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Prepared discussion contribution

INTERACTIONS BETWEEN LIQUIDS AND PAPER*

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Introduction

THE porous nature of paper can be regarded as consisting of three components, namely, an external void system, an internal void system and discontinuities. The external void system can be associated with the concept of paper roughness and is totally open in one direction. The internal void system can be regarded as that which can be observed by simple optical microscopy (e.g. paper sections cut at an oblique angle). The discontinuities can be defined as all those phenomena that deprive the voids between fibres of the characteristics which would justify regarding them as capillaries with smooth surfaces. These would include the structural elements of the fibre surface, the fines in paper, the fibrils and the fibril bundles protruding into the interfibre voids, the pits in the fibre surface and pores in the cell walls.

The interactions between the components of the model system proposed above have been investigated using thickness, light transmission and water absorption measurements.

Experimental

EXPERIMENTS were carried out using two types of paper, termed paper 1 and paper 2. Paper 1 was a cotton Whatman filter paper having a grammage of 90 g/m^2 and thickness 156 μm. Paper 2 was made of 100 per cent rayon pulp having a grammage of 75 g/m^2 and thickness 125 μm and was sized by the addition of 0·6 per cent alkyl ketene dimer. SEM pictures taken with a Jeol J50A scanning electron microscope of the two papers are shown in Fig. 1.

Roughness measurements were carried out using the Perthen system (SIOD Perthometer and DWRV-1 Perthograph). An investigation concerning the

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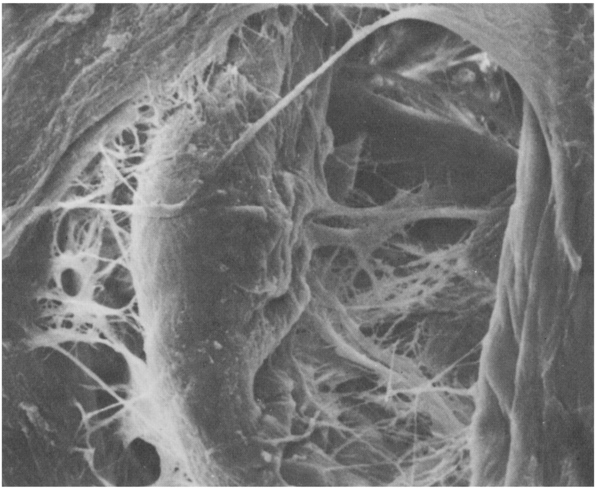
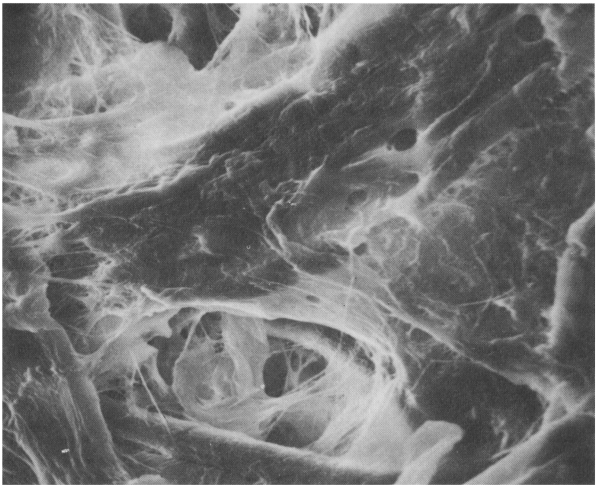
Under the chairmanship of B. W. Attwood

Paper 1



Paper 2



(The pictures were taken by A. Csonka)

Fig. 1—Electronmicroscopic pictures of the papers (× 1000)

accuracy and reproducibility of this method has been presented by Huszár and Lengyel.[1]

A double-beam Unicam SP-700 spectrophotometer was used to measure the light transmission spectra of the samples. A special sample holder with a grooved base plate was employed with a reference grating for attenuating the

