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FUNDAMENTAL PARAMETERS AFFECTING THE OPACITY AND BRIGHTNESS OF UNCOATED PAPER

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Synopsis A recently introduced theory of light reflectance based on a paper sheet behaving in its reaction to light as a stack of spaced parallel layers is described briefly. Utilising the theory, the contributions of cell wall thickness, lumen size, degree of lumen collapse, absorption coefficient of cell wall material and extent of interfibre bonding to the light-scattering ability of a sheet are discussed in a quantitative way. The conclusions are illustrated by examples of paper sheets in which there is clear evidence that their particular optical properties may be traced to one or more of the above parameters. Thus, for example, it is shown that to make sheets of high opacity while sacrificing neither brightness nor strength, fully bleached fibres with thin cell walls and narrow lumens are the most desirable.

Introduction

THE use of an increasingly larger variety of fibres for papermaking necessitates a better understanding of their optical properties than has hitherto prevailed. At present, the papermaker must rely largely upon experience in the choice of wood species and their subsequent pulping and bleaching procedures for a given optical requirement. It is generally recognised that the extent of interfibre bonding plays a fundamental role. For example, it is known that beating, which confers added tensile strength on a pulp, has, in general, a detrimental effect on paper reflectance, since a higher fraction of the surface area of the fibres is used in interfibre bonding and a lower fraction is left unbonded and available for light scattering. In addition to the degree of bonding, it is also appreciated that fibre dimensions play a part in the optical properties and that, on the whole, the finer the fibres, the more opaque the sheet will be at a given strength. These and a number of other factors were discussed at the Third Fundamental Research Symposium.(1) Yet by lack of an adequate theory for the relationships between optical paper

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properties and fibre characteristics, it was not feasible to obtain a quantitative picture of the connection between paper structure and reflectance. The physical meaning of optical 'constants' defined by the Kubelka-Munk theory (and especially the connection between specific scattering coefficient and specific surface area[2]) have been subject to much discussion without providing definite conclusions. Work on model fibres by Arnold[3] and Rennel[4] has failed to clarify fully the meaning of scattering coefficient in terms of sheet structure; the interrelationship between scattering coefficient and absorption coefficient, demonstrated by Nordman[5] at the previous symposium, has not yet been elucidated.

We have recently proposed that the optical properties of paper might be better understood if a theory of light reflectance were based on paper being a layered structure.[6] We suggested that a paper sheet could be considered as equivalent, in its reaction with light, to a stack of parallel layers of cellulose, each layer being made up of a number of bonded cell walls. The layers were regarded as being separated from one another by layers of air and as having thicknesses corresponding to the average distance through the solid between solid/air interfaces in the Z-direction of the sheet. Equations relating the basic parameters of the model to its reflectance were derived using the simple geometrical optics usually applied to describe the optical behaviour of a stack of thin transparent plates. The model, we suggest, is a more realistic description of a paper sheet than that usually applied—the continuum model of Kubelka and Munk. A particular advantage of the model and its associated theory is that it quantitatively relates the optical properties of paper to such parameters as refractive index, cell wall thickness, degree of bonding and a properly defined absorption coefficient. This is not as readily possible with the non-mechanistic Kubelka-Munk theory.

Theory

We have shown[6, 7] that the reflectance R_n of a sheet composed of n effective layers can be calculated in a stepwise manner from the equation—

$$R_n = R_1 + \frac{R_{n-1}T_1^2}{1 - R_1R_{n-1}} \quad . \quad . \quad . \quad . \quad (1)$$

where T_1 and R_1 are the transmittance and reflectance of a sheet composed of a single layer and are given by—

$$T_1 = \frac{(1-r)^2 f}{(1-r^2f^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$R_1 = r + \frac{r(1-r)^2 f^2}{(1-r^2f^2)} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $$f = e^{-2at} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus, the reflectance of a sheet composed of several layers may be calculated in terms of the number of layers in the sheet, their average thickness t and the reflectivity r and absorption coefficient a of the material that makes up the layers. The value of R_n thus calculated is equivalent to the reflectance of the sheet on a black background, which is usually denoted as R_o.

Similarly, from the same equation system, R_∞ may be calculated by stepwise calculation to such high values of n tha* R_n becomes independent of n. R_∞ is measured experimentally by determining the reflectance of a sheet when backed by an 'infinite' pile of similar sheets. It is referred to as the brightness or visual efficiency of the sheet, depending upon whether the wavelength of light used is 457 nm or 557 nm, respectively.

Further relationships that are used in the theory are those interrelating the effective number of layers in a sheet with the average layer thickness and the optically resolvable specific surface area of the sheet A_o. These have been discussed previously[6, 7] and are given by—

$$n = \frac{VW}{t} = \frac{A_o W}{2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where W is the grammage of the sheet and V is the specific volume of the solid material (0·667 cm^3/g for pulp fibres).

