molality) at different temperatures. The values of the water activity of sodium chloride solutions, calculated from the three methods described above are 0.966(0.966; 0.966; 0.966) for 1\(N\), 0.930(0.930; 0.930; 0.929) for 2\(N\) and 0.850(0.850; 0.847; 0.850) for 4\(N\).

III–7. EXPERIMENTS, RESULTS AND DISCUSSION

The osmotic flow through the films was investigated for three cases:

1. water \((a = 1)/\text{film}/1\ N\ \text{NaCl solution} \ (a = 0.966)\)
2. water \((a = 1)/\text{film}/2\ N\ \text{NaCl solution} \ (a = 0.930)\)
3. water \((a = 1)/\text{film}/4\ N\ \text{NaCl solution} \ (a = 0.850)\)

Preliminary experiments showed that the water transfer through the films was generally fast enough to allow for accurate differences in the daily readings (except for the plasticised chlorinated rubber), when 1\(N\)-sodium chloride solutions were used. At concentrations \(< 1\ N\) and for less perme-
able materials, the difference in the daily readings were in the range of the experimental error. It has been suggested in the literature\textsuperscript{21,22} that, in the presence of an electrolyte solution such as sodium chloride, some of the properties of a polar polymer could change, and consequently may affect the semipermeable characteristics of the membrane. In order to examine this, separate experiments on alkyd and epoxy resin films with a non-electrolyte solution (sucrose) were carried out. It was found that the water transport was unaffected by the type of solute, because both sucrose- and sodium chloride-solutions of the same osmotic pressure difference showed an identical water transfer rate.

The transport process started at once only if the films have been pre-soaked in distilled water for 15 days prior to the measurements. For the non-soaked films the transport process started only after a certain period of time, which depended on the nature of the film. It appears that pre-soaking of the films considerably shortens the time necessary to reach equilibrium.

For some materials, pre-soaking of the films strongly affected the water transfer rate ($W$) as well as the mean diffusion coefficient ($D$). Consequently, it was decided to determine $W$ and $D$ for both non-soaked and pre-soaked films. $D$-values of the pre-soaked films were calculated using Eq. (III–14) for the first day of flow, since $c$ at this early stage of the measurements may be considered to correspond to the water concentration in the film at $a = 1$. $D$-values of the non-soaked films were calculated from Eq. (III–6), taking into account the flux from the day the transport process started. As mentioned previously the integral was solved using the data of the sorption measurements.

The mean diffusion coefficients ($D$) together with the corresponding water transfer rates ($W$) and the mean water concentrations ($c$) are presented in the Tables III–1 and III–2. For the sake of simplicity each material will be discussed separately.

III–7.1. \textit{Chlorinated rubber with and without plasticiser}

For chlorinated rubber a good correlation between the increase in difference of water activity on both sides of the film and the water transfer (see Fig. III–2 as well as Tables III–1 and III–2) is found. As a result, the diffusion coefficient of the pre-soaked and the non-soaked films calculated from the three systems is practically the same (Table III–1 and III–2).
This result was to be expected since the increase of $c$ with $a$ is linear and small (see Chapter I), and the diffusion coefficient is independent of the water concentration.

Plasticised chlorinated rubber-films have such a low water permeability that only at a high salt concentration ($4N$) accurate daily readings could be obtained (Fig. III-3).
Table III–1. Non-soaked films

<table>
<thead>
<tr>
<th>Materials</th>
<th>$a = 1/f = 0.966$</th>
<th>$a = 1/f/a = 0.930$</th>
<th>$a = 1/f/a = 0.850$</th>
<th>$a = 1/f/a = 0.860$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta a = 0.034$</td>
<td>$\Delta a = 0.070$</td>
<td>$\Delta a = 0.150$</td>
<td>$\Delta a = 0.140$</td>
</tr>
<tr>
<td></td>
<td>$\bar{c}$</td>
<td>$w$</td>
<td>$D_{nom1}$</td>
<td>$\bar{c}$</td>
</tr>
<tr>
<td>Chlorinated rubber</td>
<td>1.59</td>
<td>0.067</td>
<td>120</td>
<td>1.54</td>
</tr>
<tr>
<td>Alkyd resin</td>
<td>41.30</td>
<td>0.525</td>
<td>36</td>
<td>39.90</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>17.50</td>
<td>0.510</td>
<td>85</td>
<td>17.20</td>
</tr>
</tbody>
</table>

Note: $\bar{c}$ ($10^{-3}$ g/cm³), $w$ ($10^{-7}$ g/h.cm), $D_{nom}$ and $D_p$ ($10^{-6}$ cm²/h), represent, respectively, the mean water concentration, the water transfer rate, and the mean diffusion coefficients as calculated from the osmotic ($D_{nom}$) and permeation ($D_p$) measurements. Experimental error: 6% to 8% for the osmotic measurements and 7% to 9% for the permeation measurements (see Chapter I).
TABLE III-2. Pre-soaked films

<table>
<thead>
<tr>
<th>Materials</th>
<th>$c_a = 1$</th>
<th>$\Delta a = 0.034$</th>
<th>$\Delta a = 0.070$</th>
<th>$\Delta a = 0.150$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$w$</td>
<td>$w$</td>
<td>$w$</td>
<td>$w$</td>
</tr>
<tr>
<td>Chlorinated</td>
<td></td>
<td>$D_{osm}$</td>
<td>$D_{osm}$</td>
<td>$D_{osm}$</td>
</tr>
<tr>
<td>rubber</td>
<td>1.60</td>
<td>0.069</td>
<td>0.140</td>
<td>0.293</td>
</tr>
<tr>
<td>Alkyd resin</td>
<td>42.40</td>
<td>0.530</td>
<td>1.071</td>
<td>1.850</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>17.80</td>
<td>0.539</td>
<td>1.080</td>
<td>2.400</td>
</tr>
</tbody>
</table>

Note: $c_a = 1 \times 10^{-3}$ g/cm$^3$, $w \times 10^{-7}$ g/h.cm and $D_{osm} \times 10^{-6}$ cm$^2$/h, represent the water concentration corresponding to $a = 1$, the water transfer rate and the mean diffusion coefficients as calculated from the osmotic measurements, respectively.

III-7.2. Epoxy resin

The pre-soaked and the non-soaked epoxy resin films behave in a markedly different way under the same conditions. From Table III-1, it can be seen that, while $D$ of the non-soaked films increases strongly with the water concentration in the film ($c$), $D$ of the pre-soaked films (Table III-2) is high and almost the same for all the three systems.

The differences between the values of $D$ of the pre-soaked and the non-soaked films can be explained in terms of the concentration dependence of diffusion. By soaking the films in distilled water prior to the experiments, the water concentration in the films at the earlier stages of the measurements in all the three cases is the same, and almost equal to the water concentration corresponding to $a = 1 (c_a = 1)$. Consequently, the initial $D$-values in all the three cases will be high and almost equal. Complete equality of the results cannot be expected, because the process...
of water desorption starts instantaneously and continues until the equilibrium concentration in the film is reached. As a result, the diffusion coefficient also decreases with the time until the constant value for the steady state is obtained. Such a situation is most marked in the case: $a = 1/\text{film}/a = 0.850$ where the difference between $c_{a=1}$ and $\bar{c}$ is the largest possible (see Fig. III-4).

---

**Fig. III-4.** Epoxy resin. Water transfer ($T$) versus time (days).

○ — pre-soaked films.
⊗ — non-soaked films.
The water concentration in the non-soaked films (c) reached at steady state in all the three cases is always lower than that corresponding to $a = 1$ ($c_a = 1$). Since the diffusion coefficient increases with the increase of the water concentration, it follows that $D$-values of the non-soaked films will be smaller than $D$ of the pre-soaked films. In the cases of high water activity and using small driving forces ($a = l/film/a = 0.966$ and to some extent $a = 0.930$).

![Graphs showing water transfer over time for different cases.](image_url)

**Fig. III-5.** Alkyd resin. Water transfer ($T$) versus time (days).
- ○ — pre-soaked films.
- ✰ — non-soaked films.
extent also \( a = 1 / \text{film} / a = 0.930 \) \( \approx \) approaches \( c_{a=1} \). Consequently, in this case similar \( D \)-values for the pre-soaked and the non-soaked films are to be expected and are indeed found (compare Table III–1 with III–2 for the two cases described above).

It should be noted that, while the dependence of the diffusion coefficient on the water concentration was expected for a hydrophilic material such as the epoxy resin, the very high \( D \)-values obtained in the case of high water concentrations are, at first sight, an unexpected result. This will be discussed in the subsequent Chapter.

