A Drop of Liquid and its Penetration into Paper

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A Drop of Liquid and its Penetration into Paper

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67/1

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List of Contents

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1) Introduction

The penetration of liquids into porous solid bodies was already subject of treatises by many researchers. We would like to mention Dr. D. Tollenaar as being representative for all others, since he considerably contributed to the better understanding of the penetration process and thereby also of the ink transfer by his publications [1, 2, 3, 4, 5].

This treatise is to elucidate processes which take place upon penetration of low viscosity liquids into porous solid bodies. Of course, in principle it will not matter just how viscous a liquid is. The penetration process will be similar in any case. The capillaries of a porous body will, however, absorb liquids of low viscosity very quickly so that the liquid during a given contact period with the drop will preferably move toward the surface of the porous body. The precondition is however, that its thickness is small compared to the dimension of its surface.

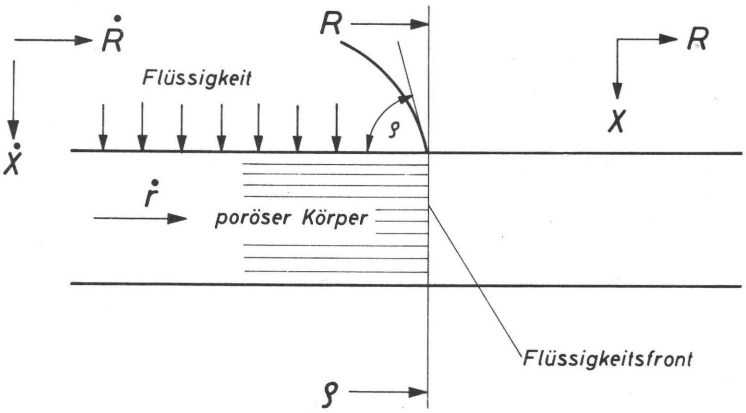
Liquids of low viscosity in addition can easily spread over the surface of a porous body.

Thus we may observe two phenomena when a drop of liquid comes in contact with the surface of a porous body.
1) The behaviour of the liquid on the surface of the body.
2) The absorption of the liquid by the capillaries of the porous body.

Finally, one has to ask whether, and if so in what way these two phenomena are related.

2) Theoretical Considerations

2.1 The behaviour of a liquid on the surface of a porous body.

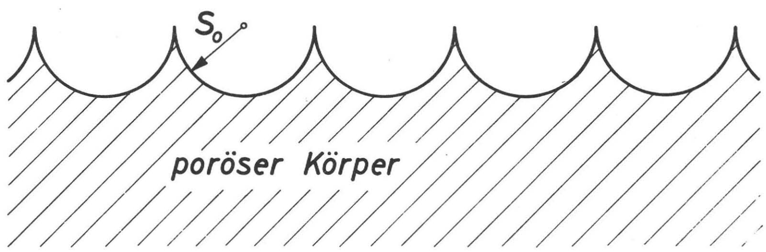


Ill. 1

Let us assume that a drop of a liquid lies on the surface of a porous body. If its radius R increases at a speed $\dot{R}$, new portions of the surface of the body are continuously wettened. Furthermore, the liquid penetrates into the pore system of the body. The radius of the saturated area of the body will be defined as ϱ . If the capillary forces in the direction of body area are lacking and if furthermore there is no pressure within the drop, the radius ϱ of the saturated area of the body will always be equal to the drop radius R if the speed $\dot{x}$ is infinitely great. All capillaries in the body from zero to ϱ are completely filled with liquid.

With an increasing drop radius R, ϱ will also increase. The speed of flow $\dot{r}$ of the liquid in the capillaries of the body on the other hand is and remains zero since according to our definition we assumed $\dot{x}$ to be infinite and the capillary forces in r-direction to be zero.

In order to be able to describe the spreading of the drop, we imagine that there are grooves in the surface of the material with the radius s_o which run radial toward the outside from the center of the drop.



Ill. 2

The liquid flows in these grooves whereby frictional forces are created. The resulting forces which act in the direction of the movement are related for simplicity's sake to the area of two grooves, i.e. to $\pi \cdot s_o^2$ so that we abtain the pressure Σ p.

If the mass forces are not considered, the frictional forces and the pressure forces should balance one another. The following relationship is obtained for the drop radius R.

$$R^2 = R_o^2 + t \frac{s_o^2}{4\eta} \Sigma P \qquad (1)$$

Herein $\Sigma P = \frac{2\varepsilon}{s_o} + P - \frac{2\alpha}{s_o}$ (1') is valid.

