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# The First Step in the Swelling of Gelatin with Water. II

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On the basis of a very simple model of the structure of gelatin and of the individual layers of the Christensen-interference plate it is possible to explain the two steps of absorption of water into the interference plate and to show that the final amount of water here is the same as in the corresponding chromated gelatin plate. Moreover it is shown that the diffusion of water throught gelatin is independent of the degree of hardening.

In the first paper in this series [1] I have examined the speed of swelling of the Christensen-interference plate with water. I was thereby forced to assume that about half of the water was taken up practically momentarily, whereas the remaining water was absorbed in the course of some days.

Continued examination of this peculiar phenomenon on various other examples of the said plates has shown its general character. At the same time it has been possible to measure the first "momentary" time and to give a plausible explanation of the two different modes of swelling on the same plate.

## 1. THE FORMULA

In the said paper was used the formula

$$v_{\mathrm{v}} - \varDelta = (v_{\infty} - \varDelta)(1 - 10^{-k.t^{0.5}}) \tag{1}$$

where $v_{\mathrm{v}}$ is the momentary volume of water, $\varDelta$ the "instantaneous" absorption of water, $v_{\infty}$ the final absorption of water, all of them per 100 volumes of gelatin, $k$ is a constant and $t$ the time (in minutes) of the slow absorption.

The examination of five other plates has shown that good agreement with this formula can only be obtained if the time $t$ is replaced by $t-t_0$, the formula therefore being

$$v_{\mathrm{v}} - \varDelta = (v_{\infty} - \varDelta)(1 - 10^{-k_2(t-t_0)^{0.5}}) \tag{2}$$

and, as the time $t_0$ is of the order of 0.1—2.0 minutes, it must be understood as the time for the first, "momentary" swelling.

Table 1 contains the results. The 1st column shows the number of the plate. Fig. 1 refers to the upper side of the "broad band"[2], Fig. 2 to the lower side. The 2nd column shows the percentage by volume of unhardened gelatin G′, the 3rd the percentage by volume of silver bromide $v_A$. Next comes $\Delta$, the first rapid absorption of water, $v_\infty - \Delta$, the second slow absorption, then the observed and calculated values of $t_0$, the observed and calculated values of $k_2$, the velocity constant of the slow absorption, and finally $k_3$ (see below).

*Table 1.*

| Plate No. | G′ | $v_A$ | $\Delta$ | $v_\infty - \Delta$ | $t_0$ |  | $k_2 \times 10^2$ |  | $k_3$ |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | obs. | calc. | obs. | calc. |  |
| $20_2$ | 22.2 | 8.3 | 94.2 | 40.2 | 1.7 | 1.8 | 2.88 | 2.50 | 23.0 |
| $20_1$ | 31.1 | 15.3 | 93.3 | 38.7 | 2.0 | 1.7 | 2.57 | 2.70 | 20.6 |
| $14a_2$ | 22.2 | 15.0 | 90.2 | 38.5 | 1.5 | 1.3 | 3.54 | 3.36 | 21.2 |
| $14a_1$ | 30.2 | 26.4 | 87.1 | 41.9 | 0.9 | 1.0 | 3.47 | 3.60 | 24.1 |
| $9_2$ | 22.2 | 14.9 | 85.7 | 43.9 | 1.2 | 0.9 | 3.41 | 3.35 | 20.0 |
| $9_1$ | 30.9 | 22.9 | 81.9 | 46.5 | 0.5 | 0.6 | 3.34 | 3.32 | 25.0 |
| $28_2$ | 21.9 | 14.2 | 82.6 | 59.4 | 0.5 | 0.7 | 3.11 | 3.30 | 24.9 |
| $28_1$ | 34.2 | 23.3 | 76.7 | 58.5 | 0.4 | 0.3 | 2.85 | 3.14 | 19.8 |
| $2_2$ | 22.2 | 17.3 | 71.7 | 76.4 | 0.1 | 0.1 | 3.77 | 3.60 | 23.7 |
| $2_1$ | 30.6 | 27.0 | 69.9 | 76.5 | 0.1 | 0.1 | 3.23 | 3.63 | 18.7 |
|  |  |  |  |  |  |  |  |  | 22.1 |

The quoted values are means of three independent experiments.

The plates were selected to give the greatest possible variations in properties and composition. No. 20 was watered before treatment with silver nitrate, No. 28 has a special thick coating, No. 2 a special high content of silver bromide, and the remaining two plates are more normal, but still with a marked difference in the extinctions of the original chromated gelatin plates.