Refractive index

THE refractive index of the material making up a sheet of paper is obviously a factor that will affect its optical properties. Although the factor has been discussed before—for example, by Giertz[1]—a quantitative appreciation of how much the optical properties would be changed by a change in this property is lacking. In the layer theory we have presented, the effect of a change in refractive index is to change the reflectivity r—that is, to change the fraction of light reflected at each encounter of a light beam with a solid/air interface. In Table 1, the reflectivities have been calculated from the Fresnel Laws for various refractive indices[8] and, from these reflectivities, the values of R_∞ and R_o/R_∞ have been calculated for sheets in which all variables other than the refractive index have been set constant.

Although it is seen that there is an increase in both visual efficiency and printing opacity with an increase in refractive index, the increases amount only to half a point in visual efficiency and three points in printing opacity for a change in refractive index from 1·5 to 1·6, a range that includes most of the materials from which paper has been made on a commercial scale. These materials include cellulose (refactive index 1·53–1·59), lignin (1·61)[9] and various synthetic polymers, including nylon (1·53), polythene (1·50–1·54) and polystyrene (1·57–1·60). The effect of a change in refractive index on the optical properties that we calculate is about half that previously estimated by Giertz using an approximate relationship.[10]

TABLE 1—THEORETICAL CHANGES IN OPTICAL PROPERTIES ACCOMPANYING A CHANGE IN REFRACTIVE INDEX

Refractive index	*Diffuse reflectivity,* r	*Visual efficiency,* R_o	*Printing opacity,* R_o/R_∞
1·3	0·061	0·895	0·628
1·4	0·077	0·907	0·685
1·5	0·092	0·915	0·727
1·6	0·106	0·921	0·760
1·7	0·120	0·926	0·786
1·8	0·134	0·931	0·807
2·0	0·161	0·937	0·841
2·4	0·210	0·947	0·884
2·8	0·255	0·953	0·911

Diffuse reflectivities were calculated from the refractive index using Judd's tables.[8] Visual efficiencies and opacities were calculated from the present theory assuming other variables were constant—that is, $W = 60$ g/m^2, $V = 0{\cdot}667$ cm^3/g, $t = 4$ μm, $a = 1$ cm^{-1}.

Thus, the refractive index appears not to be a large enough variable in conventional pulps to be worthy of extensive study with a view to improving optical properties. Furthermore, there is little to be gained in this respect by changing to synthetic polymers, although these are of interest from other points of view. It is to be noted that this is not true of the fillers that are often added to paper and whose refractive index may be very high (rutile 2·76). Because of other variables introduced, however, a consideration of fillers is beyond the scope of this paper.

In the present paper, we will use a value for the reflectivity of 0·09, which is intermediate between experimental[6] and theoretical figures for cell wall material.

Absorption index

SINCE the reflectivity r and specific volume V of cell wall material are to a good approximation constant from one pulp to another, the only variables in the equations—equations (*1*)–(*5*)—governing sheet reflectance are a, t and n. If we now fix the grammage, which is a function of n and V, equation (*5*), the only variables remaining are the absorption coefficient and the effective layer thickness. It follows that for a given grammage one should be able to calculate the theoretical reflectance of a sheet for any combination of a and t. This we have done for a standard grammage of 60 g/m^2 and the results are shown in Fig. 1.

The absorption coefficient is thus a basic variable of a pulp having a considerable effect on the optical properties of a sheet. The effect of a change in the absorption coefficient is to move a sheet either up or down a constant

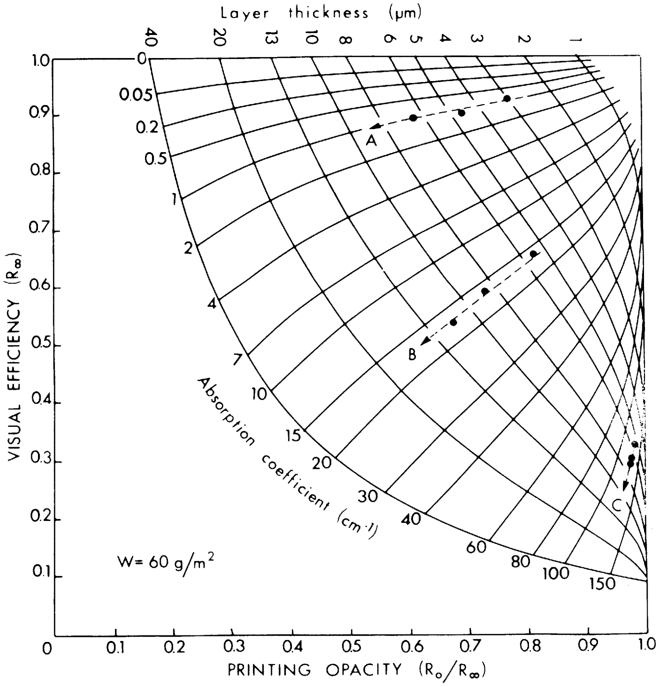

Fig. 1—Theoretical plot of visual efficiency versus printing opacity for sheets of standard weight ($W = 60$ g/m²). The figure shows the effect of varying layer thickness and cell wall absorption coefficient upon the optical properties of the sheet. Superimposed on the theoretical plot are the beater curves of (A) a fully bleached pulp, (B) a semi-bleached pulp and (C) an unbleached pulp plotted according to their experimentally determined values of R_∞ and R_0/R_∞