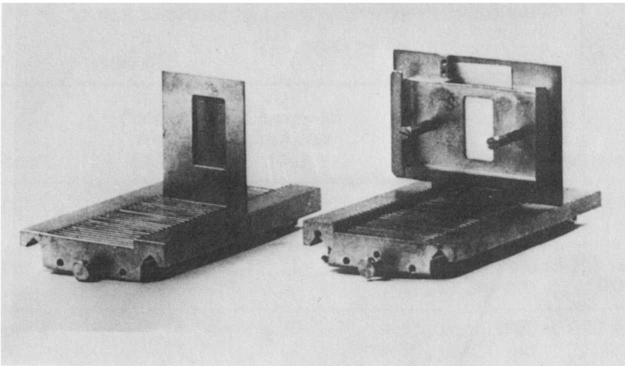


Fig. 2—The special baseplate, sample holder and the grating for attenuating the light.

light as shown in Fig. 2. For the examination of the interaction of paper with liquids the paper sample, wetted with the appropriate liquid was placed between two quartz plates and then inserted into the sample holder.

The loss of light due to optical interaction is expressed in terms of transmission decrease or extinction units, E. The transmission spectra of papers 1 and 2 are shown in Fig. 3. The reproducibility of the measurement was good, 50 independent samples were examined using an 86 mm^2 light beam and the deviation did not exceed $0{\cdot}005E$. The deviation of measurements on different areas of the samples and the selection of samples has been treated by Huszár.[2, 3]

Results

Paper 2 was subjected to various degrees of pressure, as shown in Table 1, in a flat press for 10 minutes, and the change in thickness, Δd per cent, and

TABLE 1—THE EFFECT OF PRESSING ON DIFFERENT CHARACTERISTICS OF PAPER 2

p *MPa*	Δd (%)	*Rp* µ*m*	*Rp/d* (%)	*Fibre volume* (%)	*Pore volume* (%)	*Internal pore volume* (%)
—	0	13·9	10·9	37·7	62·3	51·4
5	8·3	8·8	7·5	40·8	59·2	51·7
10	12·3	7·3	6·4	42·4	57·6	51·2
15	15·6	6·4	5·9	45·0	55·0	49·1
20	18·3	5·9	5·7	46·2	53·8	48·1
25	21·3	5·5	5·4	47·6	52·4	47·0
30	22·4	5·1	5·2	49·0	51·0	45·8

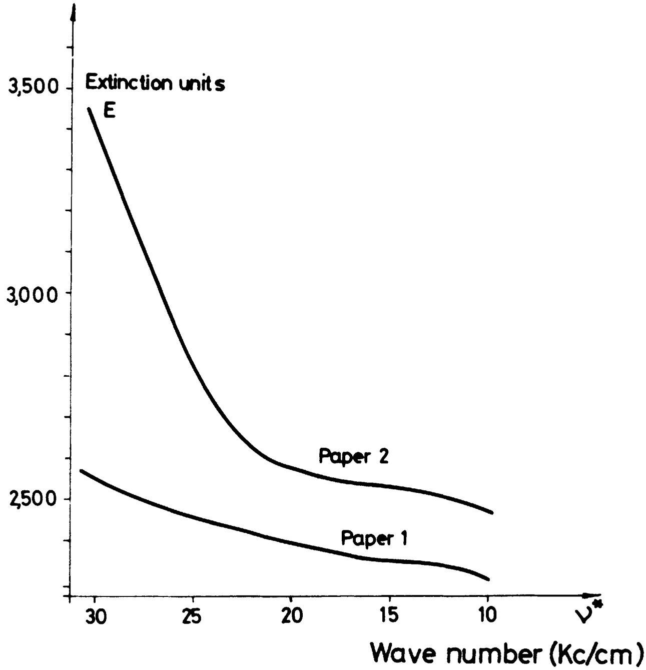


Fig. 3.—The spectra of papers 1 and 2

the roughness of the surface, Rp, were measured. The percentage of roughness related to thickness, *Rp/d* per cent, the fibre volume, assuming a fibre density of 1·56 g/m³, and the pore volume were calculated. A value called 'internal pore volume' was also calculated by subtracting the percentage of roughness related to thickness from the pore volume.

Samples were also pressed at 70 MPa and the change in light transmission which this produced is shown in Table 2.