## 2. THE STRUCTURE OF THE GELATIN LAYER

In order to penetrate into this certainly very complex subject it is necessary to use a very simplified working model. Like Sheppard, Lambert and Swinehart [3] I assume that the gelatin molecule has a length of about 100 m$\mu$ and a diameter of 0.8—0.9 m$\mu$, and that all the polar groups are found on one side of the molecule, which is therefore hydrophilic, whereas the non-polar groups are found on the other side, which is therefore hydrophobic.

The most simplified model of this structure is shown in Fig. 1, where two hydrophilic surfaces are connected, perhaps with a thin layer of water between them, as air dryed gelatin always contains some water, about 15—20 %. The mutual attraction between these hydrophilic surfaces, with or without the layer of water, will presumably be greater than the attraction between the two adjacent, hydrophobic surfaces.

## 3. THE CHROMATED GELATIN

If a gelatin layer of the suggested structure is treated with a solution of a chromate, the chromate ions must necessarily be adsorbed on the hydrophilic surfaces, and by the following hardening by light the chromate-bonds must therefore be situated between these surfaces. As to the hydrophobic surfaces, there is accordingly no difference between hardened and unhardened gelatin.

## 4. THE DIFFUSION OF WATER

In general it is assumed that the rate of diffusion of water in gelatin is independent of the degree of hardening of the gelatin, but it has not been possible to find any literature about this problem. Therefore, I have measured the rate of diffusion directly.

For this purpose four thick layers of photographic gelatin (Stoess, middle hard) were prepared on plate glass which was covered with Zaponlack so that afterwards the layers could be removed and the Zaponlack be dissolved in amyl acetate. One of the layers was hardened with formaldehyde, another, after treatment with a chromate solution, was hardened by prolonged exposure with a mercury lamp, while the two others were not treated in any way.

The thicknesses of the layers were measured directly with a micrometer. Then they were, one at a time, pressed against a Christensen-interference plate, a little water was poured out on the gelatin and the time was measured until the first sign of colour variation on the interference plate was observed. The results are shown in Table 2.

*Table 2.*

| Treatment | Thickness in $\mu$ | $t$ sec | sec/$\mu$ |
|---|---|---|---|
| Unhardened | 65 | 41 | 0.63 |
| Unhardened | 60 | 45 | 0.75 |
| Hardened with formaldehyde | 73 | 60 | 0.82 |
| Hardened with chromate and light | 80 | 45 | 0.56 |
| | | | 0.69 |

Table 2 shows that the rate of diffusion is independent of the degree of hardening. This result must be expected from the suggested model of the structure. The diffusing water must find its way through the lowest possible resistance, *i.e.* between the hydrophobic surfaces. As conditions here are independent of the degree of hardening, the rate of diffusion must be the same for hardened and unhardened gelatin, as was actually found.

## 5. THE TREATMENT WITH SILVER NITRATE

When the exposed chromated gelatin plate is treated with a solution of silver nitrate the silver ions must be adsorbed on the hydrophilic surfaces, and

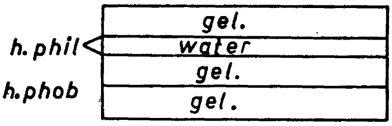

Fig. 1.

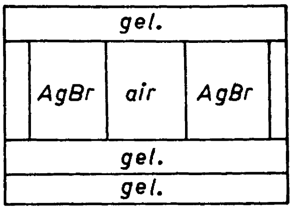

Fig. 2.

by the subsequent treatment with potassium bromide the silver bromide particles must become situated on the same places, probably linking the two adjacent surfaces together. The situation in the plate is now as shown in Fig. 2.

## 6. THE FIRST "INSTANTANEOUS" SWELLING

The experiments show that the amount of water hereby absorbed agrees with the formula

$$\Delta = 64 + k_3 t_0^{0.5} \qquad (3)$$

The values of $k_3$ and the calculated values of $t_0$ are shown in Table 1.

The number 64, which means volume of water per 100 volumes of total gelatin, is the same for all the examined plates. As it is independent of time it must refer to the almost instantaneous diffusion of water between the hydrophobic surfaces. It must therefore be independent of the degree of hardening.

In Fig. 3 are shown my earlier measurements [4] of the amounts of water absorbed in differently exposed chromated gelatin. The four curves correspond to plates which are treated with water 2, 4, 7 and 11 days after producing the

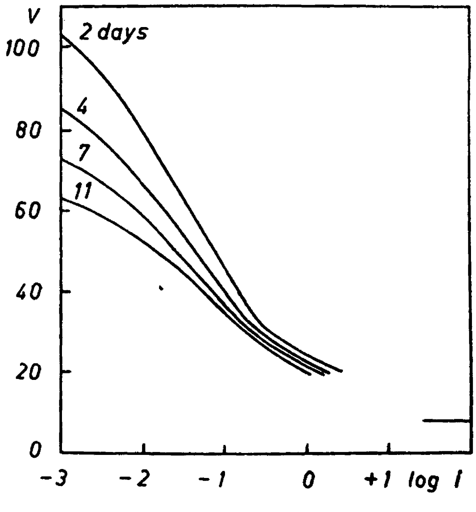

Fig. 3.