First of all, herein is

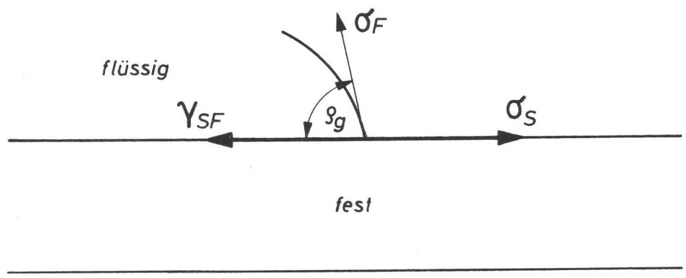
η the dynamic viscosity of the liquid in dyn s/cm^2

s_o the radius of the surface grooves in cm

R_o the drop radius at the time t=o in cm p the liquid pressure of the drop in dyn/cm^2

α the marginal line tension responsible for the marginal angle hysteresis [9] in dyn/cm

The letter ε can be defined with the aid of illustration 3.



Ill. 3

In case of equilibrium the following is valid:

$$\sigma_s - \gamma_{sf} = \sigma_f \cos \vartheta_g$$

Herein is:

σ_s the surface tension of the solid body in dyn/cm

σ_f the surface tension of the liquid in dyn/cm

γ_{sf} the interfacial tension between liquid and solid body in dyn/cm

The difference $\sigma_s - \gamma_{sf}$ is also called wetting tension σ_{sf}.

When the wetting drop is set on the surface equilibrium has not yet been reached. In the interfacial area the specific pressure energy ε can become effective.

It is defined as follows:

$$\varepsilon = \sigma_s - \gamma_{sf} - \sigma_f \cos \vartheta$$

respectively

$$\varepsilon = \sigma_{sf} - \sigma_f \cos \vartheta$$

whereby ϑ signifies the momentary marginal angle.

2.2 The absorption of a liquid by the capillaries of a porous body.

For the depth x of penetration of a liquid vertical to the body surface the relationship derived at by Lucas [6] and Washburn [7] is valid but has to be slightly altered if liquid pressure p in addition is in effect.

The relationship in that case is:

$$x^2 = \frac{s^2}{4\eta}\left[\frac{2\sigma_f \cos\varphi_g}{s} + p\right]\cdot t \qquad (2)$$

Herein is:

σ_f the surface tension of the liquid in dyn/cm

φ_g the marginal angle of the liquid with the wall of the capillaries in the interior of the body

η the dynamic viscosity of the liquid in dyn s/cm^2

s the capillary radius in cm

p the liquid pressure in dyn/cm^2

t the time in seconds

If the capillaries of a porous body are connected with one another, we have to rewrite the equation (2) with the abbreviation $\gamma = \sigma_f \cdot \cos\varphi_g$ as shown by Tollenaar,

$$x^2 = \frac{s^2}{4\eta}\left[\frac{2\gamma}{s}\left(2 - \frac{s}{s_{eff}}\right) + p\right]\cdot t \qquad (3)$$

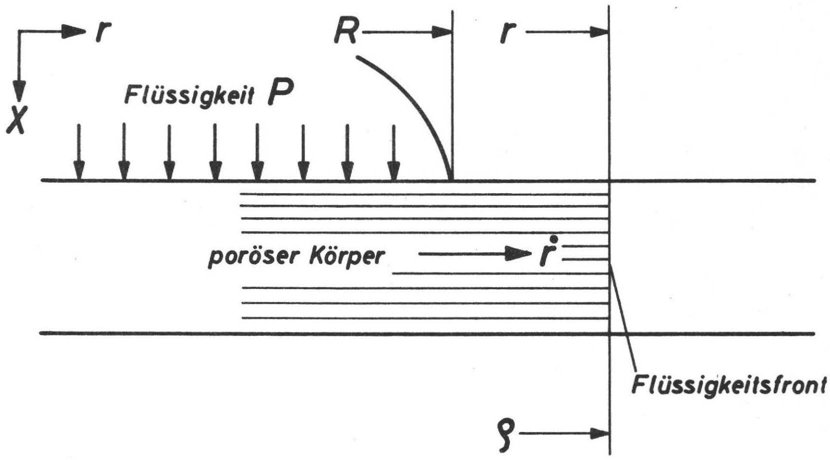
Hereby is according to [4]

$$s_{eff} = \frac{\int_0^\infty \varphi_x(s)\, ds}{\int_0^\infty \frac{1}{s}\varphi_x(s)\, ds} \qquad (3')$$

For the case p=o s_{eff} is the radius of the capillaries in which the liquid has risen the farthest.