III–7.3. Alkyd resin

The values of the mean diffusion coefficients of the alkyd resin, despite their increase with the water concentration (a behaviour which is to be expected for a hydrophilic material), are much smaller than those of the epoxy resin at equal water concentration in the film (Table III–1 and III–2). These relatively small values, when compared with those of the epoxy resin, seem to result from water cluster formation in the alkyd resin films at high water concentrations. As has been shown in Chapter II, the presence of clusters in the film decreases the mobility of the diffusible molecules. As a result, \( D \) may be less dependent on the water concentration and the differences between the pre-soaked and the non-soaked films become less marked (see Fig. III–5 and Tables III–1 and III–2).

III–8. CONCLUSIONS

The four binders investigated, when submitted to an osmotic pressure difference, behave as semipermeable membranes, since the films are virtually impermeable to the solute penetration. If any solute diffusion occurs through the films, it is much smaller than that of the water.

It was shown that, the mean diffusion coefficient (\( \bar{D} \)) of a penetrant through a film can be calculated from one of the equivalent equations, Eq. (III–10) or Eq. (III–6), with the proviso that the films behave as a semipermeable membrane.

The above equations could also be used for the concentrated solutions, because the error introduced in the calculations by assuming equality between the partial water volume of water in solution and the molar volume of water is far less than the experimental error.

For the materials with a strong concentration dependence of the diffusion (such as an epoxy resin), the pre-soaking of the films in distilled water
prior to the measurements can influence the water transport process in the earlier stages of the experiments drastically, because of a higher initial concentration of water in the film.
For the hydrophobic chlorinated rubber, $D$ is independent of the water concentration in the film. This result is in agreement with $D$ determined by means of the permeation measurement using differences in water vapour pressure (see Chapter I).
For the hydrophilic materials, $\bar{D}$ increases with the water concentration. As expected, $\bar{D}$-values when measured by means of differences in osmotic pressure for mean water concentrations higher than those used in the permeation experiments, are found to be higher. However, it should be noted that for epoxy resin the differences found are very large indeed. The explanation of this phenomenon will be given in the subsequent Chapter.

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IV. Correlation of data obtained by differences in water vapour pressure and in osmotic pressure

IV-1. SUMMARY

The mean water diffusion coefficients calculated from the water vapour permeation measurements in Chapter I are compared with the mean water diffusion coefficients calculated from the osmotic experiments in Chapter III. The dependence of the diffusion coefficient on the water concentration \( D = f(c) \) and of the concentration profile \( c = f(x) \) on the diffusion coefficient, in the steady state, have been determined. As a function of the nature of the material, \( D \) may be constant, may increase or may decrease with the increase of the water concentration. Consequently, the concentration distance curve is linear, concave or convex towards the distance axis. For the epoxy resin, the very high water transport rates found in a few osmotic measurements have been explained in terms of the \( D = f(c) \) relation. The osmotic measurements can be considered for all the materials investigated as an extension of the permeation measurements to the experimental conditions of high water concentrations on both sides of the films.

IV-2. INTRODUCTION

In the preceding Chapters, the transport of water through four binders determined by means of differences in vapour pressure and differences in osmotic pressure has been described. The transport of a penetrant through a membrane is only dependent on the driving forces acting in the film, and not on the way in which they were attained. This principle remains valid so long as the film characteristics are not changed by the environmental conditions producing the driving forces. As has already been shown for all the materials investigated such changes do not occur. It follows that it is possible to correlate the results obtained by means of vapour pressure differences with those
obtained by means of osmotic pressure differences.

The results obtained so far have been expressed in terms of the mean diffusion coefficients ($\bar{D}$) over a certain range of water concentrations. They are plotted as a function of the mean water concentration ($\bar{c}$) in the figures IV–1, IV–4 and IV–7, for epoxy resin, alkyd resin and chlorinated rubber with plasticiser, respectively. At first sight it would appear that for the epoxy resin in some of the osmotic measurements unexpectedly high $\bar{D}$-values ($\bar{D}_{osm_1}$ and $\bar{D}_{osm_2}$) are obtained. These are the cases in which the experimental conditions were such that a very high water concentration on both sides of the films, but only a small driving force, existed. Similar results were reported in the literature for the permeation of organic solvents through a number of different polymer membranes under analogous experimental conditions\(^*\). To our knowledge only in one paper\(^3\) the permeation of water through paint films under comparable experimental conditions was investigated, namely the self diffusion of water under the concentration conditions corresponding to $a = 1$. The authors limited the interpretation of the results to qualitative considerations, on the basis of theories already advanced in the literature\(^1\).

The aim of the present Chapter is to elucidate, as quantitatively as possible, the factors which might determine the relatively high diffusion of water through epoxy resin films at high water concentrations within the film. For the other materials investigated, results obtained with the two methods mentioned above will also be compared and discussed.

IV–3. THEORETICAL

As shown in Chapters I and III, an amended form of Fick's relation describing the transport process of a penetrant through a membrane was used, namely:

$$q = -Dc \frac{d \ln a}{dx} = -D \frac{c \, da}{a \, dx} \quad (IV-1)$$

The diffusion coefficient $D$, is dependent on the temperature, and may also be dependent on the concentration $c$, and therefore on the position $x$. For the sake of simplicity, the treatment has been restricted to the isothermal and steady state conditions, for which the flux $q$ is the same through each section of the membrane. Then $q$ is temperature, position and time independent, and Eq. (IV–1) can be transformed to:
\[ q \int_{0}^{L} dx = qL = \int_{a_2}^{a_1} D \frac{c}{a} \, da \quad (IV-2) \]

If \( D \) is concentration-independent, the diffusion coefficient can be calculated from the rearranged Eq. (IV-2):

\[ qL = D \int_{a_2}^{a_1} \frac{c}{a} \, da \quad \text{or} \quad D = \frac{qL}{\int_{a_2}^{a_1} \frac{c}{a} \, da} \quad (IV-3) \]

For materials with concentration dependence of the diffusion coefficient, Eq. (IV-3) gives a mean diffusion coefficient \( \bar{D} \), described in the literature as the 'integral diffusion coefficient'.

Eq. (IV-3) should then be written:

\[ \bar{D} = \frac{qL}{\int_{a_2}^{a_1} \frac{c}{a} \, da} \quad (IV-4) \]

In the preceding Chapters, \( \bar{D} \)-values of the materials investigated at different mean concentrations have been calculated. It was concluded that, for the hydrophilic materials the mean diffusion coefficient depends strongly on the water concentration. It follows that, for a better evaluation of Eq. (IV-1), the precise concentration dependence of diffusion has to be taken into consideration.

IV-3.1. Derivation of concentration dependence of the diffusion coefficient

Using a procedure analogous to that of Crank the dependence of the diffusion coefficient on the water concentration can be obtained as follows:

From Eq. (IV-2) it follows:

\[ qL = \bar{D} \int_{a_2}^{a_1} \frac{c}{a} \, da = \int_{a_2}^{a_1} D \frac{c}{a} \, da \quad (IV-5) \]

Introducing

\[ \frac{c}{a} = m \quad \text{and} \quad \int_{a_2}^{a_1} \frac{c}{a} \, da = M, \]

it follows that,
Using this equation, $D$ can be determined by two different kinds of experiments, namely: 1. by a series of experiments in which the lower activity $a_2$ (at the downstream boundary of the film) is maintained constant, while the higher activity $a_1$ (at the upstream boundary of the film) is varied. Now, by differentiation of the equation (IV–6) with respect to $a_1$, it follows that:

$$\frac{d(DM)}{da_1} = \bar{D}m + M \frac{d\bar{D}}{da_1} = Dm$$  \hspace{1cm} (IV–7)

or

$$D = \frac{d(DM)}{da_1} \cdot \frac{1}{m} = \bar{D} + \frac{M}{m} \cdot \frac{d\bar{D}}{da_1}$$  \hspace{1cm} (IV–8)

and

2. by a similar series of experiments in which the activity at the upstream boundary $a_1$ is maintained constant, and the activity at the downstream boundary $a_2$ is varied.

The same mathematical treatment is then applied, resulting in Eq. (IV–9).

$$D = \frac{\bar{D}}{m} - \frac{M}{m} \cdot \frac{d\bar{D}}{da_2}$$  \hspace{1cm} (IV–9)

The values of $m$ and $M$ can be calculated from the sorption measurements. By graphical differentiation of the curve $\bar{D}$ versus $a_1$ or $\bar{D}$ versus $a_2$ with respect to $a_1$ and $a_2$, respectively, the tangent $d\bar{D}/da_1$ or $d\bar{D}/da_2$ can be obtained. Introduction of these values in Eq. (IV–8) or (IV–9) gives the values of the diffusion coefficient sometimes called the 'differential diffusion coefficient' $D$. The calculated $D$-values can be represented either as a function of the water activity or of the water concentration, since the dependence of the concentration on the activity is known from the sorption measurements.

The two methods must, of course, give the same results. However, some small differences can be expected as a result of the errors introduced in the calculations by the inaccuracy of the graphical differentiation and integration in the determination of $d\bar{D}/da$ and $M$, respectively.

