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THE RELATIONSHIP BETWEEN STRENGTH AND LIGHT SCATTERING COEFFICIENT FOR FILLED PAPERS

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ABSTRACT

The apparent light scattering coefficient of a filler can be shown to be dependent on pulp type, freeness and sheet forming conditions. This is because a large part of this apparent light scattering is in fact due to the effect filler has on pulp. In this paper an attempt is made to provide a mechanistic model for the interaction and provide a quantitative expression relating light scattering to the effect of filler on the fibre as represented by the change in sheet strength. Examples are given of the use of this model to explain the effects of changes in wet pressing pressure and filler aggregation on the apparent light scattering of the filler.

INTRODUCTION

Fillers are a necessary part of practically all printing and writing paper. In uncoated grades the filler is essential to reduce the overall raw material costs and to improve optical and printing properties. In coated grades filler is inevitably present in the base paper as waste coating pigment, but may also be added separately to reduce costs or again improve optical properties.

In the past the choice of filler was often restricted, not only in mineral type but also in particle size distribution, by the limited sources of supply and by

papermaking practice. Improvements in mineral processing techniques and advances in papermaking, such as the introduction of neutral-alkaline sizing systems to allow the use of calcium carbonates, have completely changed this situation, and filler producers can now supply a relatively wide range of particle size distributions and in some cases can also offer a choice of mineral types. Today, therefore, it is possible to select a filler or combination of fillers to give an acceptable compromise of properties to suit practically any grade of paper, and this of course means that a thorough knowledge of pulp-filler interactions has become more important.

Several workers have reported studies on the general effects of filler particle size and shape on paper properties (1), and on more specific topics such as the optical properties of filled paper (2), and the relationship between filler surface area and sheet strength (3). In this paper attention is concentrated on the optical properties of filled paper and in particular on the relationship between optical properties and strength properties.

An attempt is made to show how established, simple (4) theories of fibre only optical and strength properties may be extended to include filled paper. A basic quantitative expression is derived, and this is used to explain how certain changes in paper making conditions, e.g. fibre beating and filler aggregation, change the apparent contribution that the filler makes to the overall sheet optical properties.

The work reported here is mainly based on a series of laboratory handsheet experiments carried out using a range of fillers in a bleached softwood sulphite pulp furnish.

THE OPTICAL PROPERTIES OF FILLED PAPER

It is widely accepted that the Kubelka-Munk analysis (5) may be applied to paper, although other methods have been proposed (6), and it has been shown that the Kubelka-Munk analysis cannot be used for strongly coloured sheets (7). These modifications and criticisms are not important here and the normal K-M approach is sufficiently accurate.

The K-M equations lead to light scattering and adsorption coefficients for the sheet, and it is customary to assume that these are weighted sums of the independent coefficients of the separate sheet components :-

$$K_{\text{sheet}} = \Sigma_i \, L_i \, K_i \,, \qquad (1)$$

$$S_{\text{sheet}} = \Sigma_i \, L_i \, S_i \,, \qquad (2)$$

where K_{sheet} and S_{sheet} are the light absorption and scattering coefficients respectively of the sheet, L_i, K_i and S_i are the weight fractions, light absorption and scattering coefficients (respectively) of component i. These simple equations are often used to predict sheet properties from known properties of individual components (8).

It is found that Equation (1), the light absorption coefficient relationship, is invariably valid regardless of the physical treatment of the pulp, filler and dried sheet; but Equation (2), the light scattering coefficient relationship, can be very sensitive to the physical treatment. Thus it is known (9) that the light scattering coefficient of the pulp changes significantly with for expample beating or refining, but it is perhaps less well known that the light scattering coefficient of the filler can also appear to change significantly, again with pulp beating and refining, and with pulp type. This is clearly shown by Fig.1 which shows light scattering coefficient plotted against loading for softwood sulphite sheets at various degrees of freeness filled with Grade C clay. The variability in pulp light scattering coefficient is attributed to bonded area changes. The apparent variability in the filler light scattering coefficient is, however, a consequence of ignoring the influence of pulp-filler interaction in the total light scattering coefficient equation.

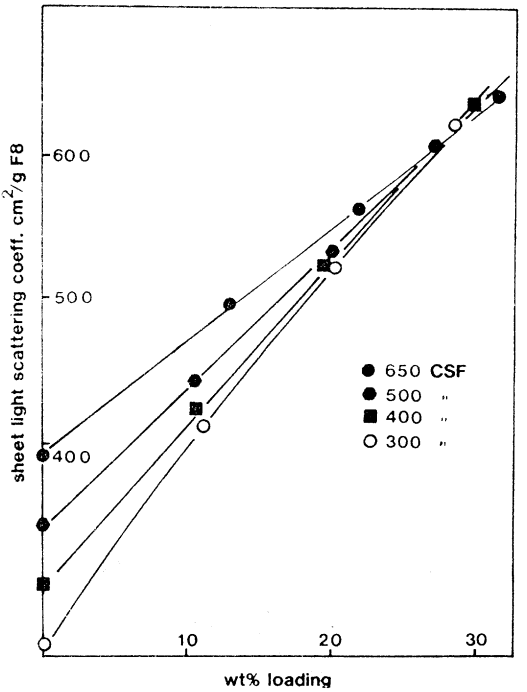


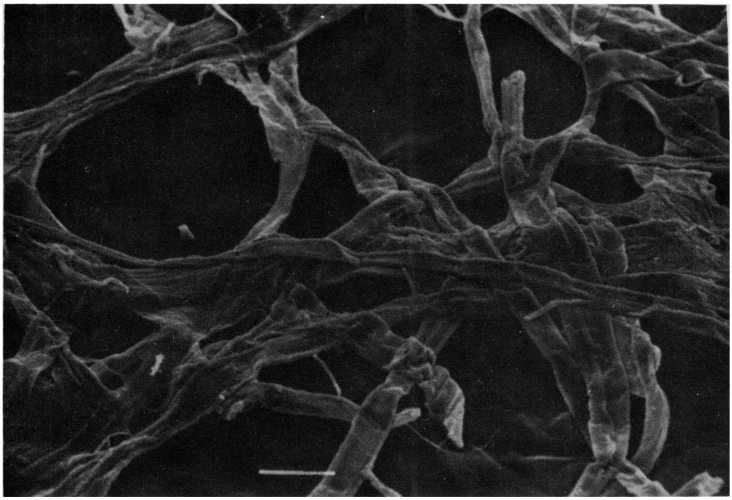
Fig 1—Effect of beating on the relationship between light scattering and loading. Sulphite pulp, grade C clay filler

A PHYSICAL MODEL OF FIBRE-FILLER INTERACTION

i. Unfilled Sheets

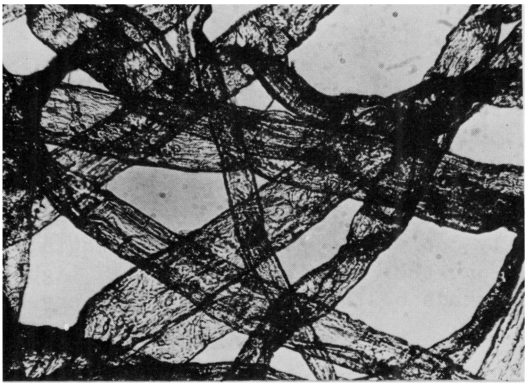
Considerable work has been carried out on the relationships between fibre strength, light scattering coefficients and bonded area (10). These relationships can be complex, but for the bleached sulphite pulp, (and most bleached Kraft pulps), used for the majority of this work, the relatively simple approach adopted by Igmasson & Thode (11) and others may be used.