It can be seen from the two tables that initially only the surface roughness decreases with increases in pressure. Above a pressure of about 10 MPa the internal pore volume starts to decrease. A large change in thickness under the impact of a comparatively high pressure is accompanied however by an insignificant decrease in light transmission in the visible range. In the ultraviolet range the transmission of the filter paper increased and the transmission of the sized paper decreased.

Transadherence isotherms of the two papers were determined following the method of Wolfram[4] applied to paper by Lengyel and Hajduczky.[5] Total

TABLE 2—LIGHT TRANSMISSION OF PRESSED PAPER

(p=70 MPa

Sample	*Pressing time (min)*	*Change in thickness (%)*	*Change of transmission*
Paper 1	10	34	± 1% from 1000 to 260 nm +5% at 250 nm
Paper 2		31	±1% from 1000 to 360 nm −8% at 260 nm
Paper 1	1	30	−5% from 1000 to 320 nm −9% at 250 nm
Paper 2		28	−3% from 1000 to 360 nm −12% at 260 nm

transadherence can be observed with a much larger drop size for paper 1 than for paper 2 and the distribution of the transadherence and retained drop is also significantly different as shown in Fig. 4.

Water vapour adsorption isotherms of the two papers were measured and the results are summarised in Table 3. In accordance with the findings of other workers[6] the water vapour adsorption is hardly influenced by sizing.

TABLE 3—WATER VAPOUR ADSORPTION ISOTHERMS OF UNSIZED AND HARD SIZED PAPER

Rel. humidity	6·5	10	13·5	24·5	31	40	52·5	63·5	77·8	91
Paper 1	1·83	2·38	2·89	3·50	4·52	4·85	5·48	6·88	9·25	14·00
	2·15	—	2·87	3·51	3·77	4·54	6·06	6·91	10·00	14·37
Paper 2	2·28	2·48	2·94	3·90	4·63	5·58	6·48	8·02	10·23	15·50
	2·30	2·88	2·94	4·05	4·86	5·50	6·83	7·60	9·94	15·41

Three methods were employed to measure the amount of liquid water uptake of the two papers. One minute Cobb tests were carried out following the standard method. A water retention value was estimated by centrifuging 10 ml of water through a 0·15 g paper sample and then determining the amount of water retained by the paper. The wet weight of the paper was also determined after soaking the paper for 10 minutes, blotting smoothly between two sheets of filter paper and then sealing between aluminium foils. The latter method was found to be strongly dependent upon the time of soaking. The effect of soaking time on the water uptake for paper 2 is shown in Table 4

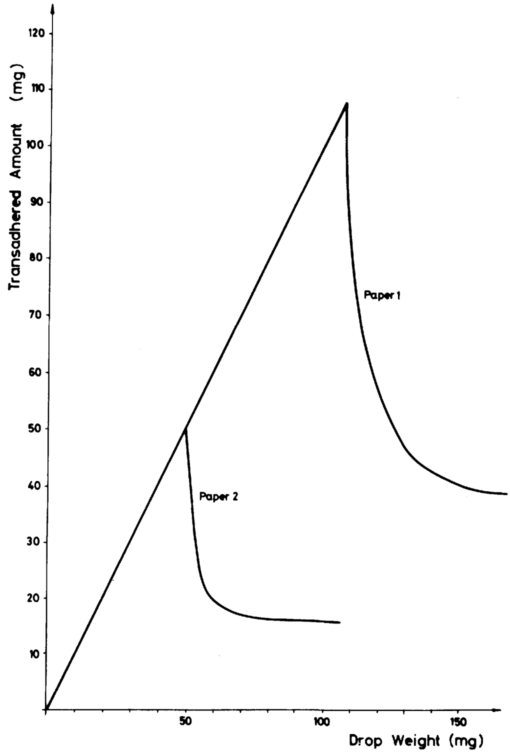


Fig. 4—Transadherence isotherms of papers 1 and 2 according to the method of Wolfram

together with the coefficient of variation for each soaking time. Similar values were obtained for paper 1. Two features of the method should be emphasised. Firstly, paper 2 is strongly water resistant and had to be kept moving in the water with a glass rod in order to ensure complete wetting. Secondly, water is removed from the surface voids by blotting with filter paper. A soaking time of 10 minutes was adopted as a standard.

