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# SOME OPTICAL CONSEQUENCES OF THE CONSOLIDATION OF PAPER

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**Synopsis**—The Kubelka-Munk equations are presented and some consequences of these regarding the influence of brightness, formation and optical bleaching agents on opacity are discussed. The main part of the paper deals with the light scattering properties of paper and the influence on the opacity of such different variables as fibre dimensions, pulping and bleaching processes, pulp drying, beating, fibre orientation, pressing and drying on the papermachine. It is shown how intimately opacity is affected by the degree of fibre-to-fibre bonding within the sheet.

## Introduction

PAPER absorbs, reflects and transmits light. Optical properties of paper of practical interest are brightness, colour, opacity, transparency and gloss. Of these, opacity and transparency—and, to some extent, brightness and colour—are influenced by the consolidation of the paper. In the following, particular stress will be laid upon opacity and it will be analysed in what way this property depends upon fibre dimensions and the density of the paper as influenced by pulping processes, beating and papermachine operation. Initially, some mathematical relationships among opacity, brightness and other optical properties will be summarised. Gloss will not be treated, but reference is made to Harrison's monograph of 1945<sup>(1)</sup> and his paper at the Oxford symposium.

#### Definitions and equations

KUBELKA and MUNK in 1931 derived the classical analysis of light distribution in a diffusing medium and Steele<sup>(2)</sup> showed that their equations can be usefully applied to paper. The application of the Kubelka-Munk theory to the scattering and absorption of light in paper has been further studied among others by Van den Akker<sup>(3)</sup> and Stenius.<sup>(4)</sup>

The following terms and symbols will be used—

R = reflectance, which is the ratio of the reflected light of the sheet under any specified set of irradiating and receiving conditions to the reflected light of a perfect diffuser under the same conditions. In most practical work, the perfect diffuser is replaced by a smoked magnesium oxide standard, which is given the reflectivity of 100.0 per cent. The ratio R is usually expressed as a decimal fraction in the absolute system and as a percentage in the system based on magnesium oxide. As magnesium oxide has the reflectivity 0.97 in the absolute system, the ratio of any corresponding R values for the two systems is 0.0097.

- $R_{\infty} = reflectivity$ , which is the reflectance of a pad of sheets thick enough to be opaque. For pulp and paper, the reflectivity is called *brightness* if determined at a specified wavelength (457 m $\mu$ ).
- $R_0 = reflectance$  of a single sheet backed by a perfect black.
- s = a general coefficient indicating the degree of light scattering and referred to as the *specific scattering coefficient*.
- k = a general coefficient indicating the degree of light absorption and referred to as the *specific absorption coefficient*.
- W = the substance of the sheet.

The Kubelka-Munk equations can be written in the following forms-

$$R_{\infty} = 1 - \frac{k}{s} - \sqrt{\frac{k^2}{s^2} + 2\frac{k}{s}} \qquad . \qquad . \qquad (1)$$

$$R_{0} = \frac{\mathrm{e}^{sW\left(\frac{1}{R_{\infty}} - R_{\infty}\right)} - 1}{\frac{1}{R_{\infty}} \cdot \mathrm{e}^{sW\left(\frac{1}{R_{\infty}} - R_{\infty}\right)} - R_{\infty}} \qquad (2)$$

In equation (2), s and W do not appear as separate variables, but rather together as the product sW. This parameter has proved to be an important term and is called the *scattering power*.

If W is given in  $g/cm^2$ , the numerical value of s will be in the range 100–700 for different types of paper, excluding translucent papers. In earlier literature, the symbol S' was used for the specific scattering coefficient. The numerical value of k ranges 1–5 for white papers to 400 for kraft papers.

For a paper composed of different constituents (1, 2...), the scattering power can be calculated as follows—

$$sW = s_1W_1 + s_2W_2 + \dots$$

The opacity of papers is expressed in two ways—as *contrast ratio* or *printing opacity*.

TAPPI contrast ratio = 
$$C_{0.89} = \frac{R_0}{R_{0.89}} = \frac{R_0}{R_{91.5}}$$
  
Printing opacity =  $\frac{R_0}{R_{\infty}}$ 

When measuring the TAPPI contrast ratio, the sheet is backed by a perfect black and by a white body having the reflectivity 0.89 in the absolute system, 91.5 in the system based on magnesium oxide. This measurement requires a specially designed apparatus, the Bausch and Lomb opacimeter being the



Fig. 1—Graph to show the dependence of the reflectivity  $(R_{\infty})$ and the printing opacity  $(R_0/R_{\infty})$  on the scattering (s) and absorption (k) coefficients, according to Stenius<sup>(8)</sup>

most commonly used. With this instrument, the ratio between  $R_0$  and  $R_{0.89}$  is given directly and the determination is thus simple and rapid.