layer thickness line in Fig. 1. It is obvious from the figure that both visual efficiency and opacity will be affected—one property being enhanced at the expense of the other, the relative effects on the two properties depending on the initial position of the pulp before the change in absorption coefficient is made. A groundwood pulp, for example, because of the small amount of interfibre bonding, will lie on a layer line of low value (about 2 μm) and will, because of the high concentration of highly coloured lignin, lie on a line of high absorption coefficient ($a = 60$ cm^{-1} approx.). Thus, it might have a visual efficiency of 0·65 coupled with an opacity of 0·98. As can be deduced from the shape of the 2 μm layer line, a reduction in the absorption coefficient to, say, 30 cm^{-1}, the pulp would gain perhaps 5 or 6 points in visual efficiency with the loss of only 1 or 2 points in opacity. That such brightening actions can be effected on groundwood with little loss in opacity is well known.

Bleaching is, of course, the usual way in which the absorption coefficient of a pulp is reduced. In practice, however, bleaching probably rarely results only in a reduction in the absorption coefficient, since the chemical reactions also affect the physical properties of the fibres, causing them to bond to a greater or lesser extent under given conditions of papermaking. Thus, bleaching usually causes not only a reduction in a, but also change in t. This has, for example, been shown to be true of the 'Paprizone' treatment of groundwood pulp.[7] This is a sequential treatment with hydrogen peroxide and ozone, which both brightens and strengthens a groundwood.[11]

It has been observed[7] that there is a limit to which the absorption coefficient may be reduced. This is $a \simeq 1$ cm^{-1}, which appears to be the absorption coefficient of 'pure' cellulose. Most fully bleached chemical pulps appear to have this absorption coefficient. Thus, combinations of R_∞ and R_0/R_∞ above the $a \simeq 1$ cm^{-1} line in Fig. 1 are inaccessible with cellulosic pulps.

Occasionally, high opacity is in practice of more importance than high brightness. In this case, dyes may be added to a fully bleached pulp—the effect is to move the pulp down a constant layer thickness line.

Fibre dimension

THE relationship between the optical properties of paper and the dimensions of the constituent fibres is perhaps best approached through their common bearing on surface area. As shown in Fig. 1, good optical properties are associated with low effective layer thickness in a sheet, a parameter which is inversely related to the unbonded specific surface area in a sheet, equation (*5*). The mathematical relationship between the optical properties and surface area in the general case, as represented by equations (*1*)–(*5*), is not readily apparent because of the complexity of the equations. For fully bleached pulps, however, it has been shown that the effect of light absorption may be neglected in the calculation of single sheet reflectance (R_0) and the equation system reduces to a single equation—

$$\frac{1}{R_o} = 1 + \frac{(1-r)/r}{A_o W} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This equation, which shows the relationship between an optical property and surface area has been verified by experimentation on sheets of up to 100 g/m^2 grammage.[6] Although this surface area is only what remains after interfibre bonding has taken place, it is initially dependent upon the area of the individual fibres. Fibres of high specific surface area in the isolated state will retain their superiority after a given amount of bonding. As with any finely divided material, the specific surface area of pulp fibres is a function of their dimensions.

Firstly, consider fibres in the unbonded and uncollapsed state. Since the cells walls of dry fibres are non-porous,[12] the surface area is that of the luminar and exterior surfaces. If it be assumed that fibres are effectively long hollow rectilinear prisms (of either circular or square cross-section for the purposes of calculation), then simple geometry leads to a specific surface area of—

$$A_F = \frac{2V}{t_c} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where V is, as before, the specific volume of cell wall material and t_c is the cell wall thickness. Neither fibre length nor lumen diameter is a factor. Thus, as V is to a good approximation constant from one pulp to another, the specific surface area depends solely upon cell wall thickness. Cell wall thickness t_c is in fact the minimum value of the effective layer thickness for sheets made from a given pulp. That is, in a 'sheet' made of uncollapsed and unbonded fibres, the effective layer would be the cell wall.

For fully collapsed fibres, the only surface contributing to the scattering of light are those of the exterior surfaces of the fibres, hence the specific surface area will be proportionally reduced to—

$$A_F{}^1 = \frac{2V}{t_c} \cdot \frac{W_F}{(W_F + W_L)}$$

or

$$A_F{}^1 = \frac{2V}{t_c} \cdot \frac{1}{(1 + W_L/W_F)} \qquad . \quad . \quad . \quad . \quad . \quad (8)$$

where W_L and W_F are the lumen and fibre widths, respectively. For high surface area in collapsed fibres, not only should the cell walls be thin, but the ratio of lumen width to fibre width must be small; in essence, the fibres should be of fine denier.

Full appreciation of the above points is best obtained from a quantitative consideration of equations (*7*) and (*8*), as shown in Fig. 2. The importance of having thin-walled fibres for high surface area is obvious from this figure, as is the drastic reduction of surface area that accompanies collapse. A thin-walled, wide-lumen fibre, such as one from the earlywood of a softwood, loses nearly half its surface area and consequently a considerable fraction of its light-scattering ability. Theoretically, it is possible to reduce the fraction lost upon collapse by choosing fibres with a low W_L/W_F ratio, which, in effect, puts a higher fraction of the total surface area on the exterior wall. In practice, however, the W_L/W_F ratio of most species of wood is too high for the effect to be great. The pulps of *Eucalyptus globulus* and esparto grass described in Table 2 are good examples of fibres for which thin cell wall is coupled with low W_L/W_F ratios and both pulps are well known for the excellent optical properties of the paper made from them.