φ_x (s) is the distribution function of the capillaries which are directed vertically to the body surface.

For the penetration of the liquid in the direction of the body surface the same laws apply in principle.



Ill. 4

We assume that the source, in our case a drop of liquid, has a constant radius R. After a certain time a liquid front with the radius $\varrho \equiv r$ has formed in the porous body which spreads with a speed $\dot{r}$.

If we do not consider the mass forces the capillary forces, pressure forces and frictional forces must be at an equilibrium.

The connection between the radius r of the liquid front and the time t is calculated analogous to equation (2) as

$$r^2 = \frac{s^2}{4\eta}\left[\frac{2\gamma}{s} + p\right]\cdot t + R^2 \qquad (4)$$

If the capillaries of the body are connected with one another, analogous to equation (3) the following is true:

$$r^2 = \frac{s^2}{4\eta}\left[\frac{2\gamma}{s}\left(2 - \frac{s}{s_{eff}}\right) + p\right]\cdot t + R^2 \qquad (5)$$

Analogous to equation (1') we now define a sum of the pressure energies

$$\Sigma p' = \frac{2\gamma}{s}\left(2 - \frac{s}{s_{eff}}\right) + p \qquad (5')$$

which becomes effective in the interior of the body. It is responsible for the advance of the liquid in the capillaries lying in r-direction.

The radius s_{eff} is calculated according to the equation:

$$s_{eff} = \frac{\int_0^\infty \varphi_r(s)\, ds}{\int_0^\infty \frac{1}{s} \varphi_r(s)\, ds} \qquad (5'')$$

whereby $\varphi_r(s)$ now signifies the distribution function of the capillaries lying in the direction of the body area.

In accordance with equation (5) the spreading radius r for each capillary radius can be calculated. It will be seen that we deal with three different cases deviating from another depending upon the relationship of the liquid pressure p to the pressure $\frac{2\gamma}{s_{eff}}$ in the capillaries with the radius s_{eff}

Case 1: $p > \frac{2\gamma}{s_{eff}}$

Case 2: $p = \frac{2\gamma}{s_{eff}}$

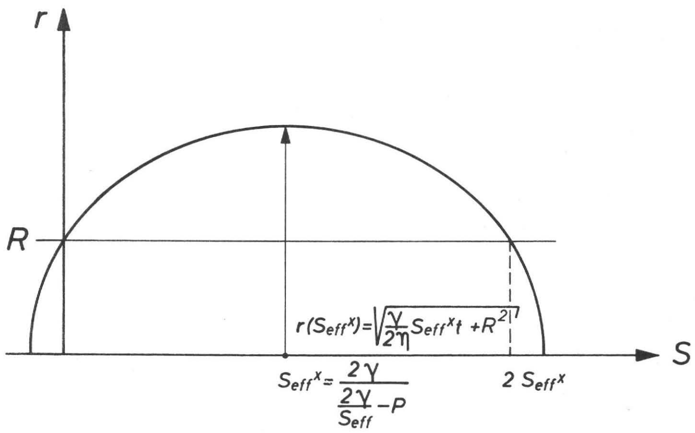
Case 3: $p < \frac{2\gamma}{s_{eff}}$

We define a radius s_{eff}^{x} as:

$$s_{eff}^{x} = \frac{2\gamma}{\frac{2\gamma}{s_{eff}} - p} \qquad (6)$$

In the case 1, $p > \frac{2\gamma}{s_{eff}}$, s_{eff}^{x} becomes < 0, in case 2, $p = \frac{2\gamma}{s_{eff}}$ s_{eff}^{x} moves toward infinity, i.e. in both cases no realizable s_{eff}^{x} exists. The liquid will advance the fastest in the capillaries with the greatest diameter.

