The First Step in the Swelling of Gelatine with Water. VI

CHR. WINTHER

Photochemical Laboratory, Technical University of Denmark, Copenhagen, Denmark

Chromated interference plates absorb a considerable amount of water in the course of one second whereafter the absorption stops for some seconds and then slowly rises again. In some plates there are for some seconds two optical systems working at the same time, one corresponding to the dry state and the other to the wet state, whereafter the first one disappears. The origin of this phenomenon was found. A model of the structure of the interference plate was proposed and discussed.

In a series of papers [1-7] I have described the properties and theory of a chromated gelatine interference plate. For the preparation of this plate (see Ref. 1) a chromated gelatine coating on plate glass is placed with the gelatine side down on a mercury surface and exposed with the blue mercury line 436 mμ for 16—24 min. Then the plate is transferred to a solution of silver nitrate (25:100), dried, then placed in a solution of potassium bromide (20:100), rinsed, then immersed for 6 min in a diluted solution of potassium metabisulphite and potassium bromide, rinsed again and dried. By the exposure the coating is divided in a series of alternating layers of hardened and un-
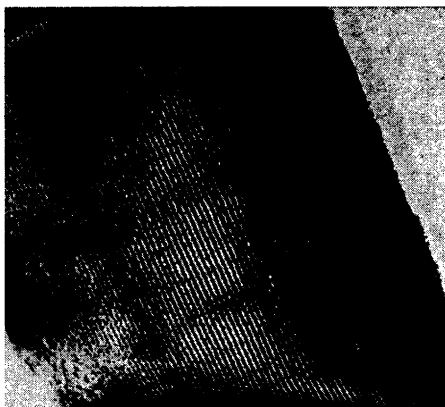

Fig. 1. Section of coating, magnification 3000.

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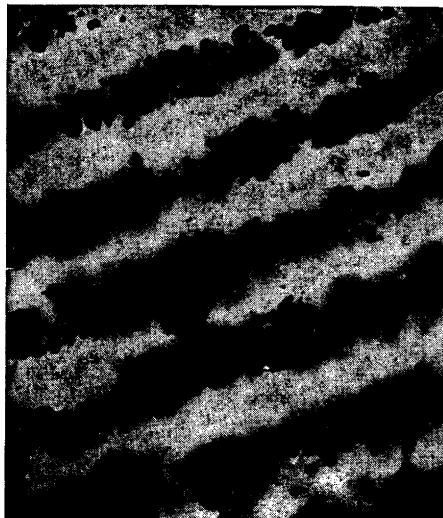Fig. 2. Section of coating, magnification 40 000, dry state.

Fig. 3. Section of coating, magnification 40 000, after bathing in water.

hardened gelatine. Afterwards the silver nitrate is absorbed by preference in the unhardened layers and the final silver bromide is distributed in the same way. The immersion in the bromide solution is discontinued at the first trace of opacity as a sign of the formation of large silver bromide particles. Fig. 1 shows a section of the whole coating, magnification 3000.

Figs. 2 and 3 show a part of the same plate, magnification 40 000, Fig. 2 in the dry state. Fig. 3 after bathing in water. The figures show that the diameter of the silver bromide particles is of the order of $10-50$ mμ.

In an earlier paper [3] I have found that a considerable amount of water is taken up in the course of one minute. In order to make a closer examination of this phenomenon a special apparatus was devised (Fig. 4).

A is a pendulum, length one metre, B a cup filled with mercury, C a switch, D a relay, E a bar supporting the photographic plate holder, and F a photographic shutter.
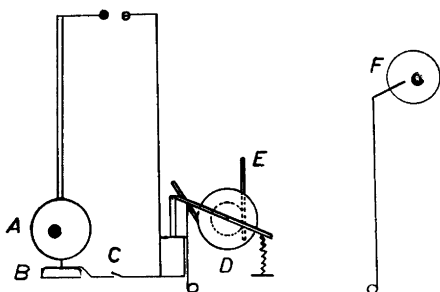

Fig. 4. Apparatus for bathing the plates.

The apparatus functions in the following way. Between the shutter and the split of the spectrograph is placed a small cuvette with water. The pendulum is set moving. A small piece of the interference plate to be examined is lowered into the water. At exactly the same moment the switch is closed, the relay starts working, the plate holder is lifted one step, and the shutter opens for 1/100 sec. In this way an exposure is made every second as long as the switch is being pressed down.

The first plate which was measured in this way gave the very remarkable result which is shown in Table 1.

In order to understand Tables 1, 2, and 3 it is necessary to discuss the spectrograms of the interference plates in detail. They consist of two different parts.