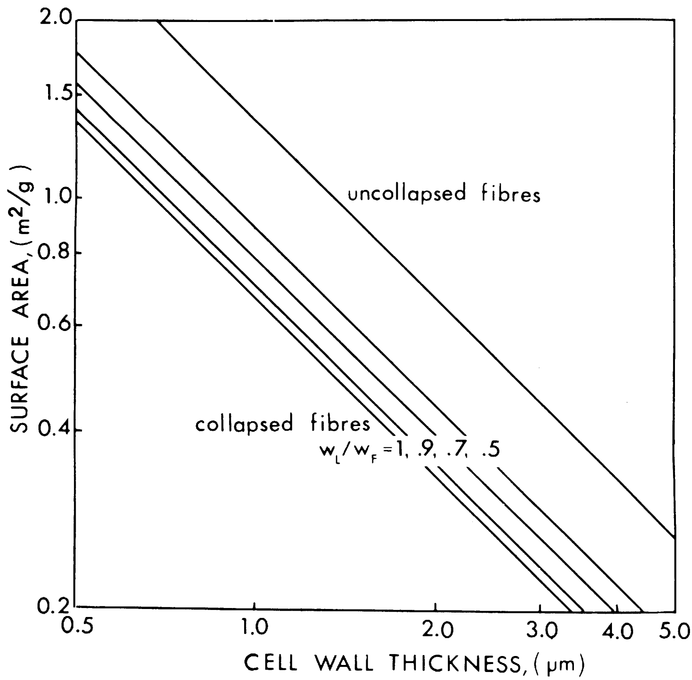

Fig. 2—Specific surface area of isolated fibres as a function of cell wall thickness. For uncollapsed fibres, the surface area depends solely on cell wall thickness, whereas for collapsed fibres it depends also on the ratio of lumen width on fibre width (W_L/W_F)

TABLE 2—PROPERTIES OF SOME COMMERCIALLY MADE FULLY BLEACHED PULPS

	Esparto grass	Eucalyptus globulus	*Spruce balsam*	*Cedar*	*Douglas fir*
Cell wall thickness, μm	0·95	0·95	1·1	1·15	1·5
Lumen/fibre width ratio	0·6	0·7	0·8	0·9	0·9
Lumen collapse, percentage	86	86	66	67	69
Calculated surface area of fibres, m^2/g	0·94	0·89	0·84	0·80	0·61
Opacity of standard sheets	0·83	0·78	0·74	0·74	0·65

The esparto pulp was prepared by the soda process and the other pulps by the kraft process. Collapse and opacity were measured on handsheets beaten to 5 km breaking length. Collapse was determined by Page's technique[16] and cell wall thickness by the method of Kallmes & Bernier, *Nature*, 1963, **197**, 1 330.

In addition to wood species, pulp yield is also a factor that affects fibre dimensions. Recent work has shown that, as lignin is removed from spruce-wood, the cell walls grow thinner in proportion to yield, while the lumen diameter stays relatively constant.[13] There are also indications that hemicellulose removal has the same effect.[14] Thus, it appears probable that cell wall thickness is reduced in proportion to yield during chemical pulping. Therefore, a wall that is 2 microns thick in wood will be only 1 micron thick when pulped to 50 per cent yield. In view of the relationship between cell wall thickness and surface area (Fig. 2), it is not surprising that quite small changes in the optical properties of the pulp.[1]

Lumen collapse

THE collapse of the lumina of fibres, as discussed above, results in a considerable loss of light-scattering ability. Unlike the loss of surface because of interfibre bonding that occurs when fibres are made into paper, lumen collapse probably does not confer strength on the paper web. It might be argued that collapse does confer strength from the fact that it converts the cylindrical fibres, with little possibility of forming extensive interfibre bonding, into flat ribbons capable of much more interfibre contact. Lumen collapse for this purpose need not be complete; partial collapse, bringing the opposing lumen surfaces to within a few microns of each other, would leave the fibres with a ribbon-like shape, yet preserve all the lumen surface. Even if this space were maintained only in the sections of the fibres between bonds, the advantage (so far as light scattering is concerned) could be appreciable. Lumen collapse is therefore a phenomenon well worth studying, with a view to finding ways of preventing it.

The collapsibility of a fibre, as of any hollow cylindrical body under a given load, will depend upon the transverse dimensions of the fibre and the plasticity of its wall. Luce,[15] drawing upon the theory for the strength of thick-walled pressure vessels, has suggested that the force necessary to collapse a fibre would be a function of the ratio of lumen width to fibre width, that is, (W_L/W_F). Thus, fibres of low W_L/W_F ratio would be expected to collapse less readily under the given loads applied during the drying and pressing of paper.