For further considerations only the case $p < \frac{2\gamma}{s_{eff}}$ is of importance. Hereby the function r (s) proceeds as follows:



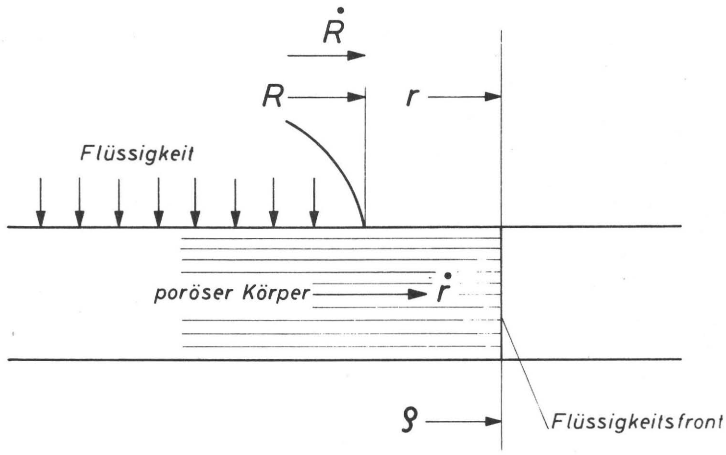
<u>Ill. 5</u>

The liquid therefore will advance the farthest in the capillaries with the radius $s_{eff}^{x} = \dfrac{2\gamma}{\frac{2\gamma}{s_{eff}} - P}$ and thus form the liquid front.

Only when the pressure p disappears, $s_{eff}^{x} = s_{eff}$

In all prior considerations we have treated the penetration into depth and the spreading in the horizontal separately and under very limiting conditions. We had assumed that a penetration into depth takes place first and that the spreading into the horizontal takes place only subsequently. Actually, after the drop is superimposed, both processes take place simultaneously and overlap. We are dealing here with an instationary flow problem which has not yet been mathematically treated. The following considerations therefore do not describe the starting process taking place in the porous body but limit themselves to the consideration of the spreading process of the drop and to the simultaneously occurring advance of the liquid front. Both these phenomena can also be observed during experiments.

2.3 The coaction of the processes as described in Sections 2.1 and 2.2



Ill. 6

Let us assume that in the above illustration $\dot{r}$ is the speed of the liquid in the capillaries which are filled the farthest. r is then identical to the radius ρ of the liquid front.

The radius R of the liquid drop enlarges itself with the speed $\dot{R}$ in accordance with equation (1). On the other hand, the liquid enters the interior of the porous body due to the pressure energies effective there at a speed $\dot{r}$ in accordance with equation (5).

A number of model concepts give rise to the supposition that despite the connection which no doubt exists between the pores on the surface and the pores on the interior of the body, the spreading of the liquid on the surface and its spreading in the capillaries proceed quite independently of one another due to the pressure energies effective there. This independence of both processes forms the basis for the following considerations.

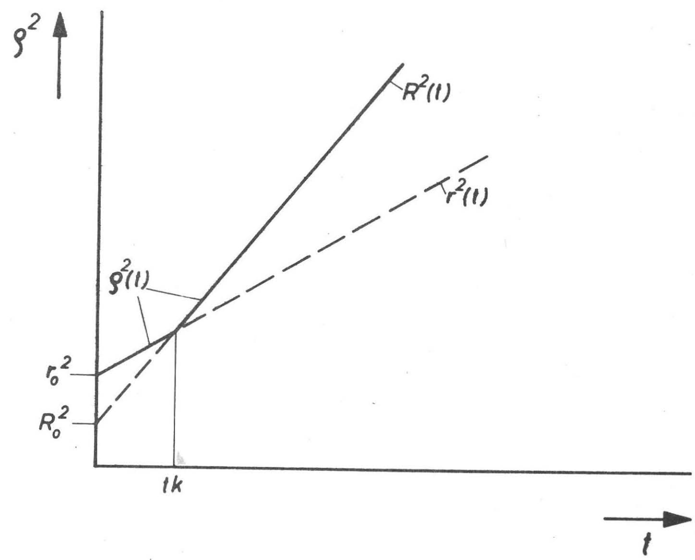
If ρ is the radius of the liquid front, we differentiate between three cases:

Case 1: $\dot{R} > \dot{r}$; after sufficiently long time $\rho \equiv R$ results.
i.e. equation (1) is valid for the calculation of ρ.

Case 2: $\dot{R} < \dot{r}$; there results: $\rho \equiv r > R$
i.e. equation (5) is valid for the calculation of ρ.

Case 3: $\dot{R} = \dot{r}$; there results: $\rho \equiv r$ or $\rho \equiv R$
i.e. equation (1) or (5) is valid for the calculation of ρ.

