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The First Step in the Swelling of Gelatin with Water

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In two earlier treatises I have examined the preparation, the properties and the theory of a chromated gelatin interference plate [1] and the treatment of this plate with water and water vapour [2] which, *i. a.*, resulted in a purely optical method of measuring the depression of the vapour pressure of diluted aqueous solutions. The examination comprised measurements of the rate of water absorption of the gelatin, either by immersion of the plate in water or by placing it over aqueous solutions of different water vapour pressure, and measurement of the absorbed water after equilibrium between the gelatin and water vapour of different pressures had been obtained.

In the following these two treatises will be referred to as I and II, respectively.

The said interference plate, which was invented by the late civil engineer J. H. Christensen, in transmitted light shows a spectrum which in part consists of a broad band, BB, in part of a number of single narrow bands with which we shall not occupy ourselves here. Through swelling with water or water vapour these bands shift towards larger wave lengths which in many instances lie in infrared. Bands photographed on an ordinary panchromatic plate must, therefore, be of the 2nd or 3rd order. In both cases it is possible by means of a previously given formula to calculate the absorbed amounts of water (*cf.* II, p. 4), which, of course, must be greatest if bands of the 3rd order are reckoned with. In the treatise I have, for a reason which will be explained below, reckoned with 3rd order, but later investigations have shown that this is not correct. These investigations were made in the following way.

The following measurements were made on small pieces of plate No. 48.

1) Photographic recording of the extinction spectrum
2) Weighing
3) Swelling in water for 5 days
4) Photographic recording of the extinction spectrum of the wet plate
5) Weighing of the wet plate in a weighing bottle
6) Fixation in 20 % sodium thiosulphate for 30 minutes, watering, drying
7) Weighing
8) Removal of the gelatin with hydrofluoric acid
9) Weighing of the glass.

From these measurements the following calculations are made:

From (1), (4), (7) and (9): the maximum amount of water v_v absorbed per 100 volumes of gelatin (*cf.* II, p. 4), corresponding to BB (*cf.* I, p. 27),

from (2) and (5): the average amount of water absorbed throughout the coating,

from (7) and (9): the amount of gelatin.

From the two last values v_M is obtained, which is the average amount of water per 100 volumes of gelatin.

Table 1 contains: 1) The plate number, 2) λ_t, the wave length of BB on the dry plate, 3) λ_v, the directly measured wave length on the wet plate, 4) and 6) this wave length converted to the 1st order under the assumption that it is of the 2nd respectively the 3rd order, 5) and 7) the corresponding percentages by volume of water, 8) the average amount of water v_M, 9) and 10) the quotients v_v:v_M, calculated on basis of the 2nd and 3rd order, respectively.

Table 1.

No.	λ_t	λ_v	2nd order		3rd order		v_M	$v_v : v_M$	
			conv.	v_v	conv.	v_v		2nd order	3rd order
4	582	588	1 170	170	1 737	342	101	1.68	3.39
8	579	615	1 228	187	1 840	364	118	1.59	3.09
10	583	529	1 050	134	1 575	286	77	1.74	3.71
12	583	599	1 195	176	1 790	348	96	1.83	3.63
13	588	596	1 186	173	1 782	345	92	1.88	3.75
14	586	615	1 228	185	1 840	362	91	2.03	3.98

In the exposed chromated gelatin plate the amount of unhardened gelatin decreases evenly from the air surface which during the exposure has been in optical contact with mercury, to the interface between the coating and the glass. The broad band, BB, is formed in the outermost part of the coating and the upper edge of BB, which always forms the basis of the calculations, accordingly corresponds to the layer which is situated closest to the air surface. Here, consequently, the amount of unhardened gelatin is larger than the average value for the whole coating. The amount of unhardened gelatin g is calculated from the formula

$$g' = 16.3—8.8 \cdot c''$$

in which 16.3 is the total amount of gelatin, c'' the amount of chromic oxide formed by the exposure, and 8.8 the proportionality factor between the amounts of hardened gelatin and chromic oxide (*cf.* I, p. 18).

For the three plates Nos. 27, 9 and 28 this calculation has been performed for the outermost layer of the coating, corresponding to BB (*cf.* I, Table 24), and for the entire coating (*cf.* I, Table 25). The results were as recorded in Table 2.

Provided the absorbed amounts of water are proportional to the amounts of unhardened gelatin, and this assumption seems reasonable, these quotients must correspond to the quotients v_v:v_M. A comparison with these values in Table 1 clearly shows that the measured spectra are of the 2nd order.

Table 2.

No.	g'		quotient
	BB	the coating	
27	5.0	3.31	1.51
9	6.0	3.82	1.57
28	7.0	4.05	1.73

This cognition of course entails alterations of some of the formulae which have been set up in II, both for the rate of the water absorption and for the relation between the absorbed amounts of water and the vapour pressures. However, it appears that the formulae are still applicable, only the constants take other values.