Page [16] has recently developed an elegant technique for the measurement of the percentage of collapsed fibres in a sheet and Fig. 3 is taken from his study. As shown in the figure, collapse of the fibres from any given pulp is less for the thicker walled fibres. Since the fibres were softwood fibres with effectively large lumina, the thicker walls imply lower W_L/W_F ratios. Collapse is increased also with increasing wall plasticity, as induced either by pulping to low yield or pulping to a given yield by the sulphite rather than the sulphate process. Page also showed that, as might be expected, extensive beating increased the degree of collapse—beating being another process increasing the plasticity of the wall.

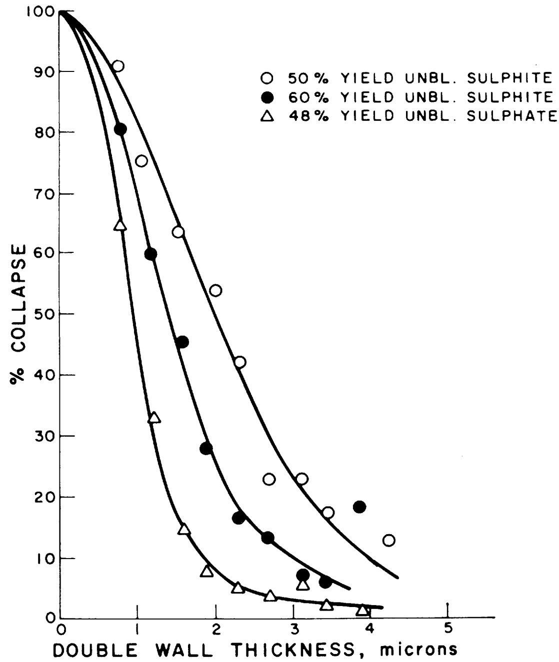

Fig. 3—The effect of cell wall thickness upon collapse [Figure taken from D. H. Page, *Tappi*, 1967, **50**, 449]

Hartler & Nyren(17) have confirmed many of the trends shown by Page, by measuring the force required to collapse single wet fibres. They showed that earlywood fibres were more readily collapsed than latewood, that sulphite fibres were more readily collapsed than sulphate and that the ease of collapse increased with decreasing yield.

There does not, however, appear to be data in the literature on the collapsibility of pulps of below 48 per cent yield. In some recent work, we examined the degree of collapse in handsheets made from several commercially prepared bleached kraft pulps. The data are given in Table 2 and it is seen that the degree of collapse for these pulps is quite high. Even the eucalyptus and esparto fibres with their low W_L/W_F ratios are extensively collapsed. It would therefore appear that a low W_L/W_F ratio serves little purpose in preventing collapse when the plasticity of the fibres is high—however, as pointed out in the previous section, a low W_L/W_F ratio keeps the fraction of the total surface area lost low when collapse does occur.

Interfibre bonding

WHEN isolated fibres are converted into a sheet of paper, a considerable fraction of the surface area that the fibres have in the isolated state becomes bonded and ineffective for light scattering. The more extensively the fibres are bonded, the less effective the sheet is in scattering light. This is, of course, the primary reason that, when pulp is beaten to increasing extents, the gains in tensile strength from increased bonding in the sheets are counterbalanced by drops in opacity and brightness. Which of the two optical properties is most affected depends on the absorption coefficient of the pulp, since, as a pulp is beaten, the optical properties moves down a constant *a* line(7) and, as is seen in Fig. 1, the slope of these lines varies with the actual value of the absorption coefficient. In all cases, the move is to greater effective layer thickness—that is, because of bonding, there are more cell walls per layer.

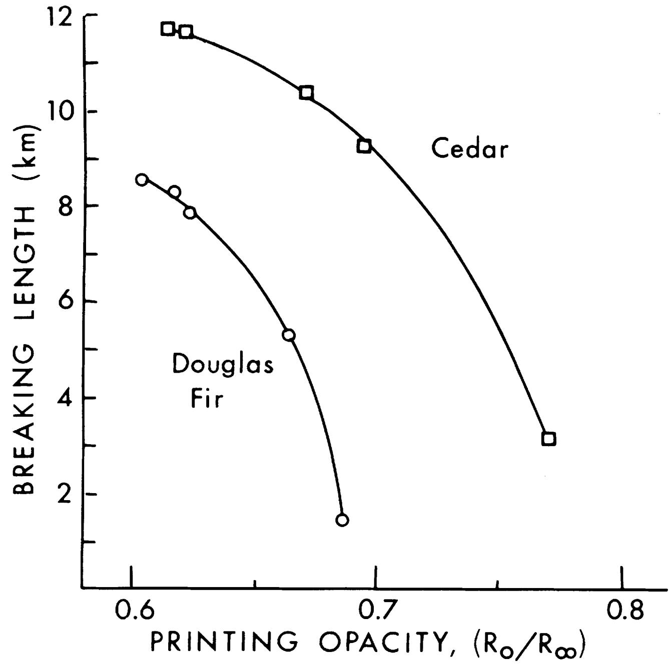

Fig. 4—The effect of beating on the optical and strength properties of fully bleached cedar and Douglas fir pulps; the pulps had very similar visual efficiencies

Although the opposing trends of tensile strength and optical properties are apparently irreconcilable for any given pulp, superior combinations of these properties may be achieved through a proper choice of pulp. If one assumes that to a first approximation the strength of a sheet depends upon the amount of interfibre bonded area, then the fibres with the largest surface area in the isolated state will be capable of forming sheets of the highest unbonded area (and therefore the highest light-scattering ability) at a given sheet strength. Some confirmation of this concept is given in Table 2, for which the surface areas of the isolated fibres of a number of pulps are calculated from their dimensions and degree of collapse. Although there is a rather narrow range in properties of the pulps examined, it is seen that there is a distinct trend for the fibres that have the highest surface area to form paper of the highest opacity at a given tensile strength. The point is further illustrated in Fig. 4, which shows the superiority of the cedar pulp over the Douglas fir pulp at a number of beating intervals, a superiority that we believe is for the most part due to the thinner cell walls of the cedar fibres.