The conditions of the experiments described in Chapter I for system I (namely: $a_1 > 0; a_2 = 0$) and system II (namely: $a_1 = 1, a_2 < 1$) are in agreement with the boundary limits required respectively by Eq. (IV–8).
and Eq. (IV-9), mentioned above. Consequently, the values of $\bar{D}$ already reported (see Chapter I) could be used for the calculations of $D$.

**IV-3.2. Concentration profiles**

If the concentration dependence of diffusion is known, the concentration distribution through a film can be determined graphically or analytically. The graphical method is by trial and error. It is a laborious method because it necessitates the examination of a large number of curves, until the tangent on the curve describing $a = f(x)$ corresponds with $\frac{da}{dx}$ as calculated from Eq. (IV-1).

Analytically, the concentration profiles can be obtained from Eq. (IV-2) if numerical expressions for $D = f(a)$ and $c = f(a)$ are known. By keeping one limit of the integrals (i.e. $a_1$ and $L$, resp.) constant, and introducing various values of $a_2$ into the resulting relationship from the integration, the distance $x$ in the film corresponding with $a_2$ is obtained. As a result $a = f(x)$ is determined. Because $c = f(a)$ is known, $c = f(x)$ can also be obtained.

The equation describing the curve $D$ versus $a$ as obtained by 'curve-fitting' for both the alkyd resin and the epoxy resin takes the form of:

$$D = K_1 - \frac{K_2}{\ln a} - \frac{K_3}{\ln^2 a} - \frac{K_4}{\ln^3 a} - \ldots$$

Unfortunately this relationship, when multiplied by $c/a = f(a)$, gives expressions which are difficult to integrate. Consequently, in the present Chapter the concentration profiles were determined by the graphical method only.

**IV-4. RESULTS AND DISCUSSION**

For the sake of simplicity the materials investigated will be discussed separately.

**IV-4.1. Epoxy resin**

The mean water diffusion coefficients of epoxy resin have been calculated from permeation ($D_v$) and osmotic ($D_{osm}$) measurements, by applying the equation (IV-4). They are presented in Fig. IV-1 as a function of the mean water concentration ($\bar{c}$). The results derived from the two methods agree satisfactorily for moderate $\bar{c}$-values. However, as mentioned before, very high mean diffusion coefficients have been obtained for two cases of
the osmotic measurements ($\bar{D}_{osm_1}$ and $\bar{D}_{osm_2}$). The two cases correspond to situations in which very high water concentrations on both sides of the film are present. It can be seen from Fig. IV–2, in which the diffusion coefficient calculated from Eq. (IV–8) and Eq. (IV–9) is plotted as a function of the water concentration, that at very high water concentrations, $D$ increases very strongly with the concentration. Such a dependence predicts very high mean diffusion coefficients for situations in which, on both sides of the film, very high water concentrations are present. This is confirmed by the very high $\bar{D}_{osm}$-values ($\bar{D}_{osm_1}$ and $\bar{D}_{osm_2}$) obtained for the cases of the two osmotic measurements described above, for which the water concentration is high but the difference in concentration is small. Because the dependence of the diffusion coefficient on the concentration directly affects the concentration profile through the film, the above results can also be interpreted in terms of the concentration distribution.
FIG. IV-2. Epoxy resin. Diffusion coefficient as a function of concentration.

IV-4.2. *Alkyd resin*

The mean diffusion coefficients as calculated from the osmotic and the water vapour permeation experiments are summarized in Fig. IV-4.

The dependence of the diffusion coefficient on the water concentration is presented in Fig. IV-5. The concentration profiles (one example is shown in Fig. IV-6), reflect this situation. The increase of $D$ with $c$ is moderate.
**Fig. IV-3.** Epoxy resin. Concentration distribution across the film, when at the upstream boundary \( C_1 = 17.8 \times 10^{-3} \text{ g/cm}^3 \) and at the downstream boundary \( C_2 = 0 \).  

**Fig. IV-4.** Alkyd resin. Mean diffusion coefficients determined from water vapour (×) and osmotic (●) measurements as a function of the mean water concentration \( \bar{c} \).
Fig. IV-5. Alkyd resin. Diffusion coefficient as a function of concentration.

Fig. IV-6. Alkyd resin. Concentration distribution across the film, when at the upstream boundary $C_1 = 42.4 \ (10^{-3} \text{ g/cm}^3)$ and at the downstream boundary $C_2 = 0$. 
and consequently the concentration profile is less concave towards the abscissa, when compared with that of epoxy resin. For the hydrophilic alkyd resin a behaviour similar to that of the epoxy resin is to be expected. However, in contrast with the epoxy resin (see Fig. IV–1), no analogous jump in the diffusion coefficient at very high water concentrations was found. This result seems to be a direct consequence of the formation of clusters of water in the alkyd resin films at higher concentrations (see also the results obtained with the plasticised chlorinated rubber.)

The presence of the clusters of water in the alkyd resin film, as already shown in Chapter II, may strongly decrease the mobility of the water molecules. As a result, the diffusion process is slowed down and lower diffusion coefficients than expected at higher concentration are obtained. In the literature, similar cases of competitive processes of specific site and cluster interactions affecting the diffusion process have already been reported for polyurethans and water as penetrant.

IV–4.3. Chlorinated rubber
The results obtained with hydrophobic chlorinated rubber have been described in Chapters I and III. They show that the diffusion coefficient is independent of the water concentration under all the permeation conditions investigated [from Table I–2 $D_e = (110 \pm 10).10^{-6}$ and from Table III–1 $D_{osm} = (120 \pm 10).10^{-6}$; these values can be considered to be the same within the limits of the experimental error]. A constant $D$ means that the concentration profile is linear.

IV–4.4. Chlorinated rubber with Chlorinated paraffin
Comparing the results obtained from the osmotic measurements (see $D_{osm}$, in Fig. IV–7) with those of water vapour measurements ($D_v$)*, it can be concluded that a good agreement exists.

As has already been shown in Chapter II, the strong decrease of $D$ with $c$ is a direct result of the immobilization of the water molecules by the formation of clusters of water in the film.

A concentration profile, from the dependence of $D$ on $c$ (see Fig. IV–8), was determined. Such a concentration profile (see Fig. IV–9) shows that, in this case, the resistance lies on the side of the high water concentration.

* The values of $D_v$ for chlorinated rubber with chlorinated paraffin were calculated from measurements carried out separately. They are smaller than those represented in Chapter I for chlorinated rubber plasticised with chlorinated di-phenyl.
Fig. IV-7. Chlorinated rubber with chlorinated paraffin. Mean diffusion coefficients determined from water vapour (×) and osmotic (●) measurements as a function of the mean water concentration $\bar{c}$.

Fig. IV-8. Chlorinated rubber with chlorinated paraffin. Diffusion coefficient as a function of concentration.
IV-9. Chlorinated rubber with chlorinated paraffin. The concentration distribution across the film, when at the upstream boundary $C_1 = 29.7 \times 10^{-2}$ g/cm$^3$ and at the downstream boundary $C_2 = 0$.

IV-5. CONCLUSIONS

The mean water diffusion coefficients ($\bar{D}$) calculated from the osmotic and water vapour permeation measurements, under steady state conditions, could very satisfactorily be interpreted in terms of the dependence of the diffusion coefficient ($D$) on the concentration.

The good agreement between the results obtained from the two methods shows that the osmotic measurements can be considered as an extension of the water vapour measurements, for the experimental condition of high water concentration on both sides of film.

For the hydrophilic materials the diffusion coefficient increases with increasing concentration. Consequently, the concentration profiles are concave towards the distance axis. For the epoxy resin at very high water concentration, $D$ increases very strongly with the water concentration. It follows that, for cases in which very high water concentrations on both sides of the film are present, relatively high $\bar{D}$-values are found, because they approach the values of $D$. For the alkyd resin, the presence of clusters of water at high water concentrations decreases the mobility of the
molecules of water. As a result, the diffusion coefficient increases only moderately with the water concentration.

The diffusion coefficient of the hydrophobic chlorinated rubber is independent of the water concentration. Consequently, the curve describing the concentration profile is linear.

For the plasticised chlorinated rubber the diffusion coefficient at first decreases steeply with the water concentration and then flattens out. As a consequence, the concentration-distance curves are convex towards the distance axis. This behaviour was attributed to the strong tendency of the water molecules to form clusters.