1) A single broad band, in the following called BB, with two edges, BB_1 against the higher and BB_2 against the lower wave-lengths. This part occupies about 0.7 of the total thickness of the coating reckoned from the air surface.

2) A series of fringes called KB which occupy most of the deeper part of the coating.

The figures in Table 1 denote the percentage by volume of water v_w at the point BB_1 at different points of time for the plate No. 300. They show that a considerable amount of water is taken up during the first second whereafter the water content remains nearly constant until after about one minute it slowly increases.

<table>
<tr><td align="center">Table 1.</td><td align="center">Table 2.</td></tr>
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Table 1.

Time		V_w
1	sec	90
2		96
5		100
8		102
12		103
16		104.5
20		106
28		106.5
36		108
44		109.5
1	min	110
2		111.5
4		116
8		120
15		124
30		130
60		135
120		141.5
180		146
1	day	169

Table 2.

Time		λ dry		V_w wet
		BB_1	BB_2	
sec	0	555	502	—
	1	568	504	81
	2	568	510	81
	3	567	510	81
	4	564	508	85.5
	5	564	508	87
	6	562	508	87.5
	8	562	506	89
	9			89
	10			90
	16			93
	30			97
	45			99.5
min	1			102.5
	2			106
	4			111.5
	8			119.5
	15			127
	30			135.5
	60			144
days	2			215

Two other plates behaved in the same manner. All these three plates had beforehand been treated with water for some days and then dried.

A series of plates which had not been treated with water behaved in a quite different way. They also took up water with the same enormous speed as the first group of plates but at the same time they retained the status of the plate for some seconds (2—10) whereafter this dry system suddenly (or in a single case more slowly) disappeared and the absorption of water continued in the usual way. This means that two different optical systems were working in the same plate at the same time.

As an example Table 2 shows the figures for plate No. 134. Columns 2 and 3 show the wave-lengths for the upper and lower edge of the band in the dry state, column 4 the percentage by volume of water in the wet state.

Table 3 contains the figures for the only interference plate (No. 47) which has shown a relatively slow transition from the dry to the wet state. The dry state has a duration of 4 sec, whereafter the absorption of water sets in. The second column shows the percentage by volume of silver bromide v_A. The following columns show the percentage by volume of water for nearly the total coating. Some of the higher fringes KB fall outside the sensibility field of the photographic plate and therefore cannot be measured.

Table 3.

	v_A	sec					min					diff.
		6	10	16	30	45	1	2	4	8	15	
BB₁ BB₂												
	32.3	54.1	55.2	55.8	56.1	56.3	56.6	56.9	57.5	58.5	60.4	6.3
	18.3	55.2	56.3	56.9	57.1	57.5	57.7	58.0	58.6	59.5	62.0	6.8
KB	13.5	52.7	53.2	53.9	54.1	54.4	54.6	55.0	55.5	56.3	58.9	6.2
	12.0	49.5	50.1	50.2	50.9	51.2	51.5	51.8	52.4	53.2	55.8	6.3
	10.6	47.4	48.0	48.5	48.9	49.1	49.5	49.7	50.3	51.2	53.9	6.5
	9.2	46.0	46.6	47.2	47.4	47.7	48.0	48.3	48.9	49.7	52.4	6.4
	8.0	45.4	46.0	46.6	46.8	47.1	47.7	47.4	48.0	48.9	51.5	6.7
	6.9	44.8	45.4	46.0	46.4	46.8	46.8	47.1	47.7	48.5	51.2	6.4
	5.8	43.9	44.5	45.1	45.4	45.7	46.0	46.2	46.8	47.7	50.1	6.4
	4.8	43.4	43.4	44.5	45.1	45.1	45.4	45.7	46.2	47.1	49.7	6.3

THE TWO OPTICAL SYSTEMS

A simple observation disclosed the origin of this remarkable phenomenon. A small piece of a red interference plate whose colour by absorption of water shifted to green was placed in water for one second and then immediately wiped and examined under the microscope. Thereby small circular red spots in green surroundings were observed. In the course of a few seconds the red spots vanished. The diameter of these red spots were of the order of $10-100$ mμ. If the interference plate had beforehand been treated with water there were no red spots visible.

The explanation of this phenomenon is that the circular spots and the corresponding extra optical system are due to the presence of microscopic

air bubbles in the surface of the coating. During the preparation of the inter-
ference plate air bubbles are unavoidable. Through filtration of the gelatine
solution and by other means attempts can be made to eliminate the air bubbles
but I consider it impossible to get rid of them altogether.