If we plot the square of the radius ρ of the liquid front over the time, we obtain in case $\dot{R} > \dot{r}$ for an example the following diagram:



Ill. 7

We see therefore, that in the range $0 \leq t \leq t_K$ the radius $r > R$, thus is $\rho(t) \equiv r(t)$, which shows that equation (5) is valid here.

In the range $t \geq t_K$ on the other hand, the radius R of the drop and the radius ρ of the liquid front are identical. Thus equation (1) is valid.

Let us now consider the capillaries with an assumed radius s in the interior of a porous body. The liquid in them has progressed to radius r(s). If the drop radius R begins to grow, in an ever increasing number of capillaries the radius ρ of the liquid front will gradually become identical with R.

In order to be able to mathematically describe this overtaking process, we form the difference

$$\Delta r(s) = r(s) - R \qquad (7)$$

In this relationship we enter equations (1) and (5) in somewhat altered form.

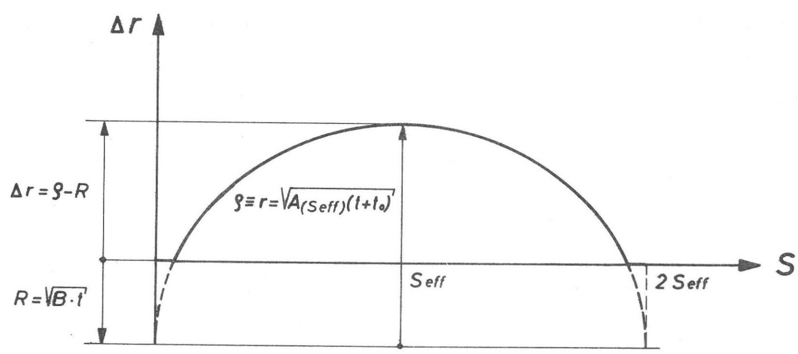
For the relationship (1) we write

$$R^2 = B \cdot t$$

and for relationship (5)

$$r(s)^2 = A(s) \cdot (t + t_o)$$

If we do not consider the liquid pressure p, we obtain the following diagram for $\Delta r(s)$.



<u>**Ill. 8**</u>

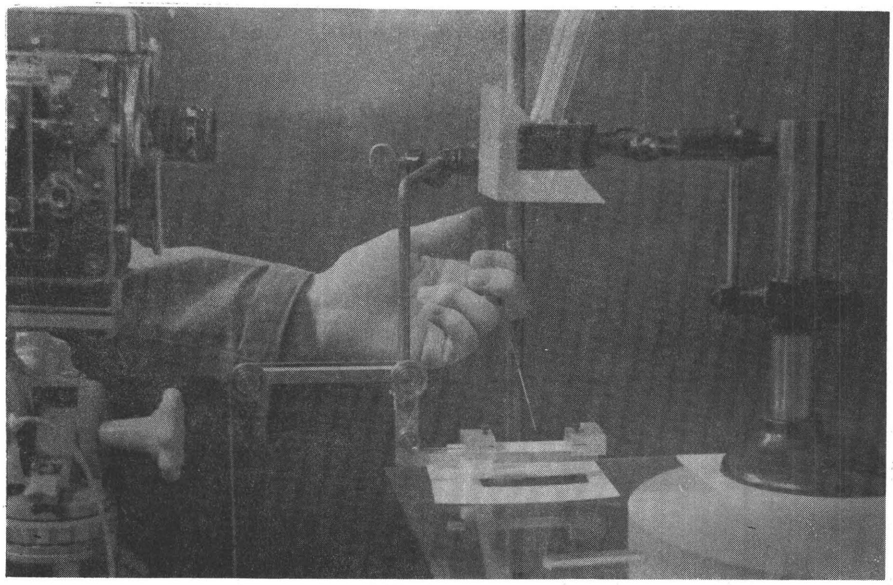
We realize that for $\dot{R} > \dot{r}(s_{eff})$ in the course of time $\Delta r = 0$ will become true for more and more capillary radii until finally after the time

$$t_K = \frac{t_o}{\frac{B \cdot 2\eta}{\gamma \cdot s_{eff}} - 1}$$

all capillaries are filled with liquid up to radius $R \equiv \rho$. In the next chapter we shall see to what extent tests confirm and supplement the theory.