Picture 1 shows an S.E.M. micrograph of a 5 g/m^2 unfilled, softwood sulphite pulp sheet and demonstrates the collapsed ribbon-like nature of the fibres bonded at points of intersection to form a 2-dimensional network. Sheets of normal basis weights may be considered as stacks of similar networks bonded together. The strength of the sheet depends partly on fibre strength and length but, for this pulp, mainly on the bonded area. The light scattering coefficient depends on the non-bonded fibre area.

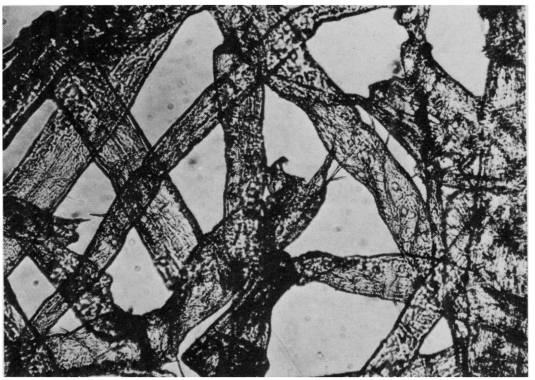


Picture 1—SEM mocrograph of 5 g/m^2 unfilled beaten softwood sulphite sheet

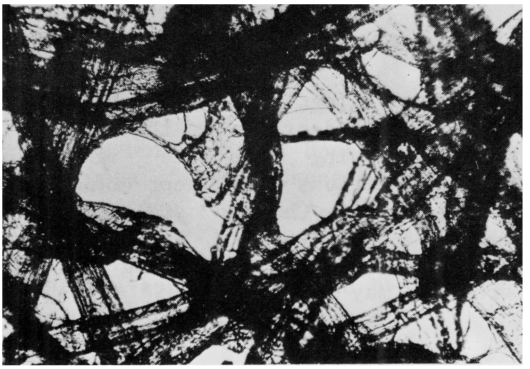
Beating or refining, and to a lesser extent wet pressing, normally decrease the light scattering coefficient by increasing the area of fibre bonded. Provided drying conditions are kept constant the exterior surface area of the fibres (bonded and non-bonded) is not greatly influenced by beating, etc. so that a simple relationship between light scattering coefficient and bonded area fraction may be assumed:-



Picture 2—Optical micrograph of 5 g/m^2 unfilled unbeaten softwood sulphite sheet



Picture 3—As picture 2, beaten softwood sulphite sheet



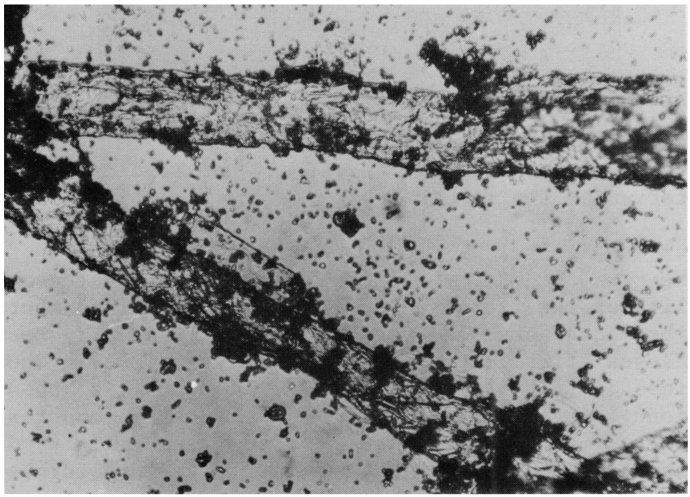
Picture 4—As picture 3, dried by removing water with acetone

$$A = 1 - \frac{S}{S_f} \qquad (3)$$

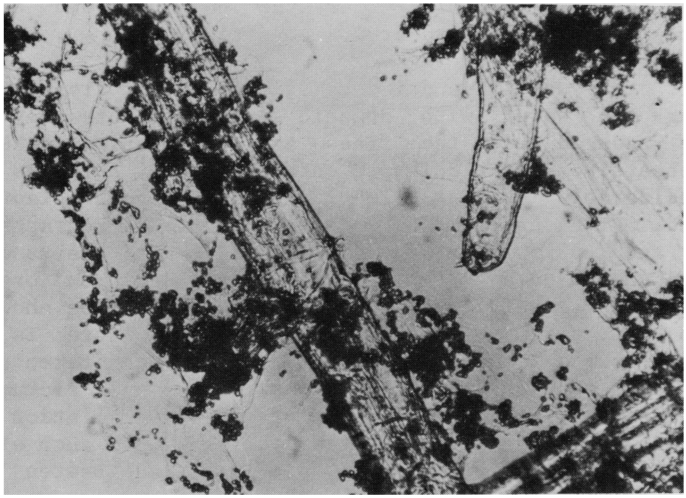
where A is the fraction of fibre bonded, S is the measured light scattering coefficient and S_f is the light scattering coefficient of a totally unbeaten, non-bonded pulp dried from water under the same wet pressing conditions as the sheet.

The major effect of beating is to increase the flexibility of the fibres which allows a greater number of fibre-fibre contacts and greater contact area. Beating also causes fibrillation and generates fines. Whether these fines and fibrils contribute to bonding is open to discussion but is not relevant here. What is important is that under normal drying conditions they are mainly drawn onto the main fibre surfaces by surface tension forces and make little or no contribution to the sheet light scattering. This is why the total dry surface area of the fibre remains approximately constant. Obviously in this simple approach complications such as lumen collapse, which may occur for beaten fibres but not unbeaten fibres, have been ignored. However, for the pulp used here the extent of lumen collapse is similar for the unbeaten and beaten pulp sheets under standard drying conditions.

If the sheet is dried by critical point drying or by removing the water with organic solvents not only is bonding reduced but the fines and fibrillation in beaten fibre sheets no longer collapse onto the fibre surfaces and a considerably greater light scattering coefficient is obtained. Pictures 2, 3 and 4 show optical micrographs of beaten and unbeaten softwood sulphite pulp sheets dried conventionally and a beaten pulp sheet dried from organic solvent respectively. (The organic solvent may be shown to have no effect on a dried sheet and therefore is not causing fibre disruption). The pictures are taken using transmitted light and the 'fuzzy' dark areas in Picture 4 show enhanced light scattering of the fibrillation and fines in the organic solvent dried sheet. No such effect is seen in Picture 3, the conventionally dried beaten pulp sheet.