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Transcription of Discussion

Discussion

Mr J. B. A. Epton In your theory, the sheet of paper is considered to be a stack of plane, parallel transparent layers of cellulose separated by air and illuminated by diffuse light. The proportion of the incident light reflected from the stack is calculated from the optical properties and the number of layers.

In your paper in *Tappi*, 1972, you said that a Zeiss Elrepho reflectance meter was used to measure the reflectance of the paper samples—that is, reflectances were measured under conditions of diffuse illumination and normal viewing.

For a parallel layer model, however, as you postulate, light incident at any angle will ultimately leave the surface with an angle of reflection equal to the angle of incidence. Therefore, a very low reflectance would be expected, since the surface is viewed normally in the Elrepho instrument—that is, the photocell sees only its own image (which is not illuminated).

We confirmed this fact by a simple experiment in which the reflectance of a stack of cellulose acetate sheets over a black background was measured on the Elrepho and the results are as shown in Table 1. The measured reflectance was approximately 3 per cent, whereas the value calculated from your theory is approximately 50 per cent.

TABLE 1—REFLECTANCE VALUES OF SHEETS VIEWED NORMALLY OVER A BLACK BACKGROUND

	Reflectance, per cent		
		Calculated from	
Number of sheets	*Measured*	*Normal reflectivity*	*Diffuse reflectivity*
5	2·7	25·9	45·7
10	3·5	37·5	57·3

In another experiment, we titled the sheets over a black tile to reflect the maximum light from the illuminated part of the sphere directly into the photocell. The measured reflectance increased as expected, since the conditions

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then approximated to normal illumination and viewing. The results are shown in Table 2 and good agreement can be seen between the measured values and those calculated from the normal reflectivity value. The values calculated from the diffuse reflectivity value, however, are much higher.

TABLE 2—REFLECTANCE VALUES OF SHEETS ON BLACK TILE TILTED TO REFLECT MAXIMUM LIGHT INTO PHOTOCELL

	Reflectance, per cent		
		Calculated from	
Number of sheets	*Measured*	*Normal reflectivity*	*Diffuse reflectivity*
0	4·0	4·0	4·0
1	11·5	10·5	18·8
2	16	15·9	29·2
3	20·8	20·4	36·6
4	24·2	24·3	42·2
5	27·4	27·6	46·5
6	31·6	30·4	49·8
8	34·6	34·9	54·5
12	40·8	40·9	59·6
20	45·1	46·4	62·9

If taken literally therefore, your simple model is valid for equal angles of incidence and viewing, but it does not predict the results given by the Elrepho.

Since the reflectances of the paper samples you measured agree with those calculated from the model, then significant scattering must occur within the layered structure in order for the light to reach the photocell.

There is no mechanism in your model by which this can occur, but the results can be explained if the sheets are considered to have irregular surfaces instead of flat ones. This would mean that light would be diffuse at *all* boundaries and total internal reflections would occur. The simplifying assumption that the reflectivity is the same for each boundary cannot then be made in this case.

TABLE 3—VALUES USED IN CALCULATIONS

Cellulose acetate film	
Refractive index	1·485
Transmitivity (f)	0·98
Reflectivities (r) —	
Normal	0·03809
Diffuse	0·08952

If the reflectance of the stack is recalculated,* using a reflectivity value at the lower interface modified to account for the substantial increase caused by

* Private communication from L. F. Gate, August 1973

total internal reflections, then the same reflectances can be obtained if the number of layers in the sheet is reduced by a factor of between 3 and 4, depending upon the refractive index.

Moreover, if the surfaces are optically rough, the nitrogen surface area per layer would be increased by a further factor of perhaps 2 or 3 over and above the factor of 2 used in your treatment. Thus, the number of rough-surfaced layers calculated from the nitrogen surface area would fall to approximately the value required by the optical considerations.

In conclusion, the model as presented is oversimplified and it is more realistic to assume that the surface of the layers are optically rough. Since surface area and light scattering per layer are both thereby increased, this leads to an agreement between observed and calculated reflections for paper similar to that given by your simple treatment.