3) Practical Tests

3.1 Description of tests



Ill. 9

A test strip is freely suspended between two clamp jaws. Normally, the pull tension amounted to 100 p/cm. We should like to mention right here that an increase from 20 to 200 p/cm did not measurably change the penetration characteristics of the liquid. A certain quantity of liquid was pushed out of the point of the needle of a syringe so that it hung suspended as a drop at the point of the needle. This drop now came in contact with the porous body. A 16 mm film camera recorded in every instance the size of the radius ρ of the liquid front. Light was passed through the sample. The films were evaluated photo-analytically so that function $\rho^2(t)$ could be plotted in a graph.

The air around the test sample was enriched with the steam of the liquid in order to reduce evaporation.

3.2 Evaluation of measurements

The tests have not yet been completed. Due to the inhomogeneity of paper a great number of tests are required in order to be able to make quantitative statements. The test results gained so far allow only qualitative conclusions.

Test liquids used are Toluole and Dioxane.

Toluole: σ_f = 27,4 dyn/cm $\quad\eta$ = 0,586 cPoise

Dioxane: σ_f = 35,4 dyn/cm $\quad\eta$ = 1,26 cPoise

The values are based on t = 20°C

The liquid volumes applied are 1 - 8 mm^3. Liquid quantities exceeding 4 mm^3 cannot be superimposed on sample in droplet form at one time. In such cases further injections are necessary.

Porous bodies used are three papers:

Paper 1 : uncoated rotagravure paper
area weight 79 gr/m^3 thickness 67 μm

Paper 2 : uncoated rotogravure paper
area weight 68 gr/m^3 thickness 68 μm

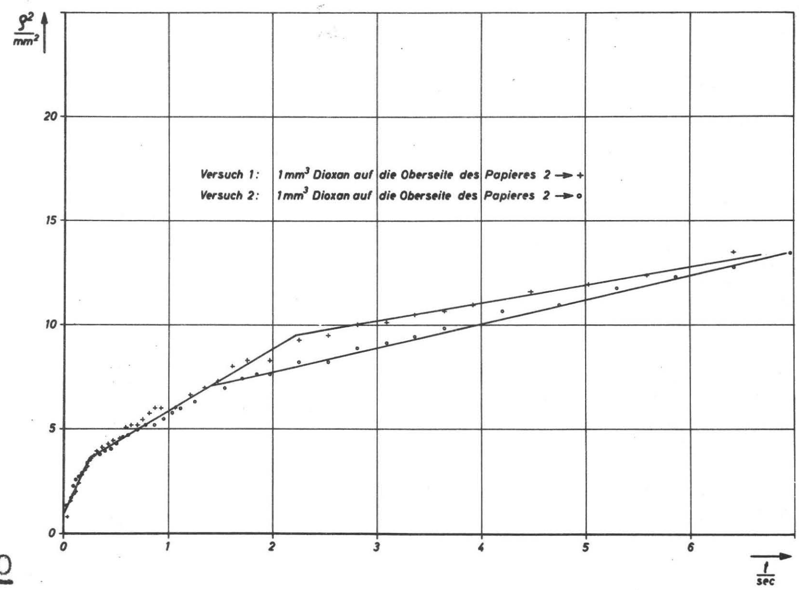
Paper 3 : raw paper
area weight 71 gr/m^3 thickness 116 μm

The liquid front at the start of the tests first spreads out on the paper in a circular form. Later on, the spot assumes the shape of an ellipse. In the graphs the square of the radius ρ of the circle equal in area to the ellipse is plotted, namely

$$\rho^2 = a \cdot b$$

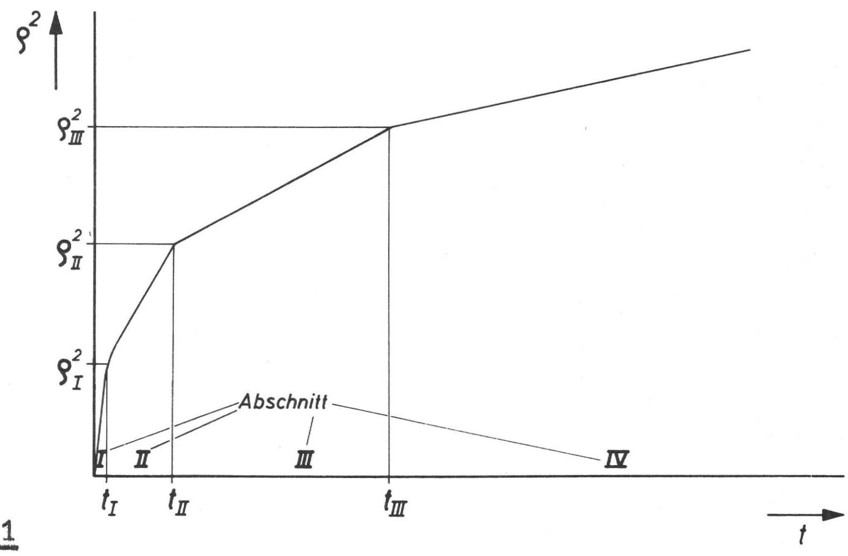
Hereby a and b represent the two semiaxes of the ellipse.