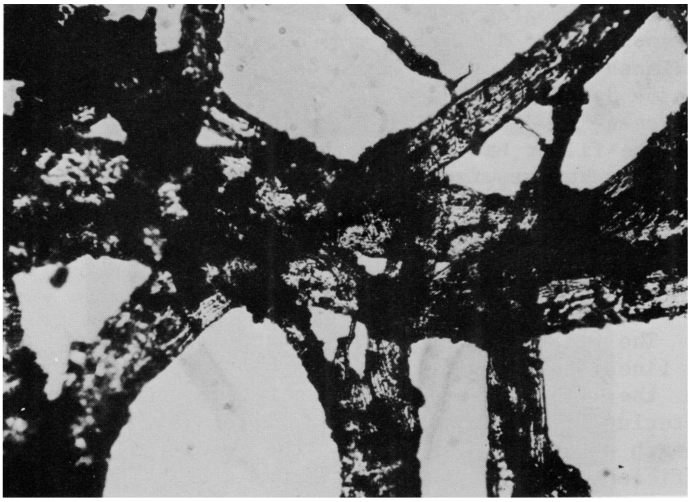


Picture 5—Optical micrograph of unbeaten softwood sulphite pulp with 25 w% precipitated calcium carbonate filler and a typical retention aid (0.02 w% Percol 292 on fibre)



Picture 6—As picture 5, beaten softwood sulphite pulp furnish

Picture 7—Optical micrograph of 5 g/m^2 sheet prepared from furnish shown in picture 5



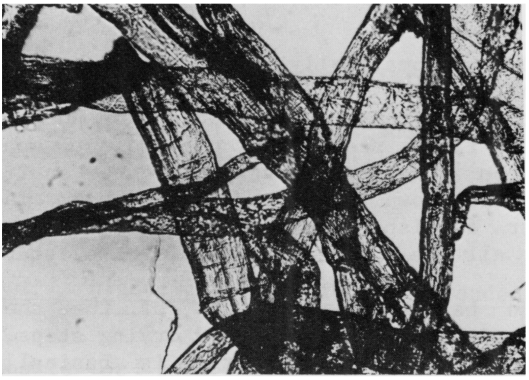
Picture 8—As picture 7, furnish shown in picture 6

ii. Filled Sheets

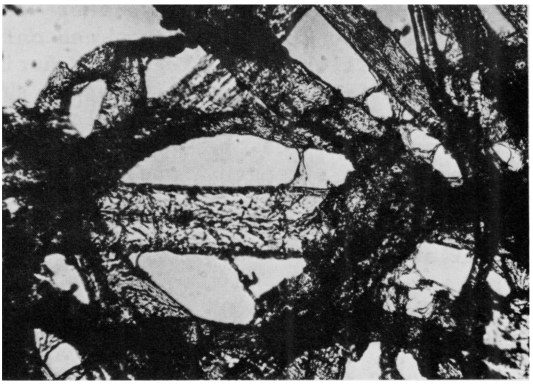
This approach may now be extended in include filled sheets. Pictures 5 and 6 show optical micrographs of furnishes containing unbeaten and beaten softwood sulphite pulps respectively with 25 wt. % precipitated calcium carbonate filler and a polymeric retention aid. For the beaten pulp furnish the filler is totally entangled in the fibrillation; but for the unbeaten pulp furnish, where there is little fibrillation, the filler is either free in suspension or closely held to the main fibre surface. Pictures 7 and 8 show optical micrographs of 5 g/m^2 sheets formed from the furnishes containing unbeaten and beaten fibre respectively. The sheets were dried in the normal way and the filler-fibril entanglement in the furnish containing beaten pulp has been drawn down onto the fibre surfaces, and the only visual difference between the sheets is a difference in loading caused by loss of some of the free filler from the unbeaten pulp furnish.

Dissolution of the filler by acid in an organic solvent, as shown earlier (12) and confirmed by experiments described below, removes the filler without greatly disturbing the sheet structure. Pictures 9 and 10 show optical micrographs of the 'filler removed' sheets corresponding to Pictures 7 and 8 respectively. Picture 9 is almost identical to Pictures 2 or 3 but Picture 10 shows the same dark areas caused by enhanced light scattering as were seen in Picture 4. Obviously for the unbeaten pulp sheet the filler has simply been removed from the fibre surface, whereas for the beaten pulp sheet the filler has been removed leaving the fibrillation intact. This is shown more clearly by Picture 11, which shows an S.E.M. micrograph of an area of the 'filler removed' beaten pulp sheet.

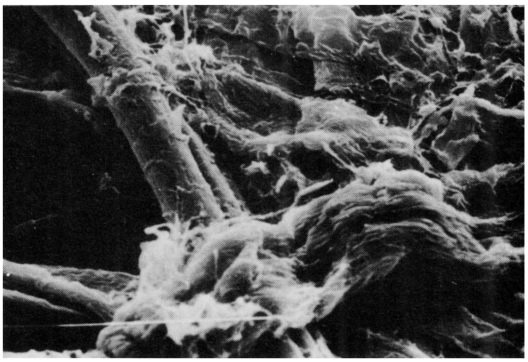
The filler therefore is assumed to prevent areas of the fines and fibrillation of a beaten pulp from collapsing onto the fibres, and thus increases the sheet light scattering coefficient. The filler also reduces sheet strength which again increases the sheet light scattering coefficient. Both these effects are, from the form of



Picture 9—As picture 7 after removal of the filler by hydrochloric acid in ethanol



Picture 10—As picture 8 after removal of the filler by hydrochloric acid in ethanol



Picture 11—SEM micrograph of 'filler removed' area from sheet shown in picture 10

Equation (2), automatically assumed to be parts of the filler contribution to the sheet light scattering coefficient. As they are dependent on pulp beating, etc. so the filler light scattering coefficient appears to be dependent on these factors. In the earlier work by Davidson it was shown that for a coarse chalk in a typical fine paper furnish these contributions may practically account for all the apparent filler light scattering.

It can be shown that most of the sheet strength develops during the pressing and drying steps, whereas the attachment of filler to the fibres is basically completed before pressing. Therefore, before pressing the fibre is partially covered by areas of filler or filler, fines and fibrillation; and if it is assumed that the filler does not move and that fibre-filler-fibre bonds either do not occur or do not create strength*, bonding can only occur when areas not covered by filler come together during pressing and drying. The effect that filler has on sheet strength gives an indication of the fibre area available for bonding and hence the area covered by filler, etc. so that a relationship between strength and light scattering coefficient basically similar to that shown in Equation (3), but extended to include the filler and its effect on fines and fibrillation, may be developed.

A SIMPLE QUANTITATIVE MODEL OF THE RELATIONSHIP BETWEEN STRENGTH & LIGHT SCATTERING COEFFICIENT FOR FILLED SHEETS

For the case of the unfilled sheet the light scattering coefficient is due simply to non-bonded fibre area and is given by Equation (3).

For the filled sheet the light scattering coefficient is assumed to have three components :-

* Whether the filler moves is difficult to measure. However, the volume created or occupied by the filler in the formed, uncalendered sheet (13) is so large, $\approx 1.4 cm^3/g$, that the assumption that fibre-filler-fibre bonding may be ignored seems valid.