The printing opacity predicts the actual show-through of the paper. It can be measured on any type of brightness tester. It grades low brightness papers in a narrower range than does the contrast ratio. A standardised procedure for measuring the printing opacity of paper is given in SCAN P8.<sup>(5)</sup>

From the Kubelka-Munk equations, it is evident that a mathematical relationship exists between the absorption and scattering coefficients and brightness, opacity and the scattering power. As calculations based on the Kubelka-Munk equations are tedious, such relationships have been given in diagrams. TAPPI Data Sheet T 425 includes  $R_0$ ,  $R_\infty$ , sW and contrast ratio; the diagram by Campbell & Benny<sup>(6)</sup> and by Giertz<sup>(7)</sup> uses  $R_\infty$ , sW and printing opacity, that by Stenius<sup>(8)</sup> s, k,  $R_\infty$  and printing opacity. The latter is reproduced in Fig. 1. All these diagrams cover values only within the commonly used limits. A complete table of corresponding values for  $R_\infty$ ,  $R_0$  and sW has recently been calculated and listed by Koller & Chapman.<sup>(9)</sup>

#### Consequences of the Kubelka-Munk equations

FROM the Kubelka-Munk equations, the following conclusions of general interest can be drawn with reference to Fig. 1—

1. The brightness of paper, equation (1), depends not only on the absorption, but also on the scattering coefficient. As shown by equations (1) and (3), the ratio k/s determines the brightness, consequently the iso-brightness lines of Fig. 1 are straight. Thus, all papermaking operations that lower the scattering coefficient of the paper such as beating, pressing and calendering (moving horizontally to the left in Fig. 1) will automatically decrease the brightness, although the k value does not change. In the same way, the colour of a paper shows up more intensively as the paper becomes denser.

2. At constant scattering coefficient, changes in the absorption coefficient (moving vertically in Fig. 1) will influence opacity. For instance, in bleaching, paper becomes less opaque and, if a pulp is bleached to a higher brightness than usual, the opacity of the paper will decrease. This can sometimes be an actual disadvantage in bleaching to very high brightness with, for example, chlorine dioxide. The opposite effect takes place when dyes are added to the furnish;<sup>(21)</sup> the opacity of, for instance, airmail papers and newsprint are increased in this manner.

3. For an equal change in substance, opacity is more affected by a fall than by a rise in substance. Here, reference is made to diagrams<sup>(6,7)</sup> or a table<sup>(9)</sup> in the literature. This fact has bearing on sheet formation, the consequence being that bad formation involves lower opacity then good formation when the comparison is made at the same sheet substance and brightness. This has been demonstrated experimentally for newsprint by Antonsen & Lorås.<sup>(10)</sup>

4. The addition of optical bleaching agents lowers the opacity.<sup>(21)</sup> With printing opacity, for instance, both  $R_0$  and  $R_{\infty}$  will increase by the addition

in reflectance as a consequence of the fluorescence in ultra-violet light, if present:  $R_{\infty}$  will increase somewhat more than  $R_0$  and this will influence the ratio  $R_0/R_{\infty}$  towards lower values.

#### Light scattering

THE absorption and scattering coefficients are the two basic parameters controlling the brightness and opacity of paper. Of these, the absorption coefficient is of secondary interest, because it is controlled by the cooking process, the degree of bleaching and brightness reversion; during the papermaking operations, it is influenced only by the addition of dyes, clay, dirt and soluble impurities such as iron compounds. The scattering coefficient, however, is influenced by the fibre raw material, the pulping conditions and most of the papermaking operations, all variables that are varied primarily in order to change certain properties of the paper other than opacity. The following study will therefore deal mainly with factors that affect the paper's scattering coefficient.



Fig. 2—Light scattering by repeated macro-optical reflection and refraction in a layer of transparent particles of irregular form

In an optically heterogeneous body such as snow and to a first approximation paper, too, the light refracting surfaces can be considered to lie in all directions. Incoming light, even if oriented, will therefore strike the various surface elements at all possible angles and will scatter diffusely inside the body. As illustrated schematically in Fig. 2, the incoming light is divided at each optical surface so that a minor portion (about 5 per cent) is reflected, whereas the major portion is refracted and penetrates deeper into the

particle. When the ray approaches the opposite side of the particle, it will, depending on the approach angle, either be totally reflected or again be divided so that a smaller portion is reflected, whereas the major portion is again refracted and penetrates further. The same process is repeated in each particle or optical surface that is struck by the light ray. After repeated reflection and refraction, one part of the penetrating light will return to the original surface and leave the body, whereas the other part will pass through the entire body and leave it on the opposite side. In addition, some light will leave the body through the side surfaces, but this latter light can be neglected when it concerns bodies of large area such as paper. The more optically refracting surfaces present inside the body, the easier it is for the incoming light to be refracted toward the original surface and the less will be the light reaching the opposite side and leaving as transmitted light.

In this way, the light scattering caused by repeated macro-optical reflection and refraction is explained. To this must be added the extra effect that is caused by true light scattering on a microscopic scale from very small bodies of the same magnitude as the light wave.

The amount of light reflected, refracted and scattered by paper is determined by the number, size and shape of the individual constituents of the paper, by the indices of refraction of these constituents and the amount of optical contact between them and by the wavelength of the light.

The proportion of light reflected at each boundary is larger the greater the difference between the refractive indices of the two materials. This explains the opacifying effect of filler materials of high refractive index such as titanium dioxide (n=2.76 for rutile and 2.55 for anatase) and zinc sulphide (2.37).

As calculated by Giertz,<sup>(11)</sup> the refractive index is higher for crystalline cellulose than for amorphous hemicellulose, resulting in a difference in the scattering coefficient of about 10 per cent. Differences that are due to the chemical composition of the cellulose material or the formation of oxycellulose are of negligible importance.

Owing to the orientation of the microfibrils, the refractive index of the native cellulose fibre is higher in its length than in its cross-direction. For cotton fibre, the refractive indices have been determined as 1.59 and 1.53, respectively. Fibre orientation will therefore make the paper anisotropic also optically and this anisotropy shows up both in brightness and opacity, if the paper is illuminated with oriented light. An example of a paper with typical fibre orientation is given in Table 1.