IV-6. REFERENCES

1. Long, R.B.,
2. Binning, R.C., Lee, R.J., Jennings, J.E., Martin, E.C.,
3. Funke, W.A., Zorll, V., Murthy, B.G.K.,
4. Crank, J.,
5. Fujita, H.,
   Volta, F.,
v. Pigmented films

V-1. SUMMARY

The water transport in paint films consisting of two binders with two different pigments has been investigated. The variation of the permeability, solubility and diffusion coefficients with the pigment volume fraction under varying conditions has been determined. The two pigments used were a non-treated titanium dioxide and a non-setting red lead, representing two quite different types of the many pigments used in paint manufacture. It was found that the two pigments caused large differences in water transport through the paint films. For a well dispersed pigment \(TiO_2\) in a binder a decrease of the permeability coefficient with increase of the pigment volume fraction was observed. When pigment aggregates are formed in the film, higher values for the permeability coefficient as compared with the well dispersed pigment were found. It could be shown that this was caused by the air entrapped in the film. For the system alkyd resin-red lead lower permeability coefficients than observed with titanium dioxide were found. This was explained on the basis that the pigment interacted with the binder. The experimental results can be described by means of a simplified model proposed to describe the water permeation in pigmented films. In this model its was assumed that the pigment is impermeable to water.

V-2. INTRODUCTION

To investigate the process of water transport through pigmented films is obviously of practical as well as of theoretical interest. However, due to the pigment incorporation, the number of factors to be considered in such investigations is greater than with non-pigmented films. In the literature a quantitative treatment has only been given\(^1\) for some penetrants such as simple gases and non-polar substances, and for media consisting of polymers and a filler of a regular particle dispersion and a well established particle form and size (see later).
For more complicated systems, only qualitative treatments could be
found in the literature\textsuperscript{2,3,4}. This holds also for water transport through
filled media.
For paints, relatively few attempts to investigate water transport through
pigmented films have been made. Most of the published work\textsuperscript{5,6,7} is only
descriptive. The possible effects of pigmentation on water permeation
was discussed by Michaels\textsuperscript{8}. He pointed out that the incorporation of the
pigment into the binder may reduce or increase the permeability of water
relative to that of the binder, depending on the pigment volume fraction,
the chemical constitution and the geometry of the pigment, degree of
dispersion, etc. Funke et al.\textsuperscript{9,10} found that the water absorbed by pig­
mented films may depend on the pigment volume fraction ($\lambda_p$) in three
different ways, namely: 1) the water absorption is independent or decreases
with the increase of $\lambda_p$. 2) the water absorption increases steadily with
increasing $\lambda_p$, and 3) the water absorption has a maximum at relatively
low $\lambda_p$. These dependencies were related to the strength of adhesion
between the pigment and the binder.
In the previous Chapters on transport of water through non-pigmented
films, large differences in the water permeation, sorption and diffusion were
found for different materials. This was due to the specific water-polymer
interaction and the formation of clusters of water in the film.
The present Chapter deals with the influence of pigmentation on the
water transport for a non-treated titanium dioxide and for a non-setting
red lead in two binders, an alkyd resin and an epoxy resin.

\textbf{V-3. A PERMEATION MODEL FOR PIGMENTED FILMS}

A model is proposed to describe water permeation through pigmented
films. The arrangement of the binder ($b$) and the pigment ($p$) in the film
is assumed to be as follows: a part of the binder is in series with the pig­
ment; while the rest of the binder is in parallel with this system.
The volume fraction of the binder in series with the pigment is denoted
by $\lambda_1$, and the rest of the binder (in parallel) is denoted by $\lambda_2$ (see Fig.
V-1). Therefore:

$$\lambda_p + \lambda_1 + \lambda_2 = 1 \quad (V-1)$$

\begin{center}
\begin{array}{c|c}
\hline
p(\lambda_p) & b(\lambda_2) \\
\hline
b(\lambda_1) & \hline
\end{array}
\end{center}

\textbf{FIG. V-1.} Permeation model for pigmented films.
The permeability coefficient of the whole system, $P_t$, is then:

$$P_t (\lambda_p + \lambda_1 + \lambda_2) = P_t = \lambda_1 P_I + \lambda_2 P_b \quad (V-2)$$

In this equation

$$\lambda_I = \lambda_1 + \lambda_p \quad (V-3)$$

$P_b = \text{permeability coefficient of the binder}$
$P_I = \text{permeability coefficient of that part of the model in which the pigment and the binder are in series. For this part the reciprocal permeabilities are additive, thus:}$

$$\frac{\lambda_1}{P_1} = \frac{\lambda_1 + \lambda_p}{P_1} = \frac{\lambda_1}{P_b} + \frac{\lambda_p}{P_p}$$

or,

$$P_1 = \frac{(\lambda_1 + \lambda_p) P_b P_p}{\lambda_1 P_b + \lambda_p P_p} \quad (V-4)$$

Introduction of Eq. (V-3) and Eq. (V-4) in Eq. (V-2), gives:

$$P_t = \frac{(\lambda_1 + \lambda_p)^2 P_b P_p}{\lambda_1 P_b + \lambda_p P_p} + \lambda_2 P_b \quad (V-5)$$

By denoting:

$$\frac{\lambda_1}{\lambda_p} = \alpha \quad (V-6)$$

and

$$\lambda_1 + \lambda_2 = \lambda_b \quad (V-7)$$

where $\lambda_b$ is the volume fraction of the binder in the film, Eq. (V-5) can be rewritten as:

$$P_t = \frac{P_p P_b \lambda_p (1 + \alpha)^2}{P_b + \alpha P_p} + (\lambda_b - \alpha \lambda_p) P_b \quad (V-8)$$

When the permeation of water through the pigment is zero ($P_p = 0$) (which for the pigments under consideration seems to be a reasonable approach) the repartition factor $\alpha$ can easily be determined. Then Eq. (V-8) transforms to:

$$P_t = (\lambda_b - \alpha \lambda_p) P_b \quad (V-9)$$

since $\lambda_b + \lambda_p = 1$, Eq. (V-9) can be rewritten as:
\[ P_t = (1 - \lambda_p - \alpha \lambda_p) P_b \]  \hspace{1cm} (V-10)

From which:
\[ \alpha = \frac{P_b - P_t}{P_b \lambda_p} - 1 \]  \hspace{1cm} (V-11)

Since \( P_b \) and \( P_t \) can be determined experimentally the repartition factor \( \alpha \) can be calculated.

If the pigment particles are incompletely wetted by the binder, pigment aggregates containing air can be formed in the film. For such a situation the model must describe a three component system. As a function of the volume fraction of air which actually takes part in the permeation process, \( P_t \) may have higher, the same or lower values than \( P_b \). This situation will be considered later. Other complications may arise if the pigment particles interact with the binder, and the resultant product has different properties from that of the bulk binder.

Another model which could be used takes into consideration the tortuosity, i.e. the increase in the diffusion length caused by the presence of the pigment particles in the film\(^1,2,3\). Thus, for a pigmented film composed of an inert pigment impermeable to the penetrant, but perfectly dispersed into a binder, for which the fraction of area occupied by the binder in any cross section is taken to be equal to the volume fraction of the binder, it follows that:

\[ P_t = \frac{1}{k} \lambda_b P_b = \frac{1}{k} (1 - \lambda_p) P_b \]  \hspace{1cm} (V-12)

The tortuosity factor \( k \), as introduced in Eq. (V-12), depends on \( \lambda_p \) and on the pigment geometry.

For a perfect dispersion of particles of a well-established form and size, such as spheres, cubes, plates, the dependence of \( k \) on \( \lambda_p \) can be calculated\(^2,3,11\).

In the case where the pigment particle size approaches zero, \( k \) will approach 1 and \( \alpha \) will approach zero. Thus, it follows from Eq. (V-12) and Eq. (V-10) that:

\[ P_t = (1 - \lambda_p) P_b \]  \hspace{1cm} (V-13)

The advantage of the model described by Eq. (V-8) when compared with the tortuosity model, Eq. (V-12), is that it can predict the minimum permeability through pigmented films without considering the tortuosity. In most cases the pigment particles in the paint films are present as aggre-
gates of different forms and sizes. Therefore, the tortuosity factor can rarely be determined accurately. The model proposed can also be used when the pigment particles (or aggregates) are permeable to the penetrant.

V-4. EXPERIMENTAL

The influence of pigmentation on the water transport was investigated using two pigments and two binders, namely:

**Pigments**
- a) a well water-washed non-treated titanium dioxide (Kronos R, \( d = 4.2 \))
- b) a reactive pigment (red lead non-setting, \( PbO_2 \) 34\%, \( d = 8.9 \)).

**Binders**
- a) an air drying medium oil alkyd
- b) an epoxy resin.

The properties of the binders were described in Chapter I. Concentrated pastes were prepared in white (porcelain) ball mills, until the fineness of grind reached 7–8 Hegman's units for the titanium dioxide, and 5–6 Hegman's units for the red lead. Paints of different pigment volume fractions were prepared by dilution of the paste with binder. The volume fraction of the pigment is:

\[
\lambda_p = \frac{V_p}{V_p + V_b}
\]

In Eq. (V-14) \( V_p \) and \( V_b \) represent the volume of pigment and binder in the dry film, respectively.

For ageing, the paints were left on a roll after milling, for 30 days. The film preparation technique was identical to that used for the non-pigmented films (see Chapter I).