1. Light scattering from non-bonded fibre area.

2. Light scattering from fibre fines and fibrillation prevented from collapse by the filler.

3. Light scattering from the filler.

i. Component 1: Light Scattering from Non-Bonded Fibre Area:

The tensile or burst strength of an unfilled sheet, T, is related to the bonded area, A. The exact relationship varies with the degree of beating and fibre length, etc. (14). However, under certain conditions:-

$$T = k\,A \qquad (4)$$

where k is a constant. This is the simplest possible relationship but fortunately applies to the bleached softwood sulphite pulp and most sulphate pulps under the range of beating and pressing condition used here. To avoid unnecessary complications this simple relationship is, therefore, used here although other relationships could be used if necessary.

For a filled sheet with loading L strength is reduced to T_L (expressed per unit fibre weight in the sheet) and the bonded area fraction of the pulp is reduced to :-

$$A_L = \frac{T_L}{T} A \qquad (5)$$

Ignoring, for the present, light scattering contributions from the filler and fibrillation or fines, the light scattering coefficient of the pulp would now be :-

$$\left(1 - A\,\frac{T_L}{T}\right) S_f \qquad (6)$$

or correcting for the fraction of pulp in the sheet, the pulp contribution to the sheet light scattering coefficient would be :-

$$(1 - L) \quad (1 - A \frac{T_L}{T}) \qquad S_f \tag{7}$$

ii. Component 2: Light Scattering from Fibrillation and Fines Prevented from Collapsing onto Fibre Surfaces by the Filler:

The filler is assumed to occupy or influence areas of the fibre surfaces and thus reduce sheet bonding. If x is the area fraction reduced by filler then (1-x) is the free fibre area, and the probability that free fibre areas coincide during drying to form fibre-fibre bonds is $(1-x)^2$. The strength of the filled sheet is related to the strength of the unfilled sheet by:-

$$(1-x)^2 = \frac{T_L}{T} \tag{8}$$

or

$$x = (1 - \sqrt{\frac{T_L}{T}}) \tag{9}$$

x is also the area over which the collapse of fibrillation and fines is prevented, and if a light scattering coefficient S_f' is defined as the scattering due to non-bonded pulp with no collapse of fibrillation, the light scattering coefficient of the pulp is increased by:-

$$(1 - \sqrt{\frac{T_L}{T}}) \quad (S_f' - S_f) \tag{10}$$

and that of the sheet is increased by:-

$$(1 - L) \; (1 - \sqrt{\frac{T_L}{T}}) \; (S_f' - S_f) \tag{11}$$

iii. Component 3: Light Scattering from the Filler:

The light scattering coefficient of the filler, S_{filler}, is assumed to be independent of the fibre, and of the beating or wet pressing conditions. This implies that

after conventional drying the filler is always attached to the fibres in the same way regardless of fibre type or sheet forming conditions. This obviously is not necessarily true. Examination of S.E.M. micrographs, however, tends to support this assumption, and with or without fines or fibrillation the filler appears to be randomly orientated on the surface and in the pore structure of the main fibre network. It should be noted that the fibre diameters are generally 2x or more the average diameter of the filler particles and that shrinkage of fibre and fibre debris during drying will probably separate fines and fibrils from direct contact with the filler leaving the filler in loose association with the fibre.

It may be expected that S_{filler} will be somewhat less than the light scattering coefficient of free powdered filler because S_{filler} allows for the loss in filler and fibre light scattering due to any filler-fibre optical contact. It is also possible that the optical 'crowding' of the filler may introduce dependence of S_{filler} on loading, but this possibility is ignored for the sake of simplicity.

The contribution of the filler to the sheet light scattering coefficient is simply :-

$$L\, S_{filler} \qquad (12)$$

iv. The Total Sheet Light Scattering Coefficient:

Summing Equations (7), (11) and (12) gives the total sheet light scattering coefficient :-

$$S_{sheet}=LS_{filler}+(1-L)(1-A\,\frac{T}{T}L)S_f+(1-L)(1-\sqrt{\frac{T}{T}}L)(S_f'-S_f) \qquad (13)$$

Following the normal assumption as given by Equation (2), for a simple pulp + single filler system :-

$$S_{sheet} = (1-L)S_{unfilled\ sheet} + L\, S_{apparent\ filler} \qquad (14)$$

where $S_{unfilled\ sheet}$ is the light scattering coefficient of an unfilled sheet and $S_{apparent\ filler}$ is the apparent light scattering of the filler under the conditions of formation. Equation (13) may be re-arranged in the same form as (14) to give:-

$$S_{sheet} = \underbrace{(1-L)\ [(1-A)S_f]}_{(a)} + \underbrace{L[S_{filler} + \frac{(1-L)}{L}\ (1-\sqrt{\frac{T}{L}})(S_f'-S_f) + \frac{(1-L)}{L}A(1-\frac{T}{L})S_f]}_{(b)} \qquad (15)$$

where (a) = $S_{unfilled\ sheet}$ and (b) = $S_{apparent\ filler}$.

The expression:-

$$\frac{(1-L)}{L}(1-\sqrt{\frac{T}{L}})(S_f'-S_f) + \frac{(1-L)}{L}A(1-\frac{T}{L})S_f \qquad (16)$$

gives the overall contribution of filler-fibre interaction to the apparent filler light scattering coefficient.

EXPERIMENTAL DETERMINATION OF A, S_f, S_f' AND S_{filler}

i. Determination of S_f and A:

Fig.2 shows a plot of tensile strength against sheet light scattering coefficient for bleached softwood sulphite pulp, unfilled sheets at different beating levels. The sheets were dried conventionally. The plot is reasonably linear and extrapolates to S_f at zero strength. Table 1 gives the value of S_f and values of A at 650 Csf (unbeaten pulp) and 300 Csf (beaten pulp) derived from the data via equation (3). Table I also gives some data for sheets dried without wet pressing.

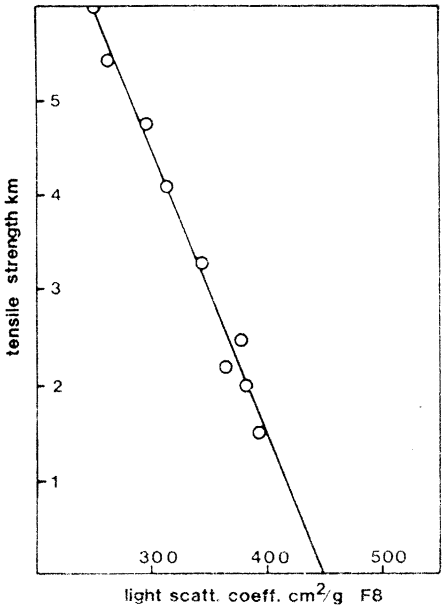


Fig 2—Tensile strength **vs.** light scattering as a function of beating for unfilled sulphite pulp sheets.