The large differences in opacity between various types of papers are first of all caused by differences in the amount of optically refracting surfaces and light scattering particles. It seems to be the general opinion that paper opacity is dependent only on light scattering caused by the outer surfaces of

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Direction	Breaking length, m	Ratio MD/CD	Brightness (Hunter), per cent	Printing opacity, per cent	Specific scattering coefficient, s
Machine (MD)	5 700	2.6	65.3	67.2	235
Cross (CD)	2 100		67.7	69.8	245

TABLE 1-OPTICAL ANISOTROPY OF MACHINE-MADE PAPER

the fibre. The form and dimensions of the fibres, the structure of the external surface and the amount of fibre-to-fibre bonding should therefore most closely influence the opacity. To this, the lumen surface of uncollapsed fibres should also be added. Finally, it has been argued<sup>(11)</sup> that capillaries and discontinuities inside the fibre wall might exist, partly arising from the dissolution of hemicellulose and lignin and partly from shrinkage cracking during drying and that these capillaries might be of such size that they will scatter the light. This question will be further dealt with in the following.

#### Fibre dimensions

WHEN dealing with light scattering units of small size in the paper such as filler particles, free fibrils (as in Fig. 7) and capillaries in the fibre wall, it should be noted that the scattering of light increases with decreasing dimensions, an optimum being passed when the dimension is about half the wavelength of the light, after which the scattering effect ceases rapidly. Opacity should therefore be measured in light of defined spectral composition, green light being recommended. Furthermore, the opacifying action of added dyestuffs will be greater for blue dyes than for yellow and red dyes.

A survey of dimensions and morphology of both woodpulp fibres and other papermaking fibres was given at the Cambridge symposium.<sup>(12)</sup>

It is difficult to characterise a fibre in such a way that it gives correct information about its opacifying properties. Fibre length and fibre width is of no meaning. For fibres of the same length, the number of fibres per 1 g could be a value of interest. Recently, more and more attention has been paid to the decigrex number, which gives the weight in mg of a total fibre length of 100 m. Thus, the decigrex number gives information about the average amount of material in the cross-area of the fibre and, if combined with the fibre width, an indication of the tendency to collapse by drying. Some examples are given in Table 2. Because of the different and unknown amounts of interfibre bonding, it is difficult to correlate fibre dimensions with paper opacity. Generally speaking, however, pulps with high decigrex number are known to form opaque sheets (see Fig. 5).

When dealing with the same kind of raw material, the yield after cooking and bleaching will be a factor of importance for fibre thickness. The lower

Pulp- wood	Decigrex number, mg/100 m	Number of fibres, 10 <sup>6</sup> /g	At 1 000 rev. PFI			Specific
			Breaking length, km	Density, g/cm <sup>3</sup>	Specific scattering coefficient, s	coefficient at 8 km breaking length
Spruce Aspen Birch Beech	20.0 8.5 10.0 9.0	3.1 20.8 11.5 11.7	8.3 7.3 4.9 5.4	0.73 0.82 0.71 0.63	230 265 365 364	240 250 255 290

TABLE 2—FIBRE DIMENSIONS AND LIGHT SCATTERING PROPERTIES FOR BLEACHED SULPHATE PULPS FROM SOME DIFFERENT WOODS

the yield, the lower the decigrex number and the higher the number of fibres in a sheet of given substance.<sup>(13)</sup> Lower yield therefore always means higher opacity. If, however, the comparison is made for the same number of fibres



Fig. 3—Scattering coefficient at 10 000 m breaking length plotted against bleached yield of acid sulphite (○) and two-stage sulphite (×) pulps prepared from the same spruce wood: comparison is made both for actual values (——) and after correction to the same number of fibres (---), a pulp with 50 per cent yield being used as a basis of comparison<sup>(13)</sup>



- Si Conventional acid sulphite; 47, 48 per cent yield
- Bi Bisulphite at pH 4; 49, 51, 55 per cent yield

2-S  $\triangle$  Two-stage sulphite;

- 51, 52, 53, 54, 55 per cent yield Sa O Conventional sulphate;
  - 46, 48 per cent yield

**Fig. 4**—Relationship between the scattering coefficient (s) and the breaking length of different types of bleached pulp prepared from the same spruce wood, the pulps having been beaten in the PEI mill

and at the same tensile strength, indicating that the degree of bonding is more or less the same, the opacity of sulphite pulps, for instance, is constant in the yield range 48-56 per cent (Fig. 3). There seems to be an extra increase in opacity for low-yield pulps that might indicate that light scattering spaces are formed inside the fibre wall as a result of far-reaching hemicellulose dissolution.

For groundwood, Parsons<sup>(14)</sup> has shown that the opacity depends directly on the fineness of the groundwood and that there exists a close relationship between the specific surface area of the pulp and the specific scattering coefficient.