During the major portion of the tests a curve path of the function $\rho^2(t)$ showed up which is depicted in the following illustration.



Ill. 10

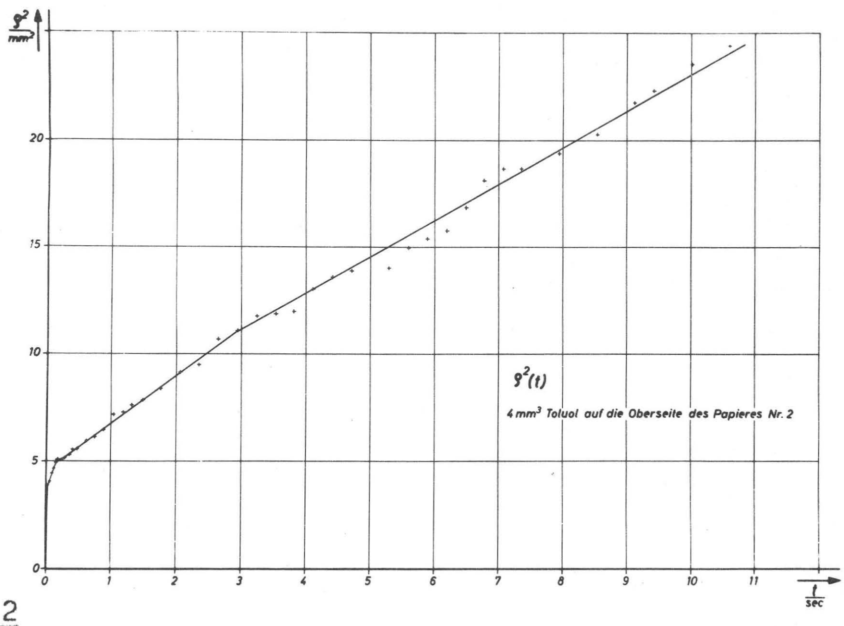
We recognize a curve path which can be subdivided into four sections.



Ill. 11

Sections I and II

At the end of both these periods of time we observe a break in the function $\rho^2(t)$. In many tests the evaluation of the photographs showed a gradation at this point.



Ill. 12

The presence of gradation allows the assumption that during the Sections I and II the radius ρ of the liquid front coincides with the drop radius R. At that time $\dot{R} > \dot{r}$ is valid. If the marginal line of the drop moves ahead on the surface of the paper, the liquid front will remain behind on the lower side of the paper due to the final penetration speed $\dot{x}$ of the liquid in the direction of the paper thickness. It takes a certain time for the liquid front to run vertical to the paper surface. The photos show a gradation during this overtaking process. Whether or not the foremost point of the liquid front is in motion or is at rest cannot be determined with certainty on the basis of the photographs, since as a result of the distribution function of the pore radii a flowing transition of the light transmission from Toluole to the paper takes place. The distribution function r(s) in the immediate vicinity of the drop will, however, be very shallow. One therefore must conclude that the gradation in the graph is real.