TABLE I:

Softwood Sulphite Pulp	
S_f F8 Normal Pressing	450 cm^2/g
S_f F8 Zero Pressing	470 cm^2/g
S_f' F8 Unbeaten 650 Csf	580 cm^2/g
Beaten 300 Csf	940 cm^2/g
Bonded Area Fraction A	
Normal Pressing 300 Csf	0.44
Zero Pressing 300 Csf	0.35
Normal Pressing 650 Csf	0.13

ii. Determination of S_f':

S_f' is dependent on beating and can be obtained by two methods. Firstly the filler may be removed from filled sheets, in which case Equation (13) reduces to:-

$$S_{sheet} = (1-A\frac{T}{T}L)\ S_f + (1-\sqrt{\frac{T}{T}}L)\ (S_f'-S_f) \qquad (17)$$

(N.B.: the sheet now only contains fibre) or secondly unfilled sheets may be dried by removing the water with organic solvents in which case strength should be practically zero and Equation (17) should again apply.

Fig.3 shows plots of tensile strength against light scattering coefficient for beaten and unbeaten softwood sulphite sheets either prepared in the normal way but from which the filler has been removed, or which have been dried from acetone. In the filler removal experiments three fillers were used, a ground marble, a precipitated calcium carbonate and ground cellulose acetate. The calcium carbonate was removed by dissolution by hydrochloric acid in ethanol and the cellulose acetate was removed by dissolution in acetone. The filler dissolution experiments had little effect on sheet strength and this confirms that the acid and evolution of gas does not disrupt the sheet. Further confirmation is provided by the excellent correlation between the cellulose acetate and calcium carbonate filler removal experiments.

Table I gives values of S_f' obtained for the beaten and unbeaten pulp obtained by fitting Equation (17) to the data and extrapolating to zero strength.

iii. Determination of S_{filler}:

The values of S_{filler} are obtained in a very similar way to that of S_f. A series of sheets is made at a fixed loading, L, but with various levels of pulp beating or freeness and a plot similar to that shown in Fig.1 is obtained. Extrapolating the plot to zero strength gives the light scattering coefficient for the sheet of loading L but with no fibre fibrillation or fines and unfilled light scattering coefficient = S_f.

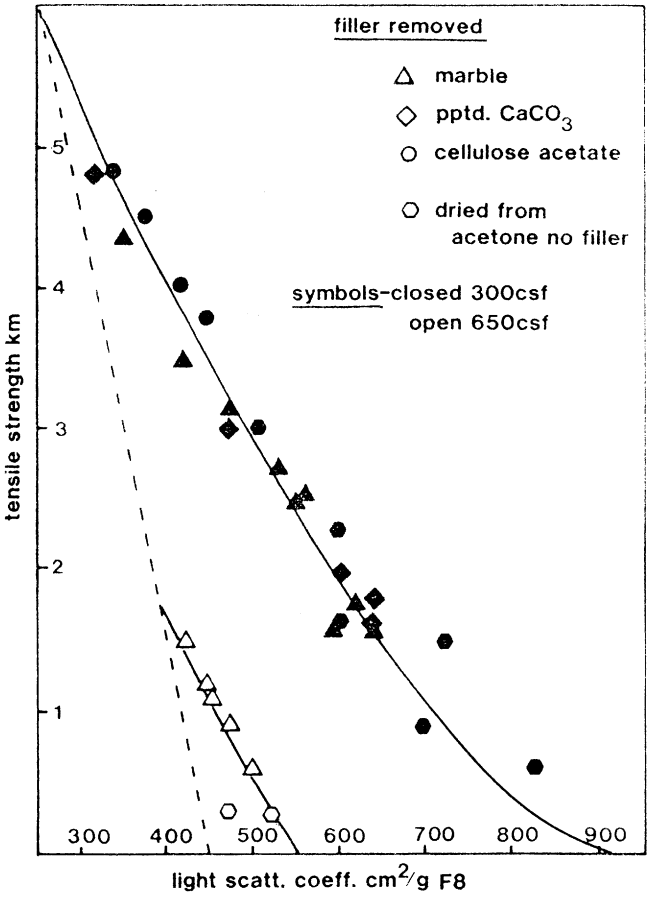


Fig 3—Tensile strength **vs.** light scattering for 'filler removed' unbeaten and beaten sulphite pulp sheets, and unfilled sheets dried from acetone

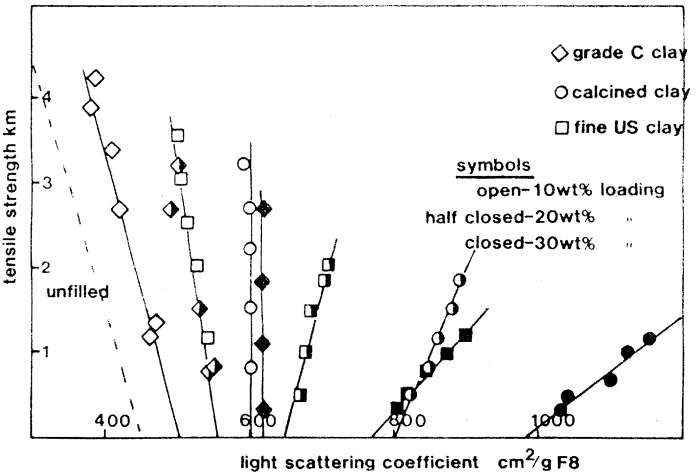


Fig 4—Tensile strength **vs.** light scattering as a function of beating for filled sulphite pulp sheets

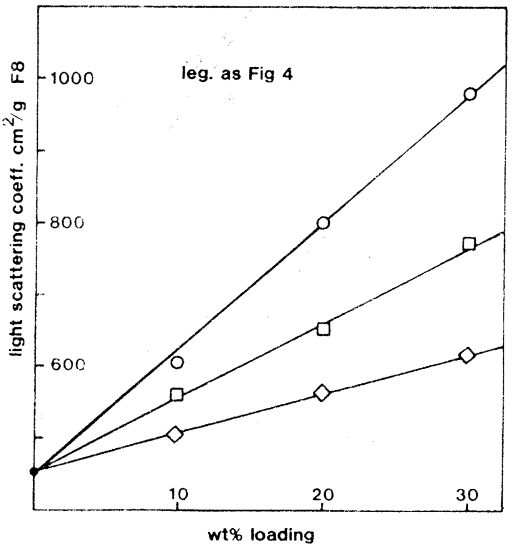


Fig 5—Light scattering **vs.** loading for 'zero strength' totally unbeaten filled sulphite sheets

The process is repeated for different values of L. In this situation Equation (13) reduces to :-

$$S_{sheet} = L\, S_{filler} + (1-L)S_f \qquad (18)$$

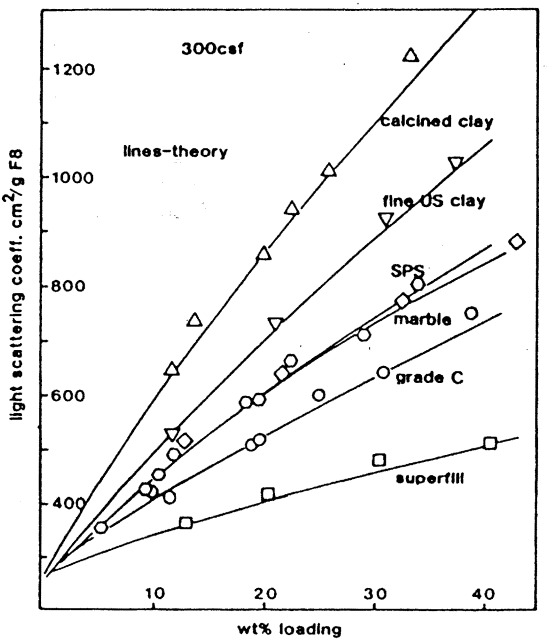
Fig.4 shows a number of such plots giving strength against light scattering coefficient for different fillers at three different loadings and various levels of softwood sulphite pulp freeness.