The amount of liquid water uptake for both papers, measured by the above three methods, is summarised in Table 5. The impact of sizing is revealed by the Cobb test results, but it is unlikely that with the hard sized paper the amount of liquid uptake is an equilibrium value. The water retention value is dependent on the magnitude of the centrifugal force applied. The water absorption value as measured by soaking was therefore taken as being a good indication of the liquid uptake.

TABLE 4—THE EFFECT OF SOAKING TIME ON THE WATER CONTENT OF PAPER 2

Soaking time (min)	*Water content (%)*	*Coefficient of variation (%)*
pulled through	14·5	25·1
1	31·9	3·3
3	32·5	4·8
5	32·8	2·2
10	33·6	1·5
60	34·8	2·6

The change in thickness with time of both papers during water absorption is shown in Fig. 5. The change in thickness was also measured after pressing the papers under a comparatively high pressure of 80 kPa and then wetting. The first moments of immersion produce a rapid increase in thickness. The difference in the degree of sizing of the two papers is clearly shown as a difference in the rate of swelling for both the pressed and unpressed paper.

TABLE 5—WATER ABSORPTION MEASURED WITH DIFFERENT METHODS

Paper	*Water taken up (%)*	*Water retention value*	*Cobb*
1	145	66·4	142
2	34	61·4	16

The pressed paper however exhibited a larger percentage increase in thickness.

The surface profiles of the unpressed and pressed paper, as well as those after soaking for 10 minutes in water and then blotting, are shown in Figs. 6 and 7. Pressing has the effect of reducing the degree of roughness. After wetting with water and the consequent fibre swelling, a significant increase in roughness is observed. The unpressed paper in the wet state differs from paper wetted after pressing merely in waviness, the highest curve peaks being almost at the same level, indicating a similar surface structure in both cases.

The two papers under consideration can be regarded as consisting of three components, namely, the volume of cellulose, the volume of water and the volume of air (the volume of the ketene dimer present in paper 2 is assumed to be negligible). The grammage and thickness measurements were carried out at a temperature of 23° C and a relative humidity of 43 per cent. From Table 3, the moisture contents of paper 1 and paper 2 are 5 and 6 per cent respectively.

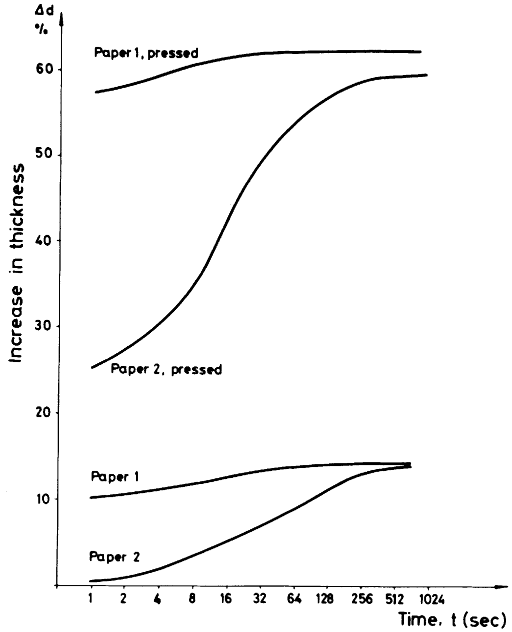


Fig. 5—The change of the thickness of paper as a function of wetting time

The pore volume of paper 1 is therefore found to be 58 per cent and that of paper 2 to be 57 per cent. Thus it can be shown that after soaking in water paper 1 is composed of 28 per cent by volume cellulose, 70 per cent by volume water and 2 per cent by volume air, and paper 2 is 32 per cent by volume cellulose, 17 per cent by volume water and 51 per cent by volume air. It is realised that the above can only be rough approximation, but the data does indicate that the main difference between the unsized and sized paper after soaking in water is the volume of air displaced by water.