#### Fibre-to-fibre bonding

THE formation of interfibre bonds and the influence of the degree of bonding on the structure and mechanical properties of paper was a main subject at the Oxford symposium and is so now. It is obvious that mechanical interfibre contact also means optical contact—whether the opposite also holds is still under discussion—and so the formation of bonds between fibres must necessarily involve a decrease of free fibre surface area and lower opacity. Formation of bonds at the same time affects the density of the paper and is the controlling factor when increasing the tensile strength of paper. Consequently, a close relationship must exist between opacity on the one hand and properties like density, modulus of elasticity<sup>(15)</sup> and breaking length on the other. As for most types of papers a certain amount of bonding is needed in order to obtain the required strength, comparison at equal breaking length would seem to be a sound and simple way of comparing different pulps for opacity. In the following, comparison will be made on this basis.

A comparison of different kinds of sulphite pulp is shown in Fig. 4. The pulps have been prepared from the same lot of spruce wood, but in different yields; the cooking processes used include conventional acid cooking, bisulphite cooking and two-stage cooking. An ordinary kraft cook is also included. Within each type of pulp, a straightline relationship exists between scattering coefficient and tensile strength. The different pulp qualities, however, grade themselves in certain groups, partly because of different yield as already mentioned. The kraft pulp is the most opaque and, among the sulphites, the bisulphite pulp is more opaque than the conventional sulphites. The two-stage pulps have the lowest opacity. The explanation for these differences has not been given, but it can be added that properties like density and tearing strength grade the pulps in the same order—thus, fibre strength and disposition to collapse might be contributing factors.

It is a common opinion that strong sulphite pulps, because of their high hemicellulose content, are less opaque than soft pulps. This is true, if the comparison is made among unbeaten pulps or after a certain beating time or at a given freeness. Beaten to the same tensile strength, however, the opacity is the same. The use of soft pulps for opaque papers is therefore only of special value, if the purpose of beating is to improve formation and not to increase the strength.

Further information about the influence of sulphite cooking on the opacifying properties of the pulp is given elsewhere.<sup>(16)</sup>

Bleached kraft pulps are produced within a very narrow yield range, the level of which depends on the wood raw material. At lower yield, the opacity is somewhat higher, but such differences seem to be the result of the greater number of fibres.<sup>(17)</sup> According to Ratliff<sup>(18)</sup> and Giertz,<sup>(17)</sup> there are no variables in the kraft cook influencing the opacifying properties of the pulp specifically.

During bleaching, the chemical reactions do not influence the cellulose material in such a way that its light scattering properties are changed.<sup>(19)</sup> At a given brightness, the specific scattering coefficient of the bleached pulp is the same regardless of the bleaching method. If the opacity is expressed as contrast ratio or printing opacity, lower values are obtained for the bleached pulp than for the unbleached: the higher the brightness, the lower the opacity. As emphasised earlier, this is a direct consequence of the decrease in the absorption coefficient.

If the bleaching involves an attack on the fibres, this can result in the paper becoming denser at a given breaking length, therefore less opaque, too. Chlorine dioxide-bleached pulps can therefore have a higher scattering coefficient than pulps bleached with hypochlorite. This is seen to be particularly the case for sulphate pulps.<sup>(19)</sup>

It should be added that, if a hot alkali extraction stage is included in the bleaching sequence, a pronounced dissolution of hemicelluloses takes place; as a consequence, the opacity increases.

As is well known, drying makes the pulp more opaque. As was stressed when dealing with soft sulphite pulps, this statement is correct only when comparing unbeaten pulps or pulps beaten in the same way. If the comparison is made after beating to a certain breaking length, however, the opacity of the dried pulp is somewhat lower than that of the slush pulp.<sup>(20)</sup>

Because of the formation of fibre fragments, fibrils and crill during beating, it could be expected that the new surfaces formed should increase the opacity. As a matter of fact, this is the case when beating very soft pulps with low hemicellulose content—such as overcooked aspen or beech sulphite pulps, cold alkali-treated dissolving pulps and purified cotton linters (Fig. 5) —or when the sheet is formed from an organic solvent such as butanol.<sup>(18)</sup> Ordinary papermaking pulps after beating, however, form a denser sheet



*Fig.* 5—Influence of beating on opacity (s): bleached commercial pulps beaten in the PFI mill and results plotted both against beating time and breaking length

with increased amount of bonding and so opacity will decrease with beating. In Fig. 5 some examples are given for different types of pulps. The amount of beating (in the PFI mill) is given on a logarithmic scale and, in this way, the decrease in scattering power follows a straight line in the same way as many other such properties of the paper as breaking length, bursting strength and density. In the same graph, the scattering coefficients of the same pulps



Fig. 6—Relationship between scattering coefficient (s) and breaking length as influenced by beating (---) and pressing (---): bleached sulphate pulp beaten in the PFI mill 500 (○), 2 000 (▽), 8 000 (△), and 16 000 (□) revolutions and, in the second pressing operation, the pressure kept at 2.5, 5, 7, 7.5, 10, 25, and 50 kgf/cm<sup>2</sup>, respectively

have been plotted against breaking length, from which can be seen that pulps of the same type are now grouped together and that the differences are due primarily to pulping process and fibre dimensions.

Pressing consolidates the sheet and will consequently decrease the opacity. At the same time, the sheet becomes stronger, but it is of interest to note that, for a certain increase in breaking length, pressing at high pressure is attended by a more marked fall in opacity than beating to the same level (see Fig. 6). In order to obtain an optimum combination of high strength and high opacity, the sheet should therefore not be pressed at high pressure. The full explanation of this well-known fact has not been given. Increased collapse because of the higher pressures could be a contributing factor.