Fig.5 shows light scattering coefficient data at zero strength obtained from Fig.4 and plotted against loading. Linear relationships are obtained which tends to support the assumption that S_{filler} is independent of fibre conditions, but also shows that S_{filler} is independent of loading and, at least for the fillers shown, optical 'crowding' does not occur. The values obtained for S_{filler} from Fig.5 and for other fillers not shown are given in Table II.

TABLE II

Filler	S_{filler}	Powder Light Scattering Coefficient
	cm^2/g F8	cm^2/g F8
Clays:		
Superfill	600	900 + 50
Grade C	1000	1600
SPS	1300	2100
Fine U.S.	1500	3200
Calcined U.S. Clay	2200	2400
Calcium Carbonates:		
Carbital 90	1200	2000
Precipitated $CaCo_3$	1800	2300 +500

Table II also includes estimates of the dry powder light scattering coefficients.



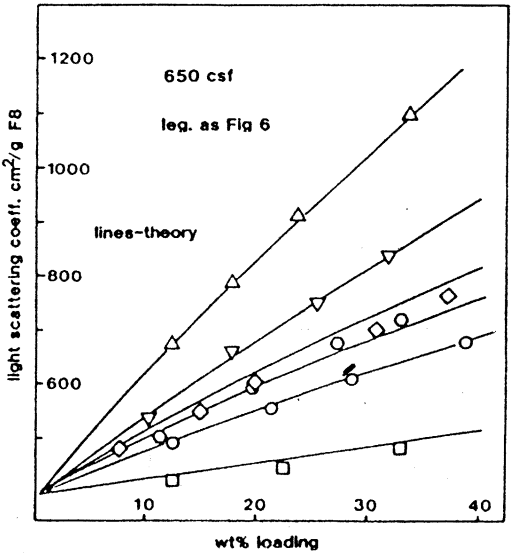


Fig 6 & 7—Light scattering **vs.** loading for beaten and unbeaten filled sulphite sheets respectively. Comparison between theory and experimental data

S_{filler} may also be obtained by controlling forming conditions to give data equivalent to that shown in Fig.5. The method is to dry filled unbeaten sheets form organic solvents and then quickly re-wet the sheets with water and dry by conventional means. This leads to sheets of practically zero strength but with an unfilled sheet light scattering coefficient very close to S_f, so that Equation (18) again applies. This was carried out for two of the fillers used here, Grade C clay and the calcined clay, and the values of S_{filler} obtained were identical to those given in Table II.

GENERAL COMPARISON BETWEEN THEORY AND EXPERIMENTAL DATA:

i. Beaten and Unbeaten Pulp Sheets:

Figs 6 & 7 show light scattering coefficient plotted against filler loading for several fillers in beaten and unbeaten softwood sulphite pulp respectively.

The lines drawn through the experimental points are obtained from Equation (13) using the coefficients given in Tables I & II and the experimental tensile strength data. The agreement is good, but this is to be expected to a certain extent as both S_f and S_{filler} are obtained from the experimental data. S_f' is, however, obtained from somewhat different data (e.g. sheets from which filler has been removed). Therefore, the fact that agreement is obtained between theory and experimental data for the beaten sheets confirms that, for this pulp system at least, S_{filler} is independent of beating conditions. If, for example, the interaction between filler and fibrillation, etc. led to increased optical contact between pulp and filler, then S_{filler} would be expected to decrease with increasing beating and amount of fibrillation. In this case the theory, which assumes constant S_{filler}, would have overestimated the light scattering coefficient for beaten sheets.

The theory in fact slightly underestimates the light scattering coefficient of beaten sheets at high loading and overestimates the light scattering coefficient of unbeaten sheets. This may, however, be a consequence of the very approximate relationships assumed between strength and bonded area.

Interestingly the area of fibre influenced by filler, x, is found to be approximately independent of beating or pulp freeness and is dependent only on filler type and loading. This probably is to be expected as the area of fibre surface (as given by the total bonded and non-bonded conventionally dried pulp surface area) is independent of beating. However, the fact that x is observed to be independent of beating supports the rather crude statistical relationship assumed between tensile strength and x.

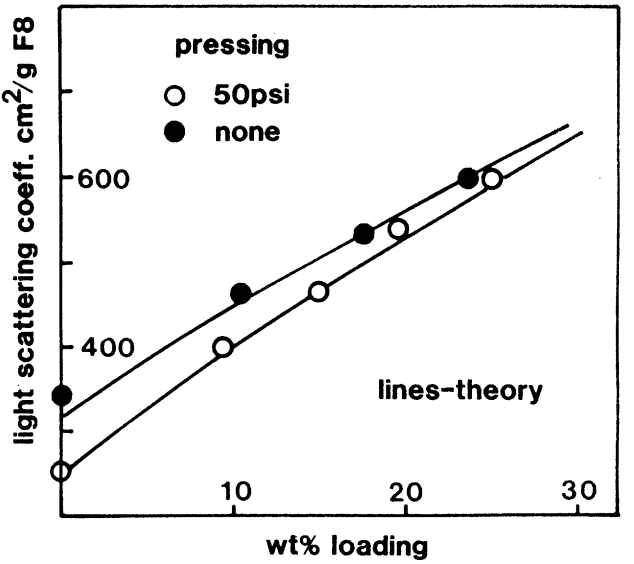


Fig 8—Effect of wet pressing. Beaten sulphite pulp with grade C clay filler. Comparison between theory and experimental data

ii. Effect of Wet Pressing Conditions:

Sheets prepared by conventional drying but without wet pressing, have higher light scattering coefficients and lower strength than sheets pressed at say 50 psi. Providing freeness remains constant the only differences expected are a small change in S_f (caused by factors such as changes in lumen collapse) and a change in bonded area. This is reflected by the tensile strength. S_f' and S_{filler} should both remain constant.

Fig.8 shows a comparison between experimental light scattering coefficient and calculated light scattering coefficient plotted against filler loading for Grade C clay filler in beaten softwood sulphite sheets dried without wet pressing or pressed at 50 psi. Again Equation (13) was used with data from Tables I & II and the experimental strength data. Agreement between theory and experiment is reasonable.

iii. Effect of Filler Aggregation:

It is well known (15) that flocculating or aggregating the filler with organic polymers improves sheet strength, but it also reduces sheet light scattering coefficient. This is often assumed to be due to a loss of filler light scattering. Aggregating the filler concentrates the filler in certain areas of the fibre surface and effectively reduces the value of x and this is seen in the increase in tensile strength.