V-4.1. Method

The sorption and the permeation measurements were carried out under the same conditions of time, temperature and relative humidities, as for the non-pigmented films (see Chapter I).

Each measurement was made in triplicate.

V-5. RESULTS AND DISCUSSION

Because the pigmented films investigated behave differently, the results will be presented case by case.
V-5.1. Films pigmented with TiO$_2$

V-5.1.1. Permeation measurements. The permeability coefficients $P_i$ as calculated from the permeation measurements are shown in Table V-1 as well as in Fig. V-2 and Fig. V-3 for the alkyd resin and the epoxy resin, respectively.

![Graph V-2](image1)

**Fig. V-2.** Alkyd resin — TiO$_2$. Permeability coefficient ($P_i$) versus pigment volume fraction ($\lambda_p$), under different experimental conditions.

![Graph V-3](image2)

**Fig. V-3.** Epoxy resin — TiO$_2$. Permeability coefficient ($P_i$) versus pigment volume fraction ($\lambda_p$), under different experimental conditions.
Table V-1. Permeability coefficients under different experimental conditions

\[ P_t (10^{-9} \text{ g/cm.h.mmHg}) \]

<table>
<thead>
<tr>
<th>Film</th>
<th>( p_1 - p_2 ) mmHg</th>
<th>( \lambda_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>AT</td>
<td>17.53 15.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.53 13.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.53 0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.63 0</td>
<td></td>
</tr>
<tr>
<td>ET</td>
<td>17.53 15.78</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>17.53 13.15</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>17.53 0</td>
<td>12.0</td>
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<td></td>
<td>2.63 0</td>
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<td>AR</td>
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</tr>
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<td></td>
<td>2.63 0</td>
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<tr>
<td>ER</td>
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<tr>
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<td>17.53 13.15</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>17.53 0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

AT = alkyd resin with TiO₂, ET = epoxy resin with TiO₂
AR = alkyd resin with red lead; ER = epoxy resin with red lead
\( p_1 \) and \( p_2 \) = water vapour pressures on both sides of the film
\( \lambda_p \) = pigment volume fraction

For the alkyd resin (AT) it was found that the experimental results fit the curves expressed by:

\[ P_t = \lambda_b P_b = (1 - \lambda_p) P_b \]  \hspace{1cm} (V-13)

As already shown such behaviour is to be expected if the pigment particles in the film are impermeable to water \((P_p = 0)\), small (\( \alpha \approx 0, \text{or} \ k \approx 1 \)), and well dispersed. An examination of a cross-section (see Fig. V-4) confirms that the pigment particles are small \((0.2-0.4 \mu m)\) and well dispersed in the binder.
Fig. V-4. Part of a cross-section (× 11.700) of an alkyd resin — $TiO_2$ film ($\lambda_p = 0.1$).
FIG. V-5. Part of a cross-section (×11.700) of an epoxy resin — TiO₂ film (λₚ = 0.1).
For the epoxy resin (ET) the results are quite different. $P_t$ appears to be equal to the permeability coefficient of the binder ($P_b$), for all $\lambda_p$-values investigated, and independent of the experimental conditions. This finding can only be explained on the basis of Eq. V-8, if the water permeability of the pigment and that of the binder are equal ($P_p = P_b$). As follows from above this can not be true, because the pigment itself is not permeable to water. However, as previously said the pigment particles may be incompletely wetted by the binder. In this case, porous aggregates which contain air may be present in the film\textsuperscript{1,2}. An examination of a cross-section, as well as density measurements of the films show that this is the case for the epoxy resin--TiO\textsubscript{2} system. Figure V-5 shows that the pigment particles are unequally dispersed in the binder. From Fig. V-6 and Table V-2 it can be seen that the determined densities ($d_t$) of the films have lower values than those given\textsuperscript{2} by:

$$d_t = \lambda_b d_b \times \lambda_p d_p \quad \text{(V-15)}$$

in which additivity of the volumes was assumed. In Eq. V-15, $d_b$ and $d_p$ represent the density of binder and pigment, respectively.

The volume fraction of air ($\lambda_a$) present in ET-films, as estimated from the values of $d_c$ and $d_t$, is about 0.06–0.07. For the system AT (see Table V-2), the values of $d_c$ are in agreement with those observed experimentally ($d_t$).

The volume fraction of air which influences the permeation process can be

<table>
<thead>
<tr>
<th>$\lambda_p$</th>
<th>0.5</th>
<th>0.1</th>
<th>0.15</th>
<th>0.2</th>
<th>0.25</th>
<th>0.3</th>
<th>0.4</th>
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<tbody>
<tr>
<td>AT</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_c$</td>
<td>1.36</td>
<td>—</td>
<td>1.66</td>
<td>1.81</td>
<td>—</td>
<td>2.11</td>
<td>—</td>
</tr>
<tr>
<td>$d_t$</td>
<td>1.30</td>
<td>—</td>
<td>1.68</td>
<td>1.80</td>
<td>—</td>
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<tr>
<td>ET</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_c$</td>
<td>—</td>
<td>1.46</td>
<td>1.61</td>
<td>1.77</td>
<td>1.92</td>
<td>2.07</td>
<td>—</td>
</tr>
<tr>
<td>$d_t$</td>
<td>—</td>
<td>1.36</td>
<td>1.51</td>
<td>1.62</td>
<td>1.80</td>
<td>1.90</td>
<td>—</td>
</tr>
<tr>
<td>ER</td>
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<td></td>
</tr>
<tr>
<td>$d_c$</td>
<td>—</td>
<td>1.93</td>
<td>2.70</td>
<td>—</td>
<td>3.48</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>$d_t$</td>
<td>—</td>
<td>1.73</td>
<td>2.38</td>
<td>—</td>
<td>3.18</td>
<td>3.85</td>
<td></td>
</tr>
</tbody>
</table>

d (TiO\textsubscript{2}) = 4.2; $d$ (alkyd resin) = 1.22

d (red lead) = 8.9; $d$ (epoxy resin) = 1.16.
approximated. For this purpose a model representing the porous aggregates will be used (see Fig. V-7). This model, in which the pigment particles ($\lambda_p$) are assumed to be arranged with air, in series ($\lambda_{A_1}$) and in parallel ($\lambda_{A_2}$), is similar to the one already described (see Fig. V-1). Therefore:

$$P_{tp} = \frac{P_A P_p (\lambda_{A_1} + \lambda_p)^2}{\lambda_{A_1} P_p + \lambda_p P_A} + \lambda_{A_2} P_A$$  \hspace{1cm} (V-16)

In this equation $P_{tp}$, $P_p$ and $P_A$ represent the permeability coefficients of water in the porous aggregate, of the pigment particles and of air, respectively. Because the TiO$_2$-particles are impermeable to water ($P_p = 0$), it follows that Eq. (V-16) can be reduced to:

$$P_{tp} = \lambda_{A_2} P_A$$

As already shown for ET-films, $P_{tp}$ is equal to $P_b \cdot P_A$ was found in the literature$^{12}$ to be $\approx 10^{-4}$ g/cm.h.mmHg. From which, $\lambda_{A_2} \approx 0.0002$.

It follows that the volume of air incorporated in the porous aggregates is more than sufficient to bring the water permeability through the porous aggregates to a value close to that of the binder.
V-5.1.2. Sorption measurements. From the sorption measurements the solubility coefficients (S) were calculated.

Some the results obtained are represented in Fig. V-8 and Fig. V-9 for AT and ET, respectively (see also Table V-3).

These figures show that the solubility coefficients, when calculated per unit volume of binder \( S_b = G/V_b \cdot p \); g/cm\(^3\).mmHg for all the materials at constant activities of the water, do not vary with \( \lambda_p \). This virtually

<table>
<thead>
<tr>
<th>Table V-3. Solubility coefficients under two experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_B, S_c, S_t ) ( \times 10^{-3} ) g/cm(^3).mmHg</td>
</tr>
<tr>
<td>( \lambda_p )</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>AT</td>
</tr>
<tr>
<td>( S_B )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
<tr>
<td>( S_c )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
<tr>
<td>( S_t )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
<tr>
<td>ET</td>
</tr>
<tr>
<td>( S_B )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
<tr>
<td>( S_c )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
<tr>
<td>( S_t^* )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
<tr>
<td>AR</td>
</tr>
<tr>
<td>( S_t )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
<tr>
<td>ER</td>
</tr>
<tr>
<td>( S_B )</td>
</tr>
<tr>
<td>( a = 1 )</td>
</tr>
<tr>
<td>( a = 0.2 )</td>
</tr>
</tbody>
</table>

\( S_B \) = experimental data, calculated per unit volume of binder
\( S_t \) = experimental data, calculated per unit volume of pigmented film
\( S_t^* \) = after the density correction; \( S_c \) = calculated from Eq. (V-18).
means that the pigment in the film does not take up or loose a significant amount of water, and that the pigment incorporation into binder does not affect the sorption characteristics of the binder.