Samples were immersed for 45 minutes in water, formamide and ethanol. The samples were then placed between two quartz plates and transmission measurements were carried out. Fig. 8 indicates the extinction changes observed for paper 2, positive values of ΔE show an increase of extinction (i.e. decrease in transmission) and negative values of ΔE show a decrease of extinction (i.e. increase in transmission) as compared with the values obtained for dry paper. After soaking in ethanol the extinction of paper 2 changes from 0·900 to 0·500 units over the wave number range used. In other words, the transmission, as compared to dry paper, increased by 3 to 8 fold. However water and formamide caused considerable swelling of the paper to take place,

A
B
C
D

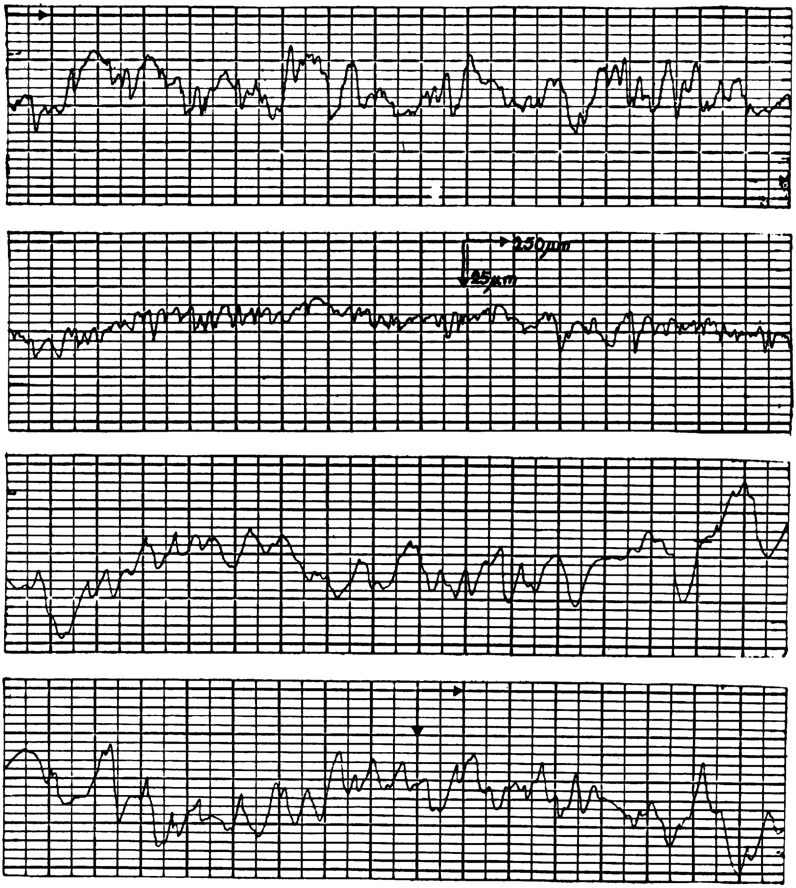


Fig. 6—The profilogram of paper 1
A—dry; unpressed
B—dry; pressed with 80 000 KPa
C—unpressed; 10 minutes soaking time
D—pressed; 10 minutes soaking time

resulting in a decrease in light transmission over the whole spectrum range in the case of formamide, and a decrease in the visible spectrum range with an increase in the ultra-violet range for water.

The effect of various organic solvents on the transmission of paper 2 was also studied and the results are summarised in Table 6. It is immediately obvious that increasing the refractive index of the wetting solution increases transmission as the values approach the refractive index of cellulose.