Fig.9 shows light scattering coefficient plotted against loading for Grade C clay either non-aggregated or aggregated, with 0.1 wt. % of a typical polyacrylamide flocculant, in a beaten softwood sulphite furnish. Also shown is the calculated light scattering coefficient which allows for the change in tensile strength for the sheets containing aggregated filler, but which assumes that S_{filler} is unchanged. The theory used in this way slightly over-estimates the light scattering coefficient especially at high loadings. This demonstrates that any loss in filler light scattering coefficient caused by polymer aggregation is in fact quite small.

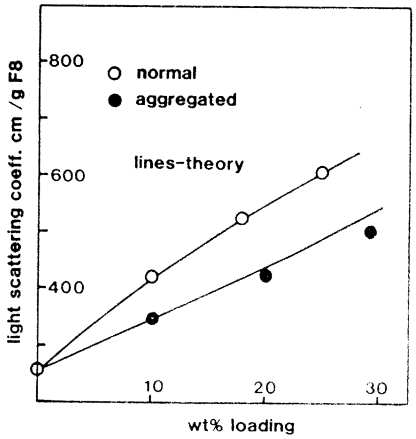


Fig 9—Effect of filler aggregation. Beaten sulphite pulp with grade C clay filler (aggregation carried out with 0.1 w% cationic PAA). Comparison between theory and experimental data

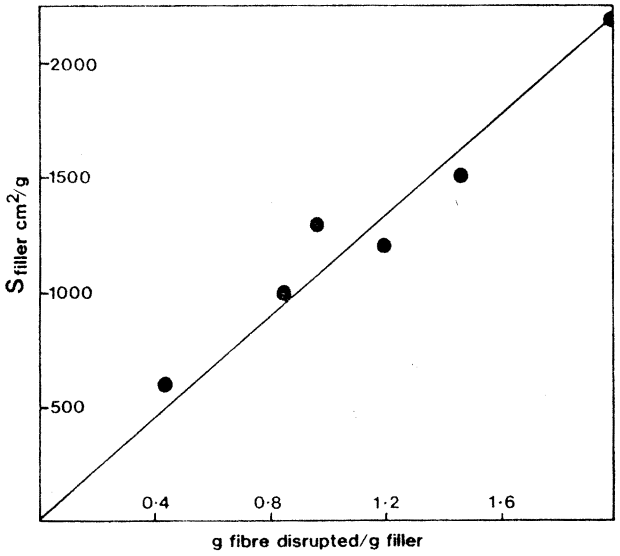


Fig 10—Relationship between S_{filler} and fibre disruption for filler shown in Table II

This is supported by the fact that this form of aggregation does not reduce the dry powder light scattering coefficient of the filler, and that S.E.M examination of the aggregated filler in a sheet shows no visual difference from normal filler except more evidence of concentration in certain areas of the sheet.

iv. The Effect of Filler Type:

The fillers discussed so far show a consistent trend in that S_{filler} increases almost linearly with increase in the effect of the filler on sheet strength.

This is shown in Fig.10 where S_{filler} is plotted against the area of fibre influenced by filler per gm of filler at a fixed sheet strength. This relationship applies to most conventional filler materials, and follows intuitively from the fact that the fillers all have similar refractive indices, and the physical properties required to give good light scattering properties such as fine particle size invariably lead to a large effect on the sheet strength.

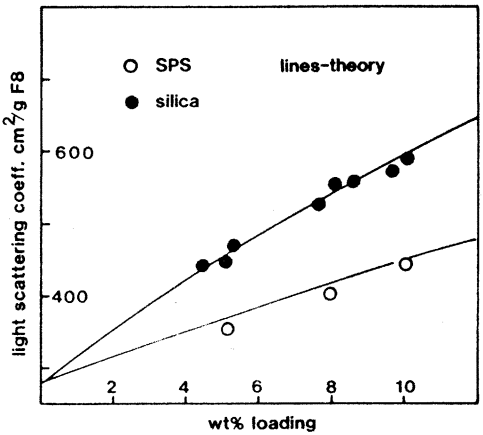


Fig 11—Light scattering **vs.** loading for beaten sulphite sheets filled with SPS clay and silica. Comparison between theory and experimental data

The relationship, however, breaks down for fillers with fine particle, or for aggregated fillers with fine primary particle size, because the effect on sheet strength continues to increase as the particles become finer but the light scattering coefficient passes through a maximum. Fig.11 shows an example of this behaviour

Sheet light scattering coefficient is plotted against filler loading for SPS clay and silica. S_{filler} is similar for both these fillers (S_{filler} for the silica is in fact 1200 cm^2/g) but the silica has far greater effect on sheet strength. Calculated lines are again shown using the sheet strength data and the data given in Tables I & II, and a reasonable fit is obtained. It is interesting to note that the apparent decrease in the contribution of silica to the sheet light scattering coefficient as loading increases is in fact due to the effect of filler on sheet strength rather than any optical 'crowding' effect of the silica particles.

Certain fillers, particularly titanium dioxide, have high refractive indices and for these fillers optical 'crowding' is important. This can only be accounted for in the present theory by assuming a dependence of S_{filler} on loading.

v. The Effect on Pulp Type:

All the work discussed above was carried out using a bleached sulphite pulp. Other systems have not been studied in detail and it could well be that the relationships shown in Equations (3) & (4) do not apply to many pulp systems, and that S_{filler} is no longer independent of fibre preparation.

Fig.12, however, shows light scattering coefficient plotted against loading for Grade C and calcined clay fillers in two beaten hardwood sulphate pulps and a softwood groundwood pulp. For these pulp systems the values of S_{filler} estimated in the manner described above are the same as those given in Table II. Values of S_f' S_f' & A were also estimated from unfilled sheets dried conventionally and by removing the water with organic

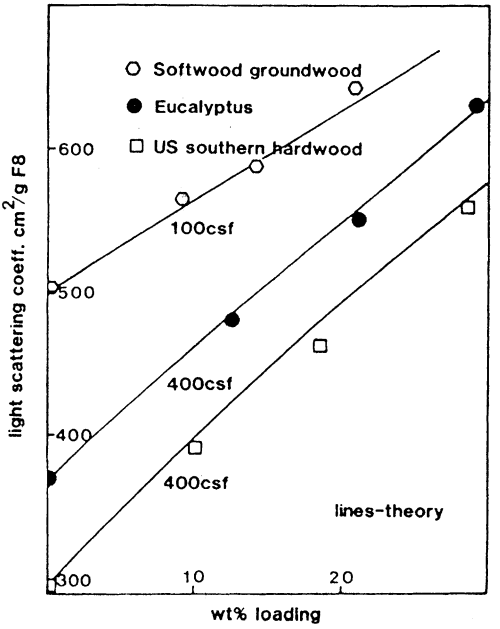


Fig 12—Light scattering **vs.** loading for various pulps filled with grade C clay. Comparison between theory and experimental data

solvents. These values are shown in Table III. Theoretical predictions were made using this data, the values of S_{filler} given in Table II, experimental strength data and Equation (13). The fit between theory and experiment is reasonable.