From the foregoing it also follows that:

\[ S_e = (1 - \lambda_p) S_b + \lambda_p S_p \]  

\[ (V-17) \]

---

**Fig. V-8.** Alkyd resin — TiO₂, \( S_b (\times) \), \( S_c (\bullet) \) and \( S_e \) (continuous line) versus \( \lambda_p \), under two experimental conditions.

**Fig. V-9.** Epoxy resin — TiO₂, \( S_b (\times) \), \( S_e \) (continuous line) and \( S_c \) before (○) and after (●) the density correction versus \( \lambda_p \), under two experimental conditions.
If the solubility coefficient of the pigment is zero \( (S_p = 0) \),

\[
S_c = (1 - \lambda_p) S_b \quad (V-18)
\]

In Fig. V-8 and Fig. V-9 the dependence of \( S_c \) on \( \lambda_p \) is represented by a continuous line, and that of the experimental data \( (S_i) \) by circles.

For AT, a good agreement between the values of \( S_i \) and those of \( S_c \) is obtained.

For ET the agreement is also obtained, but only after density-corrections have been made.

For ET this can be understood only if the air incorporated in the film (viz. 6–8\% per volume) as well as the area of pigment left unwetted by binder do not contribute noticeably to the sorption process. As already found in the literature, the solubility coefficient of the water in air \( S_A^* \) (\( \simeq 10^{-6} \text{ g/cm}^3\cdot\text{mmHg} \)) is negligible in comparison to the solubility coefficient of the water in binder \( (S_b \simeq 10^{-3} \text{ g/cm}^3\cdot\text{mmHg}) \).

It has been determined that the water taken up by the pigment alone (e.g. 0.3\% at \( a = 0.9 \) and 20°C), under equivalent experimental condition, is small in comparison to the water taken up by the binder (e.g. 1.4\% at \( a = 0.9 \) and 20°C); therefore the assumption that \( S_p = 0 \) is justified.

V-5.1.3. The diffusion coefficient. From the permeability \( (P_i) \) and solubility coefficients \( (S_i') \) the mean diffusion coefficients of water in the pigmented films, can be deduced (see Chapter I):

\[
\bar{D}_i = \frac{P_i}{S_i} = \frac{qL}{\int_{s_1}^{s_2} c \, da} \quad (V-19)
\]

where again \( q \) is the flux (g/h.cm²), \( L \) the thickness of the film (cm), \( c \) the water concentration after the density correction (g/cm³), and \( a \) the activity of water.

For AT \( \bar{D}_i \) appears to be independent of \( \lambda_p \) (see Fig. V-10) confirming that the mobility of water in the range of \( \lambda_p \) investigated, is practically unaffected by the presence of pigment in the film. As previously shown,

\[
S_A = \frac{P_A}{D_A} \simeq \frac{10^{-4}}{10^2} \simeq 10^{-6} \text{ g/cm}^3\cdot\text{mmHg}
\]

\* \( S_A \) can be calculated from the law of gases. It can also be approximated from the data of \( P_A \) and \( D_A \) (the permeability and the diffusion coefficient of the water in air), found in the literature\(^{12,13} \):

\[
S_A = \frac{P_A}{D_A} \simeq \frac{10^{-4}}{10^2} \simeq 10^{-6} \text{ g/cm}^3\cdot\text{mmHg}
\]
this is due to the fact that the pigment particles are small and well dispersed in the binder.

For ET, as a result of the air present in the film $D_i$ increases with $\lambda_p$ (see Fig. V–11).

V–5.2. Films pigmented with red lead

V–5.2.1. Alkyd resin. The dependence of $P_f$ on $\lambda_p$ is characterized by a steep decrease at small values of $\lambda_p$, followed by a slower decrease with a further increase in $\lambda_p$ (see the curves I and II in the Fig. V–12 and Table V–1). The almost abrupt break in the continuity of the curve indicates that the properties of the binder with respect to the transport of water are
Fig. V-12. Alkyd resin — Red lead. Permeability coefficient ($P_t$) versus $\lambda_p$, under different experimental conditions.

Fig. V-13. Alkyd resin — Red lead. $S_t$ (●) and $S_c$ (continuous line) versus $\lambda_p$. 
changed by the pigment incorporation in the alkyd resin. Presumably what occurs is that, from the pigment and the binder, a new component much less permeable to water is formed. Similar conclusions could be drawn from the sorption measurements (see curve I and II in Fig. V-13 and Table V-3) for the water uptake in liquid water \((a = 1)\) and \(a = 0.2\). The experimental values \((S_c)\) are below the values \((S_e)\) calculated from Eq. (V-18), showing that red lead strongly affects the sorption properties of the binder.

The viscosity measurements of the paints and an examination of a cross-section of the films indicate that red lead interacts chemically with the alkyd resin, as already suggested in the literature\(^{14,15}\). The increase in the paint consistency in the first days after milling (see Table V-4) shows that a chemical reaction can take place; while the spots around the pigment particles (see Fig. V-14 and V-15) indicate the presence of lead soaps in the film. In addition it should be mentioned that, during the process of film formation by air drying new compounds are formed which can also interact chemically with red lead.

**Table V-4. Change in viscosity (cps) of red lead paints at 20°C**

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>after 1 day</th>
<th>after 10 days</th>
<th>after 30 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkyd resin ((\lambda_p = 0.50))</td>
<td>6240</td>
<td>6560</td>
<td>10.600</td>
<td>11.200</td>
</tr>
<tr>
<td>epoxy resin ((\lambda_p = 0.55))</td>
<td>3360</td>
<td>3360</td>
<td>3360</td>
<td>3360</td>
</tr>
</tbody>
</table>

**V-5.2.2. Epoxy resin.** The sorption measurements show that the incorporation of red lead in the epoxy resin does not affect the binder properties relative to the water uptake. This can be seen from Table V-3, where the solubility coefficients calculated per unit volume of binder \((S_b)\) are given for different \(\lambda_p\). The values of \(S_b\) appear to be independent of \(\lambda_p\).

The permeability coefficients \((P_t)\), as calculated from the permeation measurements, decrease linearly with \(\lambda_p\) (see Fig. V-16 and Table V-1). Moreover the values of \(P_t\) are always above the curve described by the equation:

\[
P_t = (1 - \lambda_p) P_b \quad (V-13)
\]

Such a case is in agreement with the permeation model, as described by Eq. (V-8), but for which the pigment aggregates contain air \((P_p \neq 0)\).
FIG. V-14. Part of a cross-section (×46,000) of an alkyd resin red lead film (λ_p = 0.3). The spots around the pigment particles indicate the presence of lead soaps in the film.
Fig. V-15. A 82,500 magnification of red lead particles in alkyd resin film. The spots indicate the presence of lead soaps in the film.
Fig. V-17. Cross-section (× 9.000) of an epoxy resin — red lead film (λ_p = 0.3).
The presence of pigment aggregates and air in the films is indeed confirmed by an examination of a cross-section (see Fig. V-17), and the density measurements (see Table V-2), respectively. The mean diffusion coefficients \(D_{\lambda}\) as calculated from Eq. (V-19) are given in Fig. V-18. They increase linearly but slowly with \(\lambda_p\).

From the above results as well as from the viscosity measurement (see Table V-4) it seems that the epoxy resin, in contrast to the alkyd resin, does not interact chemically with red lead.

**V-6. CONCLUSIONS**

The transport of water through the pigmented films is obviously affected by the nature of both pigment and binder.
The different behaviour noticed experimentally could qualitatively be interpreted by a permeation model. The model predicts, for an impermeable and inert pigment which is well wetted by the binder, a linear decrease of the permeability coefficient of the pigmented films ($P_t$) with increase of the pigment volume fraction ($\lambda_p$). For small pigment particles, $P_t \simeq (1 - \lambda_p) P_b$. The alkyd resin pigmented with $TiO_2$ shows such a behaviour. When the pigment particles are incompletely wetted by the binder, pigment aggregates including air are formed in the film. As a consequence, the pigment aggregates become permeable to water.

As a function of the volume fraction of air actually involved in the water transport process, $P_t$ may increase, decrease or be independent of $\lambda_p$. For the system epoxy resin--$TiO_2$ it was found that $P_t$ is independent of $\lambda_p$, and for the system epoxy resin--red lead that $P_t$ decreases with $\lambda_p$. The presence of air in the pigmented films, however, does not affect the sorption of the binder. This is due to the fact that the water taken up by air and by the area of pigment left unwetted, is negligible in comparison with the water taken up by the binder. It also shows that the air incorporated in the film is surrounded by binder, in such a way that no direct contact (i.e. through capillaries, voids, etc.) with the exterior can be established. If capillaries had been present running through the whole thickness of the film, a very strong increase in $P_t$-values as compared with the values of $P_b$ should have been observed. This was not the case. It also follows that the presence of air in the film affects the permeability of water through the pigmented films, solely by diffusion.