When dried on the papermachine, the sheet tends to shrink and the amount of shrinkage depends on the draw in the sheet and on felt tension. When shrinkage of the sheet is prevented, which is always to some extent the case in commercial operation, the shrinkage of the single fibres will cause microcracking to take place in the bonding areas (as shown in Fig. 7) and microcracking is also likely within the wall of some fibres. In this way, new light refractive surfaces and light scattering units are formed during drying. A paper dried under tension is therefore more opaque and brighter than a freely dried paper. From the manufacture of greaseproof paper, it is also known that the centre part of the reel is less translucent than the edges.



Fig. 7—Electron micrographs of the surface of plate-dried handsheets showing micro-cracks as a result of restrained shrinkage: the microfibrils on the left will not scatter the light, whereas the larger fibril bundles of the picture on the right probably will

# Concluding\_remarks

FROM this study, it is apparent that the consolidating processes occurring in the making of paper all lead to a decrease in opacity; at the same time, consolidation of the wet web is an essential requirement for the development of strength in the final product. When both strength and opacity are specified therefore, their opposing requirements demand a proper understanding of the basic principles upon which they depend. It is hoped that the present paper will contribute to this understanding and assist the papermaker in his correct choice of furnish materials and operating conditions, which in general will require greater care in selection and a closer measure of control than for papers in which strength alone is important. From a more fundamental aspect, the light scattering properties of paper can be regarded as a partial description of its structure, providing a convenient independent means of following some of the changes occurring in fibre and network properties. Our present picture of the relationships between the structure and strength of paper owes much to the study of light scattering properties and it is clear that continued use of this valuable complementary tool will widen still further our knowledge of consolidation processes and strength development generally.

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Dr J. A. Van den Akker—We at the Institute of Paper Chemistry are among the very many technical people related to the pulp and paper industry who greatly admire the work of Nordman and his colleagues. I have only a few comments to make.

The first relates to the interesting aspect of *configuration* of the extra bonding induced by the drying of paper under compaction stress. In recent work by Wink of our staff, it was shown that a sheet that has been dried under substantial compressive stress is quite translucent (possesses a low scattering coefficient). The familiar phenomenon of opacification of paper on straining is, with this paper, most marked and one observes that the whole area of a strip under tension becomes substantially more opaque. It is apparent that some of the fibre-to-fibre bonds have been broken when the straining has been carried almost to the point of sheet failure. It seems clear that the portions of the bonds that have been broken up to this point do not contribute nearly as much to the ultimate strength of the paper as the portions that have remained intact. Accordingly, in some of our laboratory discussions of failure phenomena, we make the point that it is probably grossly erroneous to consider only the structure of the sheet as it comes to us from the papermachine or sheetforming device; one should rather consider the structure of paper rescued from a tensile test just before the moment of failure.\* Obviously, such paper has a different structure and we suggest that this structure be employed in both theoretical and experimental work on failure mechanisms.

My next comment concerns the Kubelka-Munk theory in its application to paper. As is often the case in the field of physics, a mathematical theory may imply more than one may find in the author's statement of scope. Thus, the Kubelka-Munk theory implies that the medium be comprised of a very large number of light-scattering, light-absorbing particles, in which the individual particles are so small that, for a given absorption coefficient, the intensity of scatter from the back face of a particle does not suffer significant loss because

<sup>\*</sup> Remnants after tensile failure should not be used, because, as the late Dr G. R. Sears demonstrated many years ago, a tensile test piece at the moment of break is straight enough for compressive failure to occur in the residual pieces, the energy for this coming from the strain energy in the test piece

of absorption within the particle. This condition does not obtain in paper in which the fibres contain sufficient colouring matter to result in appreciable absorption of a ray traversing a *single* fibre. It seems very likely that this consideration can account for the dependence of scattering coefficient on absorption coefficient that is illustrated in Fig. 3 of the paper by Nordman, Aaltonen & Makkonen.\*

In illustration, we may consider the absorption of radiant energy in a single fibre and compare the light flux scattered from that fibre with the flux scattered from an optically 'clear' fibre. Let us treat the fibre as a ribbon having a closed lumen and a substance of—

$$W = (5 \times 10^{-4} \text{ cm}) \times (1.5 \text{ g/cm}^3) = 7.5 \times 10^{-4} \text{ g/cm}^2$$

Treating the fibre (in the spirit of approximation) as a slab and considering only the first of the infinite number of reflections from the back face, the front and back faces of the clear fibre scatter, respectively, 51 and 49 arbitrary units—100 units in all. The front face of the dyed fibre scatters essentially 51 units, but, because of absorption, the fractional reduction of the flux in one transit of the dyed fibre is approximately  $\Delta i/i \simeq -kW$ . From Nordman's Fig. 3, the maximum value of k is about 200 cm<sup>2</sup>/g, so that the fractional drop in intensity for a single transit in the fibre is about 0.15 (strictly speaking, this is large enough to require the use of the exponential law of absorption!). This means that the scattering from the back face of the dyed fibre is approximately  $49 \times 0.85 \times 0.85 = 35$  units, so that the total scattering from the dyed fibre is 85 units, which is 15 per cent less than the flux scattered by the clear fibre. It will be noted in Fig. 3 that the scattering coefficient drops by just about this percentage on going from a wavelength of 650 to 510 nm, corresponding to which the absorption coefficient increases from a negligible value to 200 cm<sup>2</sup>/g.