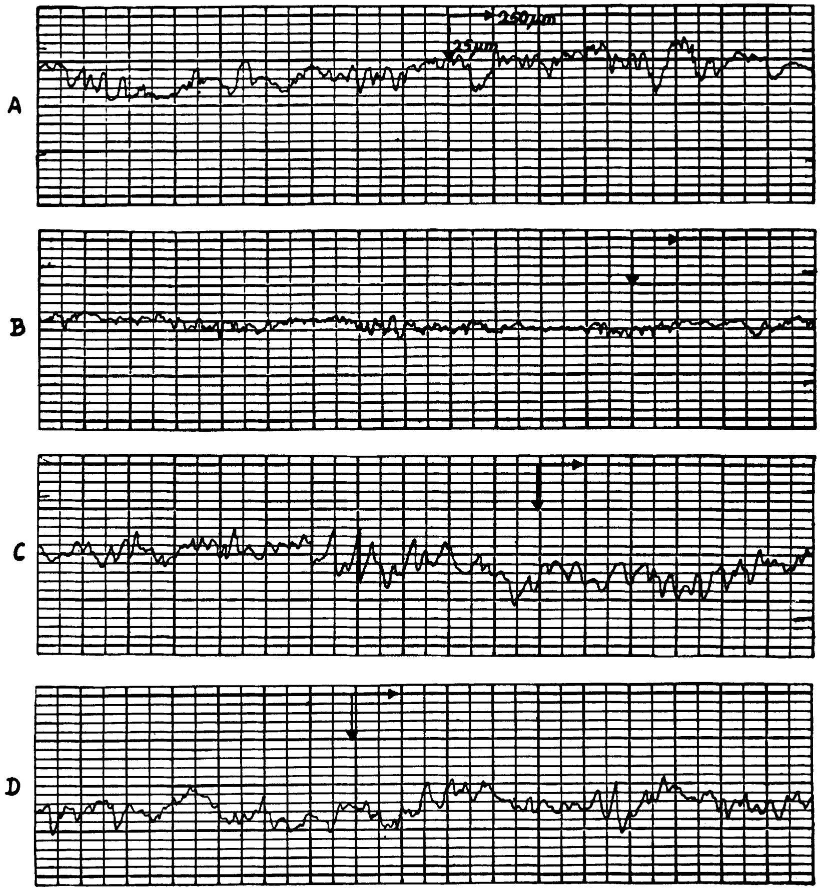


Fig. 7—The profilogram of paper 2.
A—dry; unpressed
B—dry; pressed with 80 000 KPa
C—unpressed; 10 minutes soaking time
D—pressed; 10 minutes soaking time

The light transmission of paper samples which had been redried after soaking in water was also measured. The change in transmission compared with the original dry paper is shown in Fig. 9. The change in light transmission of paper 1 is small but decreases evenly in the visible spectrum range. The light transmission of paper 2 decreases to a greater extent especially in the

TABLE 6—INCREASE IN LIGHT TRANSMISSIONS OF PAPER 2 INDUCED BY DIFFERENT LIQUIDS

Liquid	*Refractive index* ^{n}D; 20C°	$^{\Delta E}27$ kc/cm
Methanol	1·326	−0·620
Ethanol	1·359	−0·654
Acetone	1·357	−0·657
Dioxane	1·420	−0·790
Chloroform	1·444	−0·885
Cyclohexanone	1·448	−0·910
Cyclohexanol	1·465	−0·950
Paraffin oil	1·490	−1·376
Xylene	1·495	−1·387
Pyridine	1·507	−1·620
Benzylalcohol	1·538	−1·942
Water	1·333	+0·005
Formamide	1·446	+0·160