The system alkyd resin--red lead represents a special case. In earlier work on red lead in media such as linseed oil, stand oil, alkyds and the like, it was reported that an interaction pigment/binder occurred. Problems of storage, the increase in consistency, and gelation were met. Anti-corrosive properties of red lead were also investigated. It was concluded that lead soaps, the products of pigment-binder interaction, were the causes of these properties. The present investigation demonstrates that the pigment-binder interaction causes a strong decrease in the water solubility and permeability, which together with the inhibitive properties of lead soaps give good anticorrosive properties for the system red lead-linseed oil alkyds.

With respect to the dependence of the permeability, solubility and diffusion coefficients on the water concentration within the film, the experimental results showed that, for all the pigmented films investigated these were basically the same as for the non-pigmented films.
V-7. REFERENCES

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General summary

This thesis deals with some aspects of water transport in non-pigmented and pigmented free films. The main part of the work is concerned with the non-pigmented films of an alkyd resin, an amine-cured epoxy resin and a chlorinated rubber with and without a plasticiser. In addition, experiments were performed with films pigmented with a non-treated titanium dioxide and a non-setting red lead.

The sorption and permeation measurements carried out with the non-pigmented films under different experimental conditions are described in Chapter I.

From the values of the flux and the concentration of water in the film, the diffusion coefficients under steady state and isothermal conditions (20°C) were calculated from a thermodynamic relation. For materials with concentration dependence of diffusion this relation gave the integral or the mean diffusion coefficients over a range of water concentrations (\(\bar{D}\)). Using a procedure described in Chapter IV, the diffusion coefficient at a given water concentration, \(D\), sometimes called the differential diffusion coefficient, could be approximated.

From the permeation and sorption data the mean permeability coefficient \((P)\) and the mean solubility coefficient \((S)\) could also be calculated. The values of \(\bar{D}\) as well as those of \(S\) and \(P\) are presented as a function of the mean water concentration \(\bar{c}\). The four binders showed different behaviour. Because the permeability coefficient is a product of the diffusion coefficient and the solubility coefficient, the dependence of \(P\) on \(\bar{c}\) could be explained in terms of the dependence of \(\bar{D}\) and \(S\) on \(\bar{c}\).

For the alkyd resin \(P\) increased with \(\bar{c}\) as a result of the increase in both \(\bar{D}\) and \(S\) with the water concentration. For the epoxy resin the decrease of \(S\) was compensated by a higher increase of \(\bar{D}\); consequently \(P\) increased with \(\bar{c}\). For the hydrophobic chlorinated rubber pure and with a plasticiser, no change in \(\bar{D}, S\) and \(P\) with \(\bar{c}\) was to be expected since polar groups were absent. However, for the plasticised chlorinated rubber, \(P\) was independent of \(\bar{c}\), solely because the decrease in the \(\bar{D}\)-values was compensated by an appropriate increase in the \(S\)-values.
For the epoxy resin $D$ could also be obtained, using only the sorption data (the transient-method). The values of $D$ determined from the transient-method differed slightly from those obtained on the basis of the steady state-method. These differences could be explained on the assumption that a certain number of molecules of water are attached 'firmly' to the specific sites. The participation of the 'firmly'-bound molecules of water in the permeation process, at steady state, is restricted by its very low mobility, but it is indiscriminately registered in the sorption measurements on which the transient method is based.

In the second Chapter the different dependencies of $D$ on the water concentration ($D$ may increase, may decrease, or be constant) were interpreted in terms of Zimm and Lundberg's cluster theory. The clustering function $(G_{11}/V_i)$ was determined from the sorption isotherms. It was found that the three limiting cases for $G_{11}/V_i (-1; > -1; < -1)$ correspond to three cases of diffusion namely, the diffusion coefficient is independent of, decreases with, or increases with the water concentration.

When the clustering function is $-1$ over the whole range of the water concentration, it shows that the water-polymer system is ideal. This was found for the chlorinated rubber, for which the diffusion coefficient was also independent of the water concentration. For the plasticised chlorinated rubber the high positive values found for $G_{11}/V_i (> -1)$ and the decrease of $D$ with $c$, agreed with the experimental observation that the formation of clusters of water had occurred in the film. For the epoxy resin the negative values of $G_{11}/V_i (< -1)$ show that clusters have not been formed in the film. The strong interaction between water and the material prevents cluster formation, and explains the increase of $D$ with $c$.

In addition to these clearly defined cases, more complex ones may exist, when competitive processes of clustering and interaction of water with the specific sites occur. Then $D$ is the resultant of opposite effects. The alkyd resin exemplified such a case. The increase of the diffusion coefficient with the water concentration, characteristic of hydrophilic binders, was counteracted by cluster formation. As a result, the increase of $D$ with $c$ was less pronounced than in the case of the epoxy resin.

In the third Chapter the water transport under the influence of differences in osmotic pressure is described. It was found that, for sodium chloride solutions as well as for sucrose solutions, the films behaved virtually as
semipermeable membranes. It was shown that the osmotic measurements could be considered as permeation measurements for situations of very high water concentrations on both sides of the film. As a consequence, the mean diffusion coefficients ($D_{osm}$) could be calculated by applying the relationship used in the determination of $D$ from the water vapour permeation measurements.

In chapter four the mean diffusion coefficients as calculated by means of differences in water vapour pressure ($D_v$) and osmotic pressure ($D_{osm}$) are compared. The dependence of $D_v$ and $D_{osm}$ on $c$ is discussed in terms of the diffusion coefficient-dependence on the water concentration $D = f(c)$. As a function of the nature of the film $D$ increased, decreased or was constant with the increase of the water concentration. Consequently, the concentration-distance curves ($c = f(x)$) are concave, convex or linear towards the distance axis ($x$).

For the hydrophilic materials, $D$ increased with the water concentration. For the hydrophobic chlorinated rubber and the chlorinated rubber with a plasticiser the diffusion coefficient was independent of and decreased with the water concentration, respectively.

In Chapter five the permeation and sorption measurements carried out with paint films consisting of an alkyd resin and an epoxy resin with two different pigments (a non-treated titanium dioxide and a non-setting red lead) are given. The variation of the coefficients of permeability, solubility and diffusion with the pigment volume fraction ($\lambda_p$) showed that, the transport of water in the pigmented films is affected by the nature of both pigment and binder. The experimental results are in agreement with a model developed to describe water permeation in pigmented films. For an impermeable and inert pigment incorporated in a binder a decrease of the permeability coefficient with increase of $\lambda_p$ is expected. The alkyd resin with $TiO_2$ showed such a behaviour. When pigment aggregates were formed in the film, higher values than expected for the permeability coefficient were found. It was shown that this was due to the air entrapped in the film. Such a behaviour was found for the systems: epoxy resin–$TiO_2$ and epoxy resin–red lead. For alkyd resin with red lead lower permeability coefficients than expected were found. This was explained on the basis that the pigment interacted with the binder resulting in the formation of lead soaps.
Algemene samenvatting


Uit de metingen van de flux en de concentratie van het water in de film werden met behulp van een thermodynamische betrekking voor de stationaire toestand en onder isotherme omstandigheden (20°C) diffusiecoëfficiënten berekend. Voor materialen waarbij de diffusie afhangt van de concentratie leverde deze betrekking de geïntegreerde of gemiddelde diffusiecoëfficiënten ($D$) over een bepaald gebied van waterconcentraties. Door gebruik te maken van een werkwijze beschreven in hoofdstuk IV kon de diffusiecoëfficiënt $D$ bij een bepaalde waterconcentratie (deze $D$ wordt soms 'differentiële' diffusiecoëfficiënt genoemd), bij benadering worden bepaald.

Uit de permeatie- en sorptie-gegevens konden ook de gemiddelde permeabiliteitscoëfficiënt ($P$) en de gemiddelde oplosbaarheidscoëfficiënt ($S$) worden berekend. Zowel de waarden voor $D$ als die voor $S$ en $P$ worden uitgedrukt als een functie van de gemiddelde waterconcentratie $c$.

De vier bindmiddelen vertoonden een verschillend gedrag. Doordat de permeabiliteitscoëfficiënt het produkt is van de diffusiecoëfficiënt en de oplosbaarheidscoëfficiënt kon de afhankelijkheid van $P$ van $c$ worden verklaard uit de afhankelijkheid van $D$ en $S$ van $c$.

Bij de alkydhars steeg $P$ met $c$ als gevolg van de stijging van zowel $D$ als $S$ met de waterconcentratie. Bij de epoxyhars werd de afname van $S$ ge-compenseerd door een sterkere stijging van $D$; $P$ steeg dus met toenemende $c$. Bij de hydrofobe chloorrubber (met en zonder weekmaker) werd geen verandering van $D$, $S$ en $P$ met $c$ verwacht, daar polaire groepen
afwezig zijn. Voor chloorrubber met weekmaker bleek de onveranderlijkheid van $P$ echter alleen te berusten op het compenseren van de afneming van $\bar{D}$ door een toeneming van $S$.