When the plate dries the outer membrane in the air bubbles contracts
very strongly with the result that the air bubble is flattened out so that the
thin layer of air which is left constitutes a shield for the underlying part of
the coating. The water, therefore, cannot penetrate through the bubble to the
coating and this dry system can possibly survive for a short time.

In the thoroughly watered plates there are presumably just as many air
bubbles as in the others and still they do not prevent the entrance of the water.

Now by examination of some interference plates before and after treatment
with water I have shown [5] that the water eliminates about 3—5 % of soluble
gelatine which is present in the coating in the form of a 25 % solution in water.
These gelatine solutions which presumably stay on the spots where they are
created must delay the absorption of water from outside into the areas under
the air bubbles. In the watered plates these gelatine solutions are removed and
the water can therefore freely intrude into these areas.

In an earlier paper [4] I have found that the first trace of water passes through
a layer of pure gelatine, either hardened or unhardened at a rate corresponding
to about 7 sec for a thickness of 10 μ. The average thickness of the interference
plate is just about 10 μ.

Now, the only difference between the interference plate and an ordinary
layer of gelatine is the presence of silver bromide particles and this presence,
therefore, must be responsible for the enormous speed of water absorption
in the interference plate.

This enormous speed further shows that the coating of the interference
plate must contain some cavities through which the water can pass without
any hindrance. In an ordinary gelatine layer on the other hand there are only
very small cavities between the molecules.

The size of these cavities can be measured. A strip of the plate illustrated in Figs. 1, 2,
and 3 having an area of 17.00 cm² was weighed, treated with a 20 % solution of sodium
thiosulphate, rinsed, dried and weighed again. This procedure was repeated until constant
weight. The difference shows the weight of silver bromide, in this case 13.8 mg. Divided
by the density of silver bromide, 6.47, it gives the volume of silver bromide, here 2.14 mm³.

Then the strip was treated with a solution of hydrogen fluoride, rinsed, dried and
weighed. The difference gives the weight of gelatine, in this case 15.4 mg. Divided by the
density of gelatine, 1.32, it gives the volume of gelatine, 11.7 mm³.

From Fig. 1 the thickness of the coating is measured to 57 mm. The preparation
was wet, and a comparison between Figs. 2 and 3 shows that the coating gets about
the double thickness when it becomes wet. Therefore the thickness of the dry coating
must be 28.5:3000 or 9.5 μ.

The volume of the coating therefore is 17.0 × 10² × 9.5 × 10⁻³ or 16.15 mm³. Silver
bromide and gelatine together occupy only 2.14 + 11.70 or 13.84 mm³. Therefore the
cavities must occupy 2.31 mm³. The percentage by volume of the cavities is
2.31 × 100:11.70 or 19.8. The mean percentage by volume of silver bromide is 2.14 ×
100:11.70 or 18.3.

THE STRUCTURE OF THE COATING

As a simplified model of the structure I assume that the long thin gelatine molecules lie parallel to each other and parallel to the surface of the coating. When the silver bromide particles grow up between the gelatine molecules these molecules must curve around the particles to which they are chemically linked. Moreover here and there the gelatine molecules are linked together by chromic oxide which is produced during the exposure of the chromated gelatine plate.

As the gelatine molecules are inelastic they must be broken up, presumably in several places, and some of the fragments are possibly so small that they may be soluble in water and thereby constitute the soluble gelatine which has been found in the interference plates.

From these different considerations a model of the structure has been worked out as shown in Fig. 5. This figure shows a section normal to the surface of the coating of one of the layers which contains silver bromide particles. A represents a particle, G a bundle of gelatine molecules, and $\varDelta$ one of the cavities. As mentioned above the bundles of gelatine are broken up in several places when forming the small soluble gelatine fragments.
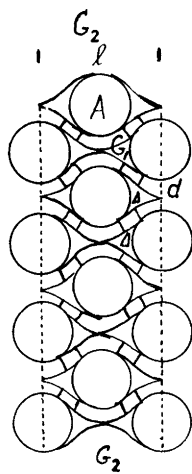

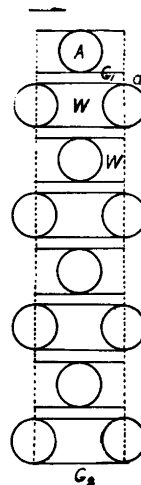Fig. 5. Section normal to the coating surface of the layers which contains the silver bromid particles.

Fig. 6. Layer after rapid absorption of water.