TABLE III.

	S_f	S_f'	A
	cm^2/g F8	cm^2/g F8	
Southern U.S. Hardwood 400 Csf	380	580	0.22
Brazillian Eucalyptus 400 Csf	460	660	0.2
Flash Dried Groundwood 100 Csf	∿ 520	580	∿ 0.04

CONCLUSION

The optical and strength properties of paper are very important, but the relationship between them, especially for filled paper, is often ignored. Davidson showed that a significant proportion of the contribution that the filler makes to the sheet light scattering coefficient is in fact due to the effect that the filler has on light scattering coefficient of the fibre. In this work it has been shown that this effect of filler on fibre is strongly dependent on sheet strength. This means that fillers which greatly reduce sheet strength often appear to give good sheet light scattering coefficients, and conversely fillers which give a good sheet light scattering coefficient (without the benefit of high refractive index) normally have very detrimental effects on sheet strength.

It has also been shown that the extent of fibre fibrillation and the presence of fines (10μm) may also be important, as the filler may prevent a certain amount of fines and fibrillation collapse onto the fibres during sheet drying and this is easily seen by 'removing' the filler. The extent of prevention may again be related to the effect that the filler has on sheet strength. The fines and fibrillation scatter light so that any prevention of collapse would enhance the sheet light scattering coefficient. Thus well beaten pulps generally show greater increases in light scattering coefficient with increasing loading than poorly beaten pulps.

In general the interaction between filler and fibre can contribute as much as 40% of the apparent light scattering coefficient normally attributed to filler in a well beaten pulp system, and practically nothing at all in an unbeaten pulp system.

The actual light scattering coefficient of the filler in the sheet is between 90% and 60% of the light scattering coefficient of the filler as a free powder and the variation reflects the effect of filler structure on the degree of filler fibre optical contact.

A simple expression has been derived here in an attempt to quantify the relationship between sheet light scattering coefficient and strength. The expression, as well as allowing the extent of interaction between filler and fibre to be estimated, also allows an indication of the mechanism of the effects of processes such as wet pressing and filler aggregation on the light scattering coefficient of filled sheets. It is shown for example that simple aggregation of the filler does not in fact reduce the filler light scattering coefficient, but merely reduces the effect that the filler has on the fibre and thus increases sheet strength and decreases the light scattering coefficient. The expression appears to apply well to softwood pulp systems, and, as far as the limited data allows, may apply to other systems.

Obviously the quantitative expression is limited to processes which are known to effect strength and light scattering coefficient. Calendering is one typical example of a process which has far more effect on light scattering coefficient than on strength. Calendering appears to create optical contact in the sheet without creating bonding contact and therefore its effects are not explained by the theories used here. There are probably more examples of such processes, but the intention here was to provide a mechanistic model of filler-fibre interaction rather than an all embracing theory.

The work described is based mainly on laboratory experiments with a bleached sulphite pulp system, but it would be interesting to study other pulp systems in more detail in the hope that physical treatments of the pulp can be identified which provide the optimum combination of strength and light scattering coefficient in the presence of a filler.

A P P E N D I X

Experimental Details:

All the sheets were prepared using a standard sheet former. The pulps were beaten using a laboratory scale Hollander beater. A retention aid, Percol 292, was used throughout at dose levels sufficient to give at least 60% filler retention, but no other chemical additions were made.

The sheets were pressed and dried, except where stated, with a total of seven minutes pressing at 50 psi followed by air drying at 23^{o}C and 50% relative humidity.

Organically dried sheets were prepared by removing the water, after formation but before pressing, by repeatedly draining ethanol or acetone through the sheets.

Filler removal experiments using acid to remove calcium carbonate were carried out using 20mls of 15% hydrochloric acid dissolved in 500 mls of ethanol. The sheets were left in the acid for at least 1 hour and then washed carefully in ethanol. Filler removal using acetone to remove cellulose acetate was carried out using a Soxhlet apparatus.

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Transcription of Discussion

SESSION 4 FILLERS

Chairman B. Radvan

The Relationship between Strength and Light Scattering Co-efficient for Filled Papers

by R. Bown

Prof K.J. Ebeling Helsinki University of Technology, Finland

Two questions; first, have you carried out similar studies for other fibre types besides the bleached sulphite which was described here? Would you expect similar fibrillar contribution if you used mechanical pulp?

What type of mechanical pulp - according to you - would be most effective?

Dr. R. Bown The work we have done with other pulps is very limited. What I suspect will happen is that the S_{filler} terms that we use will be slightly different because we are accounting for the physical contact between the filler and the pulp. This may not be the same for all pulps. From our limited work, it would not appear to be too different.

Ebeling The second question; did I understand correctly one of your conclusions that the agglomeration of the filler particles does not have an effect on the optical activity of the filler? In other words, whether or not you use retention aids, the optical efficiency of the filler is the same?

Bown Yes, if anything, you change the strength of that system and you change the position of the filler. One thing that I must emphasise, is that we have assumed that the filler doesn't move. If we have a system in which the

retention aid is not very efficient, say a magazine type paper with high drainage rates, then the filler may not end up in a random manner in the sheet; it may concentrate in some areas. This will change the effect it has on the scattering of the pulp system which must be taken into account.

Ebeling Practical experience with magazine papers containing mechanical pulps shows that the optical activity of the filler would change. I do not know if this is due to fines. For a well dispersed system, you have better opacity, than if you have a heavily flocculated filler system.

Bown In that system, you are probably measuring the scattering co-efficient on a highly calendered paper, which tends to reduce the scattering of the filler, and most of the differences you see are due to changes in the scattering coefficient of the pulp.

Prof J. Silvy Ecole Francaise Papeteries, Cedex, France

One other problem for the extrapolation in the relation between tensile strength and scattering co-efficient, is the conditioning of the fibres in tension during drying. This must change the value of the extrapolation. If you displace the links between fibres with fillers, the tensile strength is lower. This effect, like pressing or beating, modifies the value of tensile strength. In this case, when you increase the percentage of fillers, you have an effect on fibre tensile strength with respect to sheet conditioning. Is this so?

Bown This may be the case. All these cases are refinements to my basic approach. I am not attempting to say that in this case we have a rigorous approach. This bonding effect is not really one of the major contributions to the scattering co-efficient. The changes you are proposing, may well be right, but will not change the conclusions we have drawn from the way the filler works in the system. What it might do, is slightly change the results we get.

Prof W. Scott Miami University, Oxford, U.S.A.

I would like to comment on the aggregation aspects. We have looked at a wide range of carbonate fillers that were differentiated by morphology, from rhombohedral particles looking like titanium dioxide to scalenohedral and aragonite crystals that were very irregular in shape. I think we found something that supports your findings, i.e. when we had the rhombohedral, spherically shaped particles, there was a very strong effect of aggregation on scattering factor with increased loading. With the aragonites and scalenohedral particles, which are more rosette or irregularly shaped, we could load to very high levels with essentially no effect on filler scattering.

Bown The data shown was in fact with a clay filler which gives a loosely packed structure when flocculated. Obviously, if you are using blocky pigments, you may start to greatly increase pigment contact areas.