Voor de epoxyhars kon $\bar{D}$ ook worden gevonden uit sorptiemeningen onder niet-stationaire omstandigheden (de z.g. ‘transient-method’). De waarden van $\bar{D}$ bepaald bij niet-stationaire omstandigheden verschillen slechts weinig van die bepaald bij de stationaire toestand. Deze verschillen konden worden verklaard door de aanneming dat een zeker aantal moleculen water stevig aan bepaalde plaatsen is gebonden. De deelneming van de stevig gebonden watermoleculen in het permeatieproces bij stationaire toestand is beperkt door de lage beweeglijkheid; bij de sorptiemeningen waarop de ‘transient-method’ is gebaseerd wordt de aanwezigheid van dit vast gehouden water uiteraard wel geregistreerd.

In het tweede hoofdstuk worden de verschillende afhankelijkheden van $\bar{D}$ van de waterconcentratie ($\bar{D}$ kan stijgen, dalen of constant zijn) geïnterpreteerd in termen van de cluster-theorie van Zimm en Lundberg. De clustervormingsfunctie ($G_{11}/V_1$) werd bepaald uit isotherme sorptiemeningen. Gevonden werd dat de drie gebieden voor de waarde van $G_{11}/V_1$ (n.l. $-1$, $> -1$, $< -1$) overeenkomen met drie vormen van diffusie, n.l. met een diffusiecoëfficiënt onafhankelijk van, afnemend met, of toenemend met de waterconcentratie.

Als de clustervormingsfunctie $-1$ is over de gehele reeks van waterconcentraties, dan is het systeem water-polymer ideaal.

Dit werd gevonden voor chloorrubber, waarbij de diffusiecoëfficiënt ook onafhankelijk was van de waterconcentratie. Voor de chloorrubber met weekmaker kwamen de hoge positieve waarden gevonden voor $G_{11}/V_1$ ($\gg -1$) en de afneming van $\bar{D}$ met $\bar{c}$ overeen met de experimentele waarneming dat er clustervorming in de film plaats vindt. Voor de epoxyhars bewijzen de negatieve waarden van $G_{11}/V_1$ ($< -1$) dat clusters niet zijn gevormd in de film. De sterke wisselwerking tussen water en materiaal verhindert dit en verklaart de toeneming van $\bar{D}$ met $\bar{c}$.

Naast deze goed gedefinieerde gevallen kunnen ook meer ingewikkelde bestaan, waarbij processen van clustervorming en wisselwerkingen van water met specifieke polaire groepen naast elkaar voorkomen. Dan is $\bar{D}$ een resultante van tegengestelde effecten. De alkydhars is een duidelijk geval. De toeneming van de diffusiecoëfficiënt met de waterconcentratie, karakteristiek voor hydrofile bindmiddelen wordt tegengegaan door clustervorming. Het resultaat is een minder uitgesproken stijging van $\bar{D}$ met $\bar{c}$ dan bij de epoxyhars.

In hoofdstuk 3 wordt het watertransport onder invloed van verschillen
in osmotische druk beschreven. Gevonden werd dat voor natriumchloride-oplossingen, zowel als voor rietsuikeroplossingen, de films zich feitelijk gedroegen als semi-permeabele membranen. Aangetoond werd dat de osmotische metingen beschouwd konden worden als permeatiemetingen voor situaties met hoge waterconcentratie aan beide zijden van de film. Bijgevolg konden de gemiddelde diffusiecoëfficiënten \( D_0 \) worden berekend door toepassing van de betrekking gebruikt voor de bepaling van \( D \) uit metingen van de waterdampdoorlatendheid.

In hoofdstuk 4 worden de gemiddelde diffusiecoëfficiënten, berekend m.b.v. verschillen in waterdampspanning \( D_v \) en osmotische druk \( D_0 \) vergeleken. De afhankelijkheid van \( D_v \) en \( D_0 \) van \( c \) wordt behandeld in samenhang met de afhankelijkheid van de diffusiecoëfficiënt van de waterconcentratie \( D = f(c) \).

Hierbij zijn drie gevallen te onderscheiden: \( D \) stijgt, blijft gelijk of daalt met toenemende waterconcentratie. Dit uit zich in de concentratie-afstandskrommen die dan resp. hol, lineair of bol zijn t.o.v. de afstandsas. Voor de hydrofiele bindmiddelen steeg \( D_0 \) met de waterconcentratie \( (c) \). Voor de hydrofobe chlorrubber was de diffusiecoëfficiënt onafhankelijk van de waterconcentratie; bij chlorrubber met weekmaker daalde zij met de waterconcentratie.

In hoofdstuk 5 worden de permeatie- en sorptiemetingen gegeven die zijn uitgevoerd met verfilms op basis van een alkydhars en een epoxyhars met twee verschillende pigmenten (een niet behandelde titaandioxidewit en een niet-uitzakkende loodmenie). De variatie van de permeabiliteits-, de oplosbaarheids-, en de diffusiecoëfficiënt met de pigmentvolumeconcentratie \( \lambda_p \) toonde aan dat het transport van water in de gepigmenteerde films wordt beïnvloed door de aard van het pigment en het bindmiddel. De experimentele resultaten zijn in overeenstemming met een model, ontwikkeld voor de beschrijving van de waterdoorlatende in gepigmenteerde films. Voor een niet-doorlatend en inert pigment, aanwezig in een bindmiddel, wordt een afneming van de permeabiliteitscoëfficiënt met een stijging van \( \lambda_p \) verwacht. Dit gedrag werd inderdaad gevonden bij de alkydhars met TiO2. Bij aanwezigheid van pigmentagglomeraten in de film werden permeabiliteitscoëfficiënten gevonden die hoger waren dan was verwacht. Aangetoond werd dat dit een gevolg was van opgesloten lucht in de film. Dit gedrag werd gevonden voor de systemen epoxyhars-TiO2 en epoxyhars-menie. Voor de alkydhars met menie werden lagere permeabiliteitscoëfficiënten gevonden dan verwacht. Dit werd verklaard door de wisselwerking tussen pigment en bindmiddel, waarbij loodzepen worden gevormd.
List of principal symbols

\( a \) = activity of penetrant (in all cases water), \( p/p_0 \)

\( c \) = concentration of sorbed water in film (g/cm\(^3\))

\( c_{a=1} \) = concentration of sorbed water in film at \( a = 1 \) (g/cm\(^3\))

\( \bar{c} \) = mean water concentration over a range of activities (g/cm\(^3\))

\( d \) = density

\( d_b, d_p, d_c, d_i \) = density of binder, pigment, pigmented film (calculated) and pigmented film (determined), respectively.

\( D \) = diffusion coefficient (cm\(^2\)/h)

\( \bar{D} \) = mean diffusion coefficient (cm\(^2\)/h)

\( \bar{D}_v, \bar{D}_{osm} \) = mean diffusion coefficient as obtained from the permeation and osmotic measurements, respectively (cm\(^2\)/h)

\( \bar{D}_t \) = mean diffusion coefficient of pigmented films

\( G_{11} \) = cluster integral

\( L \) = thickness of film (cm)

\( m \) = molality

\( N \) = normality

\( p \) = vapour pressure (mmHg)

\( p_o \) = vapour pressure of pure solvent (mmHg)

\( P \) = permeability coefficient (g/cm.h.mmHg)

\( P_b, P_p, P_i, P_{rp}, P_A \) = permeability coefficient of binder, pigment, pigmented film, pigment agglomerate and air, respectively (g/cm.h.mmHg)

\( q \) = flux of water (g/cm\(^2\).h)

\( R \) = gas constant

\( RH \) = relative humidity

\( S \) = solubility coefficient (g/cm\(^3\).mmHg)

\( S_b, S_p, S_c, S_{rp}, S_A \) = solubility coefficient of binder, pigment, pigmented film (calculated), pigmented film (experimental) and air, respectively.

\( t \) = time (hour, unless otherwise specified)

\( T \) = temperature (°K)
\( T \) (Chapter III) = water transfer (g/cm)
\( \bar{V}_i \) = partial molar volume (cm\(^3\)/mole)
\( W \) = water transfer rate (g/cm.h)
\( \lambda_b, \lambda_p, \lambda_a \) = volume fraction of binder, pigment and air, respectively, in pigmented films
\( \mu \) = chemical potential
\( \mu_o \) = chemical potential in standard state (of pure water in all cases)
\( \pi \) = osmotic pressure (cmHg)
\( \phi_1, \phi_2 \) = volume fraction of penetrant (water) and polymer, respectively
\( \text{AT} \) = alkyd resin with \( TiO_2 \)
\( \text{AR} \) = alkyd resin with red lead
\( \text{ET} \) = epoxy resin with \( TiO_2 \)
\( \text{ER} \) = epoxy resin with red lead