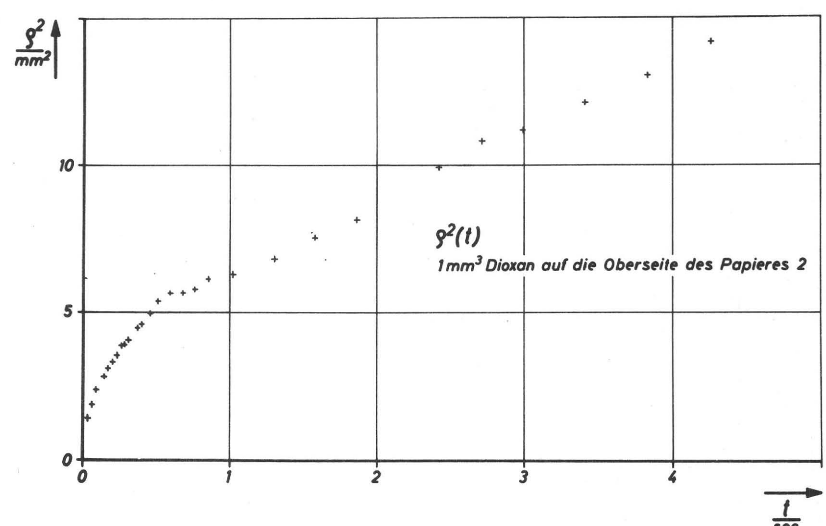
A noticeable deviation of the curve path of the function from reality can only occur after long periods of time, when the course of the distribution function r(s) has become very sharp.

If during sections I and II the marginal line of the drop is at the same time the front line, i.e. $R \equiv \rho$ we may describe the course of the function $\rho^2(t)$ with the aid of equation (1).

Equation (1) is: $$R^2 = R_o^2 + t\,\frac{s_o^2}{4\eta}\,\Sigma p$$

whereby $$\Sigma p = \frac{2\varepsilon}{s_o} + p - \frac{2\alpha}{s_o}$$

As soon as the liquid touches the paper, a marginal area is created between the two media. The marginal angle φ , under which the surfaces of the liquid and the paper meet, will strive toward an equalization value φ_g . If this marginal angle of equilibrium is reached, ε becomes Zero by definition; Section I is ended. The tests show that the Sections I and II continuously merge. This is understandable since φ cannot suddenly become equal to φ_g , i.e. ε cannot discontinuously become Zero. This was particularly evident in the tests with Dioxane as shown in the next graph, since the processes with this liquid which has a higher viscosity proceed slower than with Toluole.



Ill. 13

During Section II the following is valid since $\varepsilon = 0$:

$$\Sigma p = p - \frac{2\alpha}{s_o}$$

Section III

On the bases of visual observations which are to be verified photo-analytically, the drop does not further noticeably change its radius. Any further advance of the front is now necessarily determined by processes in the interior of the body, i.e. the equation (5) and thus $\rho \equiv r$ applies.
Since the capillaries of the paper continue to absorb the drop, the marginal angle φ_g at a constant radius R drops from a maximum value $\varphi_{g\,max}$ at the end of Section II to a minimum value $\varphi_{g\,min}$ at the end of Section III. The marginal angle hysteresis [9] permits this angle change.
If during the tests the minimum quantity of 1 mm^3 was superimposed, Phase III either was absent altogether or at least could no longer be clearly observed.

The pore radius $s^{\times}_{eff}$ can be determined from the slope of the function $\rho^2(t)$ in Section III. According to definition it is the radius of the capillaries in which the liquid has progressed the farthest.

The following values for $s^{\times}_{eff}$ for each type of paper were received from tests hitherto carried out:

Paper 1 $\quad s^{\times}_{eff} = 2,7 \cdot 10^{-5}$ cm

Paper 2 $\quad s^{\times}_{eff} = 1,7 \cdot 10^{-5}$ cm

Paper 3 $\quad s^{\times}_{eff} = 1,8 \cdot 10^{-5}$ cm

These values lie slightly above the radii measured by P.A.H. Ernst [8] which can be attributed to the effect of the liquid pressure in the interior of the drop.

Section IV

If the processes in Section IV are observed visually it can be determined that the drop radius reduces itself until no more liquid is found on the surface of the paper. The physical relationships have not as yet been dealt with.

4) Summary

The behaviour of a liquid on the surface of a porous body and the absorption of the liquid by its capillaries was theoretically and experimentally examined. In this treatise all the problems could not be completely discussed.

Theoretical considerations and tests proved, however, that the penetration process and the spreading of a liquid on the surface of a porous body represent two phenomena which proceed as though they were completely independent of each other. It is therefore, reasonable to apply independent formulas for both processes. The tests show that in the beginning phase the drop radius R is identical with the radius ρ of the liquid front, whereas later on the pressure energies in the capillaries of the body determine the advance of the liquid front. Further tests are necessary in order to be able to make clear qualitative statements about the individual sections of the function of $\rho^2(t)$.

The aim of this and subsequent treatises will be to arrive at a better understanding of the absorption behaviour of liquids as a whole, respectively, of printing inks.

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