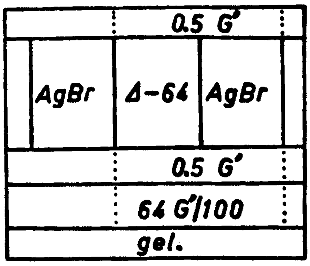

*Fig. 4.*

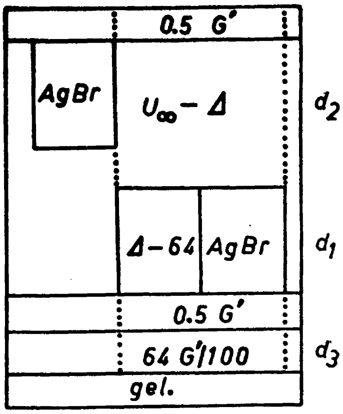

*Fig. 5.*

plates. The abscissae are the logarithms of the quantities of light, the ordinates the amounts of water per 20 mg of coating. Obviously the curves are not going to zero but are approaching a certain positive value. To the right is marked out the amount of water which corresponds to 64 %. These measurments therefore confirm the conclusion that the very rapid diffusion is independent of the degree of hardening.

When this rapid diffusion has finished the water proceeds to fill the interstices between the gelatin and the silver bromide particles. It is quite natural that the time for this absorption increases with the amount of absorbed water, as shown in formula (3). The measured values, 0.1—2.0 minutes, are in agreement with my earlier measurements, which have shown that the swelling of chromated gelatin is completed in less than 2.5 minutes. Further treatment with water up to 15 minutes shows no difference.

The situation is now as shown in Fig. 4.

## 7. THE SECOND SWELLING

In my earlier experiments with swelling of exposed layers of chromated gelatin [5] I have found that the adsorption of silver nitrate is somewhat greater than could be expected from the concentration of the solution, so that a selective adsorption of silver nitrate must take place. In other words, the forces between silver ions and gelatin are somewhat stronger than those between water and gelatin. Through the competition between the bonds water-gelatin and AgBr-gelatin, which consequently are not very much different, there will in every moment occur a number of ruptures between gelatin and silver bromide, so that there will always be a very small, but constant, number of free gelatin surfaces. This situation can be written as an equilbirium

$$\text{gel.AgBr.gel.} \rightleftharpoons \text{gel. AgBr} + \text{gel.}$$

The two "concentrations" on the right side are equal, therefore

$$\text{gel.} = K\ (\text{gel.AgBr.gel.})^{0.5}$$

Now, after the first rapid absorption water continues to enter. Thereby the process must be furthered, and the speed must be proportional to the existing free gelatin surface. In accordance herewith the experiments show that

$$k_2 = k_4 \left( \frac{v_A}{G' - \dfrac{64}{9.3}} \right)^{0.5}$$

The number 9.3 is the swelling factor for this particular type of gelatin [4]. For the results see Table 3 (for $k_4$) and Table 1 where the observed and calculated values of $k_2$ are compared.

Now the situation is as shown in Fig. 5. In this figure are indicated the thicknesses of

the gelatin molecule (assumed to be 0.8 mμ),
the silver bromide particle, $d_1$,
the layer $v_\infty$—$\Delta$, $d_2$, and
the layer "64", $d_3$.

These three numbers are given in absolute measure, if the thickness of the gelatin molecule is taken as 0.8 mμ. The following two lengths are only relative.