It can be seen at once that, just as the result calculated above depends upon whether or not the lumen is collapsed into optical contact, the scattering coefficient of a dyed sheet depends upon the relative bonded area. Carried to the ultimate of a completely bonded, perfectly transparent sheet, it is seen that the scattering coefficient of a colourless sheet depends simply upon the reflection of light from its two surfaces, whereas that of a deeply dyed (but transparent) sheet reflects light from essentially its front surface only and thus has a scattering coefficient of only slightly more than half that of the colourless sheet.

The Kubelka-Munk theory remains fairly accurate and certainly very useful in connection with white or lightly tinted papers. When the absorption coefficient is appreciable, the present discussion would seem to indicate that a more exact theory would consist of some sort of numerical analysis. It may be that, with the evolution of a more realistic theory, suitable dyes could be

<sup>\*</sup> See also Foote, W. J., *Paper Trade J.*, 1939, **109** (25), 31–38 21–-C.P.W. II

employed in connection with light-scattering techniques to yield information on the extent of bonding in a sheet.

Dr P. Luner-Nordman and his associates published a most interesting paper in 1952, describing a new method of determining the strength of interfibre bonding in paper. The term bond strength was given to the ratio of irrecoverable energy to the change in the scattering coefficient observed on straining paper. The bond strength value was found to be independent of beating and wet pressure, hence it was interpreted to be a property of the pulp rather than of the sheet. This work proved so interesting that quite a number of people took up this technique. These include Sandborn, Kärnä, Stone and others. A number of investigators have pointed out that the energy consumed in bond breaking is only a small fraction of that necessary to produce the new surface as observed optically and that most of the irrecoverable energy is consumed in processes related to plastic deformation of the fibre network. In view of this, I feel the term *bond strength* is a misleading term to apply to this ratio. Perhaps a better term would be the specific rupture energy of paper. This is a more common way of expressing fracture phenomena and would at the same time help to recognise the similarity or dissimilarity between paper and other materials.

My first question is related to this point. Has any attempt been made to sort out the various theories on fracture to see whether bond strength bears any relation to theoretical treatments on fracture? My second question is whether bond strength value has been correlated to fibre properties such as fibre dimensions or fibre mechanical properties?

*Mr D. H. Page*—Nordman suggests, referring to his results of Fig. 4, that the effect of wavelength on scattering coefficient for lightly pressed, lightly beaten sheets is due to a slight separation between contacting fibres, which affects light of 4 000 Å wavelength, but not light of 7 000 Å wavelength.

I wonder whether this can be correct. Over the wavelength range 7 000– 4 000 Å, the scattering coefficient changes enormously—from 275 to 430 cm<sup>2</sup>/g. If we assume that for such a bulky sheet the relative bonded area is at most 30 per cent, the increase can barely be explained, even if the whole of the optical contact areas are visible to 7 000 Å light, but invisible to 4 000 Å light.

Perhaps this large increase in scattering coefficient at low wavelengths can be explained better in terms of the presence of structural features that are light scattering in the Rayleigh sense, since this type of scattering is highly dependent on wavelength. Such structural features might well be the wrinkles on the outer secondary wall of the fibres. They are of the order of a ten thousands of Ångströms in diameter and would be present in abundance on the fibres of a lightly beaten, lightly pressed sheet.

I would like while discussing optical contact to correct a misquotation of the work by Tydeman and myself made by Nissan on the first day of this conference. He said that we believed the whole of the optical contact areas between fibres to be completely hydrogen bonded. We have never said this either orally or in print: we still hold the view that we put forward in 1961\*—'It is clear that these optical contact areas contain the sites of action of the hydrogen bonds—and perhaps other forces of adhesion—that are principally responsible for the mechanical strength of paper. The distribution of adhesive forces within these optical contact areas may by no means be an even one, but it seems highly unlikely that, over appreciable areas within this optical contact zone, there should be a total absense of bonding.'

**Mr P. A. Tydeman**—I should like to ask a question relating to the scanning of specimens for  $R_0$  and for mass that results in a very close relationship between the two (Fig. 8). If the values of  $R_0$  are converted to specific scattering coefficient, does this show a reasonably constant value along the strip length?

Dr H. G. Higgins—We tried to devise an experiment to distinguish between the effect on paper properties of lateral conformability of the fibres and of their surface texture. The results have been published<sup>†</sup> and I shall mention them only very briefly. Three types of pulp were prepared—A had never been dried up to the time of papermaking, B was dried in the usual way and C was dried in the presence of a cationic starch, which was subsequently removed by salivary amylase. The fibres of pulp A will be laterally conformable and of an 'open' surface texture (as can be seen microscopically). The normally dried fibres (B) will be rendered less conformable in that drying leads to irreversible structural changes and their surface texture will also be changed as the fibrils dry down on to the surface. The fibres of pulp C will also be less conformable than those of A, in the same way as B, for they have undergone the same internal changes as a result of drying; but the surface texture of the fibres is similar to that of pulp A, because the surface has been protected by the cationic starch. When one compares the effect of conformability (A against C) with the effect of surface texture (B against C), one finds that the mechanical strength of the paper is influenced much more by the change in lateral conformability than by the changes in surface texture.

*Mr J. A. S. Newman*—It is useful to know the number of particles involved in a fibre particle system before one considers what effect the loading particles may have on the available fibre bonding area.