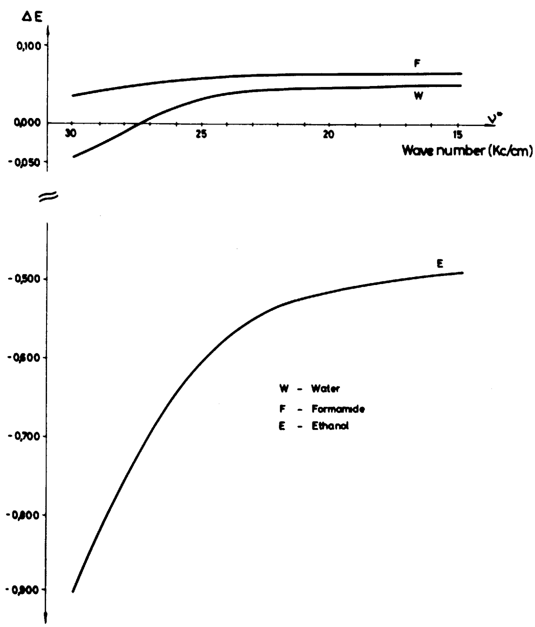


Fig. 8—The effect of solvents on transmission of paper 2

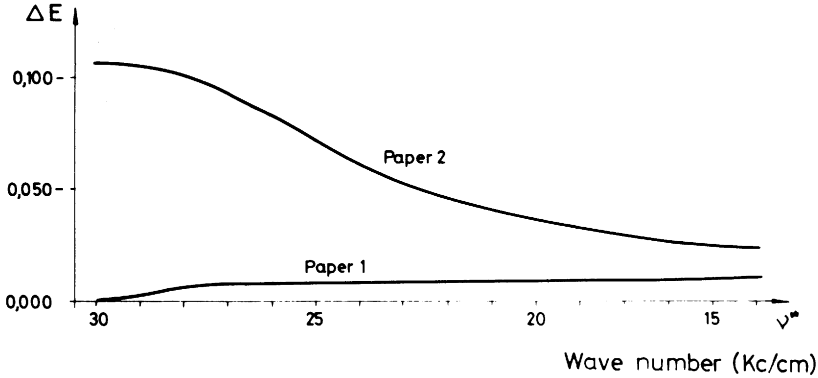


Fig. 9—The transmission of the redried papers

ultra-violet range. This indicates that the samples after soaking and then redrying do not revert to their original structures.

The effect of various water-ethanol mixtures on the light transmission of paper 2 is summarised in Fig. 10. There is no linear dependence between the optical properties and the composition of the water-ethanol mixture. In order to achieve an increase in transmission a mixture of approximately

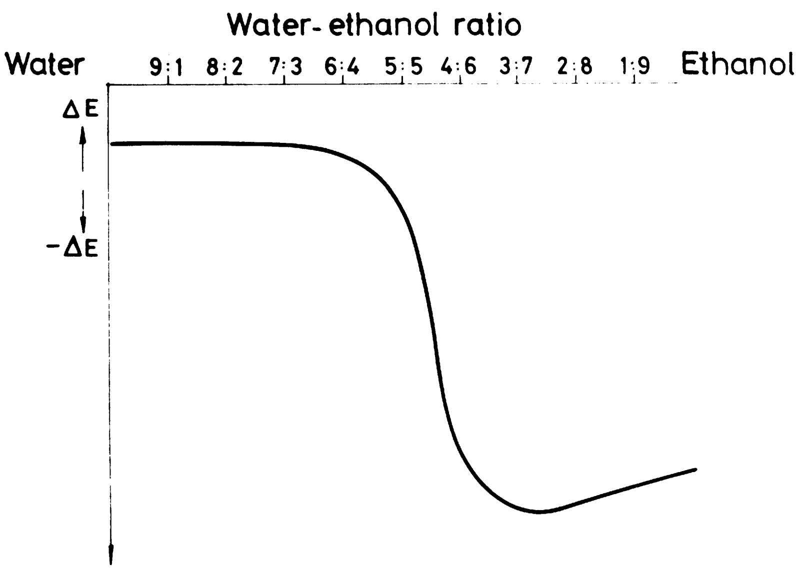


Fig. 10—The effect of water: ethanol ratio on the transmission of paper 2 at a constant wave number