For the rate of swelling with water the formula will be:

$$v_{\mathrm{v}} - 84.1 = (v_{\infty} - 84.1)\ (1 - 10^{-0.028 \cdot t^{0.5}})$$

and Table 3 will be:

Table 3.

t	λ_{BB}		v_{v}	
	obs.	calc.	obs.	calc.
0	558	—	—	—
1	868	873	89.3	90.9
2	881	881	93.1	93.0
4	889	891	95.4	95.9
8	906	905	100.5	99.9
15	923	921	105.2	104.6
30	950	945	113.0	111.4
60	975	974	120.1	119.9
120	1 010	1 010	130.3	130.3
240	1 047	1 050	141.0	141.8
1 920	1 158	1 157	173	172.7
4 320	1 182	—	180	—

The new formula has the great advantage over the previous one that the time *t* will have the same exponent as was previously found for the swelling with water vapour for which the formula reads:

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

Add to this the altogether unexpected information that 84.1 % by volume of water is absorbed instantaneously — at any rate in the surface of the coating —, whereafter the absorption of water continues after the same law as in the treatment with water vapour.

The original calculation had been performed on basis of spectra of the 3rd order just to avoid this instantaneous absorption of water which already at

Table 4.

t	λ_{BB}		v_v	
	obs.	calc.	obs.	calc.
5	618	626	17.8	19.7
10	656	652	28.6	27.2
20	692	687	39.0	37.2
45	740	741	53.1	52.8
60	765	764	60.0	59.5
90	798	800	69.7	69.8
120	834	829	79.6	78.0
180	868	871	89.6	90.1
∞	1 182	—	180	—

that time was found as the result of the calculation on basis of spectra of the 2nd order. However, the new experiments have shown the impossibility of avoiding this assumption.

Also the formula for the absorption of water from saturated water vapour must be altered. The constant will now be 0.0225, and the corresponding parts of Tables 3a and 3b will be as recorded in Table 4.

It will be seen that after the first film has been formed the absorption of water proceeds more slowly than the absorption of saturated water vapour. Presumably this must be due to the fact that this film of water restrains the diffusion of water into the interior gelatin coating.

In Table 5 are the values of k for a number of varying vapour pressures.

Table 5.

$\frac{p}{p_0}$	k	v_∞
1	0.0225	180
0.9964	0.0250	140
0.98	0.0521	58.6
0.95	0.1001	26.0
0.84	0.1376	14.8

For the equilibrium with the vapour pressure formula (4) will be:

$$v_v = v_1 \left(1-10^{-0.0126\left(\frac{p/p_0}{1-p/p_0}\right)^{0.7}}\right)$$

The corresponding values are found in Table 6.

The measurement of the depression of the vapour pressure is based on the fact that the curve whose abscissa is the degree of moisture p/p_0 and whose ordinate is the corresponding amounts of water in the gelatin (*cf.* II, Fig. 5) rises very sharply when p/p_0 approaches 1. In Table 7 are stated some (now

Table 6.

$\frac{p}{p_0}$	λ_{BB}		v_V	
	obs.	calc.	obs.	calc.
1	1 182	—	180	—
0.9964	1 044	1 047	140	141
0.98	753	783	58.6	65
0.95	672	687	26.0	37.1
0.88	624	627	19.1	20.0
0.84	609	614	14.9	16.0
0.795	599	604	12.1	13.2
0.726	592	593	9.7	10.1
0.66	591	586	9.5	8.1
0.58	582	580	7.1	6.4
0.45	580	574	6.3	4.5
0.323	572	569	4.3	3.1
0.20	562	565	1.3	1.9

corrected) values of the shift of v_V and of the wave length of BB as compared with the value for $p = p_0 = 1$ for various values of p/p_0 near 1.

Finally, Table 8 shows the result of a number of measurements of the depression of vapour pressure. Four pieces of a plate were first saturated with water for several days and then placed over water and 0.01, 0.03, and 0.1 *M* solutions of potassium chloride, respectively, until equilibrium had been established. Table 8 contains the depression of vapour pressure in question and the corresponding directly observed wave lengths and the wave lengths converted to 1st order.

Table 7.

$-\log\left(1-\frac{p}{p_0}\right)$	Δv_V	$\Delta\lambda_{BB}$
1	155.2	538
2	85.2	295
3	4	14

With a plate which is strongly sensitized to infrared a direct measurement of the bands of the 1st order should be possible. Incidentally, it may be men-

Table 8.

	$1-\frac{p}{p_0}$	λ_{BB}	
		obs.	conv.
water	0	525	1 040
0.01-KCl	0.00036	517	1 025
0.03-KCl	0.001026	501	990
0.1 -KCl	0.00328	443	870

tioned that attempts are being made to avoid the photographic recordings entirely and instead to measure the differences directly by visual, optical means.

SUMMARY

By treatment of gelatin with water the surface instantaneously absorbs a considerable amount of water whereafter the swelling proceeds slowly and after the same law but at a somewhat lower rate than in the case of absorption of saturated water vapour.

REFERENCES

1. Winther, Chr. *Trans. Danish Acad. Tech. Sci.* **1953** No. 5.
2. Winther, Chr. *Ibid.* **1953** No. 6.

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