- \* Formation and Structure of Paper, Ed. F. Bolam (Technical Section, B.P. & B.M.A., London, 1962), 174
- † McKenzie, A. W. and Higgins, H. G., Paper Tech., 1964, 5 (2), 155-158

With an unbeaten pulp of specific surface  $15\,000\,\,\mathrm{cm^2}$  and  $10^7$  fibres per gram, 1 per cent of retained loading gives the following results—

	Titanium dioxide	Chalk	Precipitated 'chalk'
Diameter	0.3	3.0	0.3
No. particles/fibre	$1.4 \times 10^{4}$	30	$3 \times 10^{4}$
Projected area of particles		4 14 50	1 / 1 7
on a fibre/fibre area	1/40	1/170	1/1/
Separation between particles	10 diameters	20 diameters	7 diameters

This is, of course, assuming completely uniform dispersion of the filler over the available fibre surface. From numerical estimates like these, one can see more clearly whether it might be possible for leading particles to interfere appreciably with the rebonding of microfibrils during the drying and consolidating processes.

**Dr H. K. Corte**—Please clear up for me one small point of terminology. We all remember from the introductory talk how important it is to understand the correct meaning of a word. The Kubelka-Munk theory does not contain the word substance, but it does contain the word thickness. The scattering coefficient therefore has the dimension  $cm^{-1}$ . Van den Akker suggested for convenience introducing substance for paper instead of the thickness, in which case, the scattering coefficient has the dimension of the reciprocal substance,  $cm^2/g$ . This, very curiously, was taken to be the specific fibre surface and the increase in the scattering coefficient was taken to indicate an increase in the specific fibre surface, but it has nothing to do with it. It is the reciprocal value of that sheet substance that by scattering reduces the intensity of transmitted light to a defined degree. If the substance is  $1 g/m^2$ , the specific surface will be  $1 cm^2/g$ ; if  $100 g/m^2$ , it will be  $100 cm^2/g$ . The specific internal surface, on the other hand, is something quite different and all the energy data are based on the former type of surface.

It did not surprise me in the least therefore that values found by Stone using nitrogen adsorption for various increases or decreases of the specific surface resulting from various degrees of bonding agreed not at all with those from optical measurements. Not only that, but there was not even a constant factor of proportionality.

**Dr Van den Akker**—The introduction of substance W as the independent variable (in place of thickness)—not done for convenience, by the way, but to overcome some conceptual difficulties about the composition of paper, compressibility and analysis—has introduced to s the *dimensions* of cm<sup>2</sup>/g. The numerical expression of s has never been interpreted as an actual specific surface area of some sort; it is only accidental that changes in s, being used to

obtain relative measures of changes in surface area, are expressed in  $cm^2/g$ . On the basis of a model in which a linear connection was assumed to exist between s and specific surface area, Swanson & Steber\* experimentally determined the numerical relationship between s and fibre area based on the gas adsorption technique. This provided us, for the first time, with the means for comparing the energies per unit of broken-bond area (Nordman technique) with theoretical estimates, a subject that has been discussed elsewhere.

**Dr J. Grant**—Davidson's rather revolutionary theory depends very much on his experiment of removing calcium carbonate with acid. I have already expressed the view that the results can be explained by the action of the acid on the carbonate producing carbon dioxide *in situ*. This could adequately explain the loss of rattle and strength, because of a certain amount of debonding by the gas and, of course, an increase in sheet bulk. I suggested some further experiments to clear this point up and wonder if they were done.

His paper referred to Schwalbe's work on which I have already commented, but Davidson now confirms that his experiments do not apply to titanium dioxide, because Schwalbe told us that this was exceptional.

*Mrs R. Marton*—Have you examined high-yield pulps or groundwood pulps, because, when very coarse groundwood is refined, the scattering coefficient increases with decreasing freeness and the breaking length increases at the same time. Can this be explained reasonably by your new approach?

Mr R. R. Davidson—I would first like to criticise Newman's use of the term precipitated chalk. Chalk is a 90 million year old geological deposit that cannot be precipitated. Precipitated calcium carbonate (P.C.C.) has a completely different structure. This use of the word chalk in the paper industry for a number of completely different fillers causes a degree of confusion that should no longer be tolerated among chalk whitings, ground limestones and P.C.C.s.

The second point is that for the 3 micron diameter particles (a quite normal size for a paper filler), Newman's calculations give a distance of 20 diameters between the particles with 1 per cent filler addition. For high opacity in printings, 20 per cent filler may well be added. A good coverage of the fibre area would thus be expected.

I assure Grant that the carbon dioxide bubbles were not the cause of the change in sheet structure. Similar results were obtained when the acid was added so slowly that no bubbles arose; the carbon dioxide dissolved in the surrounding liquid. Addition of filler increased the caliper at constant pulp

\* Tappi, 1959, 42 (12), 986-994

substance. Moreover, the acid treatment tended to reduce the caliper; it was the filler, not the bubbles that opened up the sheet.

*Mr L. Nordman*—Several of the questions have been concerned with terminology and dimensions. As was stated in the transactions of the first symposium at Cambridge, the strength of the bonds is given in terms of the energy required to decrease the bonded area by one unit of scattering coefficient. The scattering coefficient is a component of reflectance, the other being the absorption coefficient. The scattering coefficient has been shown by various authors to correlate the surface area. References to works of this type have been given in the written contribution. A knowledge of the proportionality factor that exists between the scattering coefficient and surface area measured according to some other method allows conversion of our bond strength to a corresponding bond strength value expressed in other units of surface area as obtained, for example, in nitrogen absorption measurements.