As I have shown in an earlier paper [3] the thickness of the single layer is $264(1 + v_m)$ mμ, where 264 is the thickness of gelatine plus chromic oxide and v_m is the mean percentage by volume of silver bromide. Generally the value of v_m is about 17, the total thickness therefore equal to 264×1.17 or 310 mμ. The half of the layer which contains all the silver bromide therefore has a thickness of 155 mμ. Assuming that the average size of the silver bromide particles is 30 mμ there will be about 5 particles in the single layer, a result that corresponds very well with the direct observation of Fig. 3. Fig. 5 therefore represents that half of a single layer which contains the silver bromide particles. Above and below the illustrated layer are layers of pure gelatine of the same thickness.

As the great speed of water absorption is the same for the original as for the watered plates there must be direct spatial connection between adjacent cavities perpendicular to the surface or parallel to the section. This is easily understood. When the bundles of gelatine are curved around the silver bromide particles perpendicular to the section they must necessarily be spread over a larger area and must thereby be separated into smaller units. Between these smaller bundles there must be direct connection from each of the cavities to the adjacent ones.

Fig. 6 shows the same part of the layer after the first rapid absorption of water. A and G have the same meanings as before and W is the water content.

So far we have only been occupied with the layers containing silver bromide particles. As to the layers which are free from these particles it is more difficult to understand the way in which water can pass through the pure gelatine with a much higher speed than usual.

In an earlier paper [1] I have found that the original distribution of silver bromide in the layer after treatment with silver nitrate and potassium bromide is quite different from the final distribution after the treatment with the mixed solution of metabisulphite and bromide. Table 4 contains the calculated values. Z/λ is the phase fraction in the stationary wave, v_A the percentage by volume of silver bromide for BB.

Table 4.

Z/λ	0.25	0.275	0.30	0.325	0.35	0.375	0.40	0.425	0.45	0.475	0.50
V_A	31.5	28.3	25.6	23.5	21.8	20.5	19.6	19.1	18.4	18.1	18.0

Presumably the size of the silver bromide particles must decrease from the upper to the lower part of the table. The immersion into the mixed solution of metabisulphite and bromide causes the smaller particles to be dissolved and deposited on the greater particles with the result, as seen in Figs. 2 and 3, that all the silver bromide is collected in one half of the double-layer while the other half consists of pure gelatine. But the particles which originally were present in the gelatine layer had exercised their effect in stretching the gelatine molecules and thereby in producing spaces between the fragments through which spaces the water can freely pass.

CALCULATIONS

For calculation we shall work with the area within the dotted lines in Figs. 5 and 6 which comprises the silver bromide containing half of the layer. The thickness of the section under discussion is supposed to be equal to the radius of the silver bromide particles. When

l is the horizontal width of the section,
A is the total amount of silver bromide,
d is the thickness of the gelatine bundles,
G_1 is the amount of gelatine in the silver bromide layer,
G_2 is the amount of gelatine in the pure gelatine layer,
G is the total amount of gelatine,

A is the sum of all the cavities
W is the amount of water and
v is the percentage by volume of water that dissolves the soluble gelatine

then

$A = 16/3 \cdot \pi\, r^3$

$G_1 = 7ldr, \quad G_2 = lr(8r + 7d), \quad G = lr(8r + 14d)$

$A = 8r^2(l - \tfrac{2}{3} \times \pi\, r)$

$W = 16r^2(l - \tfrac{1}{3} \times \pi\, r) - vG,$

As an example we shall calculate the values for BB_1 in Table 3.

Here $v_A = 0.323 = A{:}G$. We assume $r = 1$, then $A = 16.8$ and $G = 52.2$. The percentage by volume of soluble gelatine is from 3 to 5. The amount of water that dissolves this gelatine is four times as great. Taking the value of 5 for gelatine the percentage by volume of water is 20, then $v = 20$ and $vG/100 = 60.4$. From these values and the three equations for G, A, and W the following data are obtained:

l	A/G	d	G_1	vG
3.48	0.213	0.50	12.2	10.4

As mentioned before the value of A/G was found from Figs. 1, 2, and 3 to be 0.198 so that the value now found seems quite reasonable.

The amount 10.4 of water corresponds to the amount of 2.6 for soluble gelatine. There remain 9.6 volumes of insoluble gelatine, a little less than the volume of the gelatine solution, which seems reasonable. With so great a volume of aqueous solution there is plenty of room for horizontal migration of water in the thoroughly watered plates where this solution is removed.

REFERENCES

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4. Winther, Chr. *Ibid.* **10** (1956) 1124.
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6. Winther, Chr. *Ibid.* **12** (1958) 1643.
7. Winther, Chr. *Ibid.* **12** (1958) 1652.