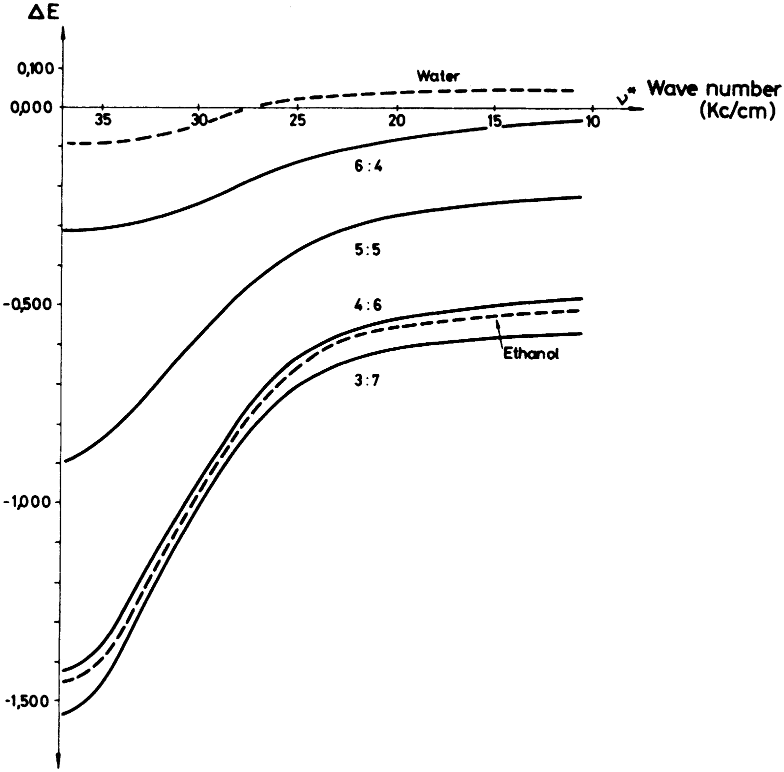


Fig. 11—The transmission of paper 2 vs. wave number at different water: ethanol ratios

50 per cent water–50 per cent ethanol has to be used and the greatest change in ΔE occurs with only a small change in the composition of the water-ethanol mixture. The influence of water-ethanol mixtures on the light transmission of paper 1 was also studied and similar trends were observed, but the measured differences in transmission were far less than those recorded for paper 2.

The magnitude of the optical change is of course dependent on the wave number. The influence of the wave number is shown in Fig. 11. Extinction decreases with increasing wave number, but the same general trend, as shown in Fig. 10, is observed for any given value of wave number.

The following solvent exchange experiment was carried out with paper 2. Samples were immersed in ethanol for 30 minutes after soaking in water, formamide or with no pretreatment, and thereafter the transmission was measured. The results are summarised in Table 7. The column marked 'diff 1' shows the difference in extinction between the samples pretreated with water and those pretreated with formamide. This difference appears to be random and negligible. The transmission of the solvent exchanged paper appears to be independent of presoaking in water or formamide. The transmission of pretreated and ethanol exchanged samples was, however, substantially greater than the transmission of samples which were immersed in ethanol without pretreatment as shown in the column marked 'diff 2'.

TABLE 7—DIFFERENCE IN EXTINCTION OF PRETREATED AND UNPRETREATED PAPERS INDUCED BY ETHANOL

Wave number (kc/cm)	*Diff.* 1	*Diff.* 2	*Wave number (kc/cm)*	*Diff.* 1	*Diff.* 2
45	−0·003	0·216	27	0·005	0·121
44	0·004	0·206	26	—	0·127
43	0·008	0·183	25	−0·003	0·127
42	0·000	0·183	24	−0·007	0·126
41	0·000	0·176	23	−0·004	0·127
40	0·005	0·168	22	−0·012	0·124
39	−0·003	0·166	21	−0·003	0·132
38	−0·004	0·161	20	−0·006	0·137
37	−0·006	0·159	19	−0·002	0·143
36	−0·007	0·161	18	−0·002	0·147
35	−0·010	0·162	17	−0·005	0·154
34	−0·012	0·159	16	−0·002	0·155
33	0·002	0·145	15	−0·002	0·157
32	0·006	0·130	14	−0·003	0·168
31	0·011	0·130	13	0·003	0·170
30	0·013	0·129	12	0·005	0·172
29	0·012	0·133	11	0·010	0·160
28	0·012	0·127	10	0·012	0·161

Concluding Remarks

THE effect of pressing the papers results initially in a decrease in the external void system followed at high pressures by a decrease in the internal void structure. This produces only a small change in the light transmission properties of the papers indicating that the character or quantity of the cellulose-air interfaces is unchanged by pressing.

When the sized paper is soaked in water a considerable time is needed for the swelling and the water uptake to reach their final values. However the light transmission decreases almost instantly to its final value. It is postulated that the internal void system takes up water quickly but this water does not wet the discontinuities, thus creating an additional water-air interface which increases the light scattering to a small extent.

Wetting the papers with water and the subsequent swelling was found to reverse the effects of pressing the sheets at high pressure. In the swollen condition the roughness differences between the pressed and unpressed samples become insignificant.

Swelling the paper in water or formamide followed by solvent exchange with ethanol was found to increase transmission. The magnitude of the change cannot be attributed to effects produced by changes in refractive index.

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