*Table 3.*

| Plate No. | $k_4 \times 10^2$ | $d_1$ | $d_2$ | $m$ | $n$ | $v_1$ | $v_2$ | $D$ | $k_5$ |
|---|---|---|---|---|---|---|---|---|---|
| $20_2$ | 3.92 | 2.78 | 2.90 | 13.4 | 3.0 | 4.37 | 5.68 | 11.9 | 2.73 |
| $20_1$ | 3.23 | 2.28 | 1.98 | 12.8 | 6.8 | 5.75 | 4.26 | 11.9 | 2.55 |
| $14a_2$ | 3.57 | 2.96 | 2.78 | 8.8 | 5.0 | 5.18 | 5.74 | 15.0 | 2.35 |
| $14a_1$ | 3.27 | 2.62 | 2.24 | 8.8 | 10.1 | 5.75 | 4.86 | 15.0 | 2.36 |
| $9_2$ | 3.45 | 2.64 | 3.16 | 8.2 | 5.6 | 5.18 | 5.80 | 14.8 | 2.45 |
| $9_1$ | 3.40 | 2.28 | 2.60 | 7.8 | 10.0 | 6.27 | 4.88 | 14.8 | 2.52 |
| $28_2$ | 3.08 | 2.36 | 4.28 | 7.8 | 6.0 | 5.07 | 6.64 | 19.3 | 2.10 |
| $28_1$ | 3.08 | 1.68 | 2.74 | 7.4 | 13.9 | 5.96 | 4.42 | 19.3 | 2.28 |
| $2_2$ | 3.55 | 1.80 | 5.52 | 4.2 | 9.6 | 5.18 | 7.32 | 15.8 | 2.06 |
| $2_1$ | 3.51 | 1.80 | 3.90 | 4.2 | 15.0 | 5.76 | 5.70 | 15.8 | 2.12 |
|  | 3.40 |  |  |  |  | 5.45 | 5.53 |  | 2.38 |

The length of the silver bromide particle, $n$, and
the length of the water filled interstice $\Delta - 64$, $m$.

As $$0.5\,G' = 0.8\ (m + n) \tag{5}$$

and $$\Delta - 64 + v_A = d_1\ (m + n)$$

then $$d_1 = 1.6\,\frac{\Delta - 65 + v_A}{G'} \qquad m = \frac{\Delta - 64}{d_1} \qquad n = \frac{v_A}{d_1}$$

Further

$$d_2 = d_1 \frac{v_\infty - \Delta}{\Delta - 64 + v_A} \qquad\qquad d_3 = 1.6 \frac{64}{100} = 1.0 \text{ m}\mu$$

The last number $d_3$ must have a constant value as the amount 64 comprises both hardened and unhardened gelatin.

The values of the other quantities are given in Table 3.

For pure chromated gelatin with the swelling factor 9.3 the amount of water in the second slow swelling is 9.3 G′ — 64. The length $m + n$ is calculated for 0.5 G′ (see formula (5)). The amount of water per (relative) unity of length therefore is

$$v_1 = \frac{0.5(9.3 \text{ G}' - 64)}{m + n}$$

For the interference plate the corresponding quantity (see Fig. 5) must be

$$v_2 = \frac{(v_\infty - \Delta)\frac{m}{m+n} + \Delta - 64}{m} = d_1 + d_2$$

The values of $v_1$ and $v_2$ are shown in Table 3. The values of $v_2$ must be less exact than those of $v_1$ because so many different observations take part in the calculations of them, each with its own uncertainty. As a whole there can still be no doubt about the identity of the two series of numbers. The slow absorption of water, therefore, proceeds to the same end in pure chromated gelatin and in the interference plate, indicating that the elastic forces between the gelatin molecules which terminate the absorption are of the same magnitude in the two different cases.

## 8. THE SPONTANEOUS DRYING OF THE WET PLATE

After the measurement of the final amount of water by the swelling process the plate was with the utmost speed wiped with filter paper and then spectrographed 0.5, 1, 2 . . . minutes after wiping.

During the drying process the water does not need to overcome any elastic or other forces, but the process is a simple diffusion and evaporation. Accordingly the speed of drying must be inversely proportional to the thickness of the coating and directly proportional to the remaining amount of water. Therefore

$$-\frac{dv}{dt} = k_5 \frac{v_V}{D}$$

where $D$ denotes the thickness of the coating in $\mu$. Through integration it follows that

$$v_V = v_\infty 10^{-k_5 t/D}$$

Table 3 contains the results. It seems that the constant $k_5$ decreases a little with increasing thickness of the coating. It must, however be taken into account that the half period for $D = 11.9$ $\mu$ is only 1.3 minutes. As the first spectrograms were taken after 0.5 and 1 minute and the time of exposure must be at least 5 seconds, there must be a systematical error which tends to an apparent increase of the speed of drying, *i.e.* the value of $k_5$ in this case tends to be too great. For the greater values of $D$ the half period increases up to 2.8 minutes and the measurements are therefore apt to be less erroneous.

After completion of this work I have learned that Bagley and Long[6] have examined a quite analogous case by the sorption of acetone vapour in cellulose acetate. Thereby they have found, first a rapid and thereafter a slow stage of sorption, and they have explained the former as due to diffusion and the latter to breaking of the interchain bonds in the polymer network, just as I have proposed.

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