Dr A. M. Scallan We have in our previous work (*Tappi*, 1972, **55** (4), 583) calculated the reflectances of sheets of paper from their surface areas and found the calculated values to agree with the experimentally determined ones. I think therefore that your question should be 'Why do the equations that apply to paper not apply to cellulose acetate sheets?' To this, you have provided your own answers. The surfaces of the cellulose acetate sheets are smooth and the photocell of the Elrepho, viewing the surfaces normally, picks up very little light, since the photocell itself occupies the part of the sphere wall necessary to irradiate the sample. Tilting the sample brings light to the sample from an area of the sphere beside the photocell. The reflectivity that one should substitute in the equations in this case is that for the angle of incidence induced by tilting. Unless the angle is very large, the reflectivity will be close to that for normal reflectance. Thus, the results obtained on the cellulose acetate sheets are quite in accord with the equations presented by us, but modified for the type of illumination.

We find that your system does not exactly duplicate the layered structure of paper. Although our model does not have a built-in mechanism for maintaining the diffuseness of light after it has been refracted and reflected, we presume that, in paper itself, the surfaces are sufficiently disaligned to do this. Light, which is diffusely incident from the sphere of the Elrepho meter, is diffusely scattered. Since the angle of incidence of the light to the plane of the sheet does not necessarily equal the angle of reflection, the photocell picks up a representative fraction of the radiation scattered from paper. Having made the surfaces irregular, we do (as you point out) have the problem that total internal reflections could raise the reflectivity of alternate surfaces in the model. Nevertheless, we find good agreement between calculated and experimental reflectances using the usual value for diffuse reflectivity. Therefore, we must conclude that total internal reflections rarely occur: this could again be due to the roughness of disalignment of the surfaces, which prevent the conditions for internal reflection to be met.

Dr J. A. Van den Akker It would not take much waviness in the layers—the fibres already have it—to distribute the light in a sufficiently random way to eliminate the difficulty. The scattering and randomising of the light by the fibres is what makes a sheet of paper different from a stack of regenerated cellulose sheets.

I believe that the Stokes analysis would apply to smooth wavy sheets—that is, *randomly* wavy sheets, the surfaces of which deviate from the horizontal by only a few degrees. The waviness would introduce only small cosine errors and would not significantly modify (in my opinion) the amount of light absorbed; nor would it significantly influence the amount of light reflected. Yet it would create in very few layers the desired randomness of the distribution of the light and do this without significantly changing the surface area. On the other hand, a *fine-scale* roughness would indeed change the specific surface area.

Dr D. Atack I suggest that you consider introducing some factor to account for fibre delamination. We know that such delamination often occurs and, in fact, it is possible in some cases to have an increase in both breaking length and opacity.

Dr Scallan First of all, I know that you are specifically interested in groundwood, whereas our concepts are centred on chemical pulps, for which there is usually a drop in optical properties with increased strength induced by beating.

I believe that delamination of the fibre wall exists only while the fibres are in the wet state. In dry pulps, the fibre wall is non-porous, hence there are no solid/air interfaces to interfere with light. I consider therefore that delamination is not a cause of any optical effects.

Dr Atack Nevertheless, one does get an increase in strength together with an increase in opacity.

Dr Scallan At the beginning of beating with some chemical pulps and sometimes with groundwood, yes.

Dr Atack In some cases, the lamellae must continue to exist in the dry state, too.

Mr Epton The cellulose sheets experiment does exactly represent the theoretical treatment given in your paper in *Tappi,* 1972 and we used independently determined values of refractive index and absorption coefficient. You also say that the surfaces of the layers are rough, but you refer in your paper to a sub-optical roughness that is picked out by the surface area measurement and cannot be seen by the light scattering effect. The roughness that I am talking about, however, would be a surface roughness that could be seen and would scatter light.

Moreover, if you use a rough surface model, then your equations are incorrect, because the model must be modified to account for the different reflectivities on either surface and you have assumed that the reflectivities are the same.

Finally, the table of results that you have presented is based on a set of assumptions. If you changed those assumptions—that is, different reflectivity values and a different number of layers—a very similar set of results could be produced that could still agree with your measured results.

Dr Scallan On the first part of your question, I have nothing to add to my earlier comments. Our calculated values of reflectance for bright handsheets are indeed based on a set of assumptions. They are calculated from the equation—

$$\frac{1}{R_o} = 1+\frac{(1-r)/r}{AW}$$

where R_o = single sheet reflectance
A = specific surface area
W = grammage
r = reflectivity

In this equation, one may use the uncorrected nitrogen adsorption surface area for A coupled with the r value for normally incident light (0·05). Alternatively, one may use the nitrogen adsorption surface area divided by a roughness factor of 2·0 for A coupled with the r value for diffusely incident light (0·10). Close to the same result is obtained for R_o; however, it seems most reasonable to assume that the illumination is diffuse and the surfaces are rough.

Mr J. R. Parker I think that the point to bear in mind is that, although the illumination of the top surface of the fibre might be diffuse, if the top surface is planar, the light is refracted into a cone of rays and the illumination of the lower surfaces of the fibre is not diffuse. This is according to your model. If there is any waviness in the fibre surfaces, then the angle of this cone would be increased so that total internal reflection could occur at the lower surface of the fibre. If it was indeed diffuse, the reflectivity on that surface would go up by a factor of about seven. This takes a little reconciling with your statements.

Dr Scallan I think that paper has the unique optical properties that it has because of its structure. Its composite fibres are very small, the wall thickness approaching the wavelength of light. Thus, the surfaces of the layers are effectively rough in their reaction with light and certainly rough enough, as Dr Van den Akker says, to maintain the light in an approximation to a diffuse condition.

Perhaps, it is misleading to think about the problem in a macroscopic way, as with cellulose acetate sheets. For total internal reflection to occur at a cell wall/air interface, the surface must be perfectly parallel to the paper plane and the incident light perfectly diffuse. Both conditions are unlikely to occur simultaneously; in fact, measurements of reflected and transmitted intensity distributions suggest that a perfectly diffuse light distribution is seldom if ever obtained.

We agree with Epton that there are probably deficiencies in our assumption that the boundary reflectivities are the same at both the upper and lower surfaces, but we have no evidence that these are significant enough to affect our calculations.

Dr C. T. J. Dodson I would like to direct a question to Dr Scallan via Professor Wahren, using one of his figures, Fig. 34. This may throw some light (if I may use that expression) on the subject. The point is the remarkably different spectral distribution measured optically for differing paper surfaces.

Dr B. Norman The results in Fig. 34 were obtained by a rather rough method of estimating the surface structure and could not apply in Dr Scallan's case. It is not really the coarseness of the fibres that is recorded, but rather the macro surface structure of the sheet.

Prof. J. Silvy This is about the formal choice of the variables in your graph. Do you think that the choice of the printing opacity is the best from a practical point of view? I think it is better to use the reflectivity R_o of a single sheet. What do you do when the grammage of your paper changes? Are there other curves? If you use the reflectivity of the single sheet, the grammage must be put in your graphs. I think that would be best from a practical point of view, because the grammage, the scattering and absorption coefficients trend in the same direction when we are considering the opacity of paper and we must take these variables in association, not separately, don't you think?

Dr Scallan We dealt with single sheet reflectances (R_o) in our earlier paper in *Tappi*. Today, I have preferred to deal with the measurements of visual efficiency and opacity to bring out the effect of variables governing the optical properties of paper other than grammages.

Mr D. J. McConnell In your paper, you mentioned that you could possibly deal with dyes and to change the absorption coefficient by using dyes. Was this in fact done and how did the absorption coefficients of dyes in handsheets relate to the absorption coefficients of the dye solutions before they were added?

Dr Scallan We have studied the effect of putting increasing amounts of dye in handsheets. This was particularly to see whether, as we went to very high absorbances, we obtained a better or worse description of optical behaviour than the Kubelka-Munk theory. It is at very high absorbances that the Kubelka-Munk theory has been most criticised, but our theory did not predict optical behaviour in this region any better than the Kubelka-Munk theory. Perhaps, when absorption is high, the light reaching the lower layers in the sheet is no longer diffuse, because the rays at a high angle to the normal (and therefore long path length) are reduced to negligible proportions by absorption.

Whether the absorption coefficient of a dyed sheet as calculated from our theory agrees with that of the dye in solution, we believe it should, but we have no evidence to this effect as yet. We have, however, measured the absorption coefficient of regenerated cellulose sheets after embedding them in a liquid of matching refractive index and found a value close to the 1 cm^{-1} predicted by our theory.

Prof. D. Wahren I would like to comment on Mr Radvan's paper. It is not a criticism, just something to point out.

You have been careful to use the expression 'layered structure' of paper and the consequence of this. That is very correct. A non-layered structure should not be mixed up with a three-dimensional fibre orientation in the paper. I will try and demonstrate this. Consider the fibre orientation in a perfectly random field. All angles with the horizontal are equally probable. What is then the average angle of a fibre? This can be quite simply calculated. It turns out that the average angle of the fibre in a random suspension is 32·7°.

Suppose now that we produce a perfectly random suspension, then compress this structure, which can be of unit thickness from the start. We compress it to the density of the final paper. What will happen? Of course, the average angle will decrease. The mathematics work out so that, in a low density sheet of, say, 30 g/m^2, the average angle is approximately 4°; at a density of 60 (normal for a kraft paper), the average angle is approximately 2°. So, in a microtome section, we will observe fibres that on the average are practically parallel to the plane of the sheet, not at all the 3-D structures of the fibres in pig skin. The interweaving may be there anyway and may be important.

Dr E. L. Back Just one comment on the layered structure of the paper or the layered structure of the bonds. Bonding agents added have a much larger effect on the Z-direction strength than on the strength in the plane of the sheet. What might be forgotten is that the reverse is true as well for hydrophobic additives. When wax or rosin size is added to the stock, the tensile strength might be reduced 5 or 10 per cent, but the Z-direction strength might be reduced as much as up to 50 per cent. This data refers to building boards, but it certainly should be checked for some grades of fine papers.

Mr B. Radvan I agree with what Prof. Wahren said before that this question of structure is topological, not geometrical.

I cannot really comment on Dr Back's remark. I have had no experience of measuring these effects. Needless to say, before coming here, I tried my hardest to produce a three-dimensional sheet, but I failed. There were some indications in this work, however, that the effects on strength may be much greater because of secondary effects—that is to say, even a small degree of displacement of the fibre from the horizontal or layered arrangement will interfere with the bonding. I wonder if the effect of additives is not something similar.