That the term *bond strength* should be suggested to replace the term *specific rupture energy* emphasises the fact that all of the energy is not associated with bond breakage, but part of it may be used in other processes leading to rupture. It seems, however, that the ratio between energy required for bond breakage and other energy dissipation is a constant, judging from the fact that the relationship between energy consumption and increase in scattering coefficient is linear in the plastic region of the stress/strain curve.

The optical method does not afford any scope for actually localising and studying the rupture of a single small section of the structure, but we get only the total changes over the aperture of the measuring instrument. Therefore, we have not tried to relate the results to known theories of fracture. No particular influence by fibre dimensions has been found.

I can advise Mrs Marton that we have tested pulps up to a yield of about 70 per cent, but no higher. No groundwood sheets have been tested.

The interpretation of Fig. 4 in the written paper is that the two-phase system fibre/air in a bulky sheet contains a large amount of phase separations of the order of magnitude that is detectable by short wavelengths of light only. Compaction of the sheet either by beating or wet pressing causes a decrease in the light scattering areas and, in particular, closely spaced phase boundaries are removed. Page's suggestion that these small-scale irregularities are microcompressions in the fibre surface may well be true.

For practical reasons, we cannot by scanning the strip obtain more than one reflecting value, in this case  $R_0$ . It seems that we are unable to calculate the scattering power and scattering coefficient according to the Kubelka-Munk equations. Small changes in  $R_0$  are, however, nearly proportional to the corresponding changes in scattering power. This means that the scanning results

give an approximate picture of the changes in scattering power over the strip. The  $R_0$  curve for the unstrained strip is more or less a constant.

Finally, Van den Akker's remark that the sheet as it comes is not the same as it is just before rupture is very appropriate: this is clearly illustrated in our scanning results, particularly for highly beaten sheets.

**Prof. H. W. Giertz**—Before yesterday's session, I prepared a plan for the discussion and asked Nissan kindly to make a contribution about mechanical properties and molecular structure. Unfortunately, we had no time for it and this seems to be the case again today. To save time, I have not presented my paper on optical consequences of the consolidation of paper, but wish to take this opportunity of presenting some new results not included in my paper that concern the mechanical properties of paper and therefore belong to the present discussion.

Dealing with the same types of pulp, as is well known, a close relationship exists between opacity and tensile strength as is shown in Fig. 4 (page 152). When comparing different types of pulp, the same relationship does not exist. So, for instance, sulphate pulps are more opaque than are sulphite pulps, but if the comparison is made at the same extential stiffness (that is, the slope of the first part of the stress/strain curve), both sulphite and sulphate pulps have the same opacity. These results might be of interest when correlating mechanical properties with other paper properties and it seems likely that the extensional stiffness is a more fundamental strength property than is rupture load.

This was a contribution of my own and I now want to proceed by handing over to Nissan. During the earlier sessions, there was some opportunity for discussing the influence of the network, the fibres and the bonds on the mechanical properties of paper. I think the few minutes left are best used by giving some attention as well to what is taking place on a molecular and atomic level when paper is broken.

**Dr** A. H. Nissan—It has been suggested that I contribute on the synthesis of the structural and molecular approaches to the mechanical properties of a paper network. Giertz asked me whether I saw any chance of unifying the two major approaches to the understanding of the mechanical properties of paper. On the one hand, a body of theory and observation has grown around the concept that paper consists of fibres and fibrils of known or measurable properties, joined together at discrete junctions to give a network of calculable properties. On the other hand, there is the basic concept that ultimately all mechanical properties of materials will be functions of deep underlying molecular parameters and their interactions. To this general rule, it is improbable that paper will prove uniquely an exception.

I believe there is a trend towards unification and that the first steps in that direction have already been taken during the present conference. First comes the realisation that the *bonded areas* at the junctions are microcompressed and corrugated. Thus, the apparently uniformly bonded areas now appear to be bonded only at discrete points. This fact takes the structural unit down in dimensions from the fibre level to the smaller dimensions of fibrils. Yet, there is no valid reason to think that the fibrils will prove to be the ultimate structural units in the network, since we know that they are invariably composed of microfibrils. The appearance in the fibrils of 'voids' full of water, described in an early paper during this conference with dimensions of 35 Å, indicates that most probably the ultimate structural unit in the network theories will be the microfibril.

The microfibril has received intensive consideration over the last few years. Dr R. St. J. Manley, for example, finds it to be of the order of  $35 \text{ Å} \times 35 \text{ Å} \times (200-400 \text{ Å})$  in dimensions. He believes it to consist of single crystals of folded cellulose molecules bound internally by hydrogen bonds. Because of the high degree of order within the microfibril, it is highly resistant to disruption by mechanical means. The bonds between these structural units are also hydrogen bridges; but, since the degree of order is not high, these bonds are more easily broken piecemeal. (It had been shown many years ago, in a thermodynamic paper to the Faraday Society, that, if a large number *n* of hydrogen bonds were to be broken together, the energy required would be about 5n kcal/mole, even if they were broken successively as in a zip fastener. Thus, if n = 100 in a microfibril, the energy required would be 500 kcal/mole to disrupt the microfibril.)

Clearly, if the basic structural unit is the microfibril, we may then postulate that there will be N bonded areas per cm<sup>3</sup> joining the microfibrils together. We need not specify the nature of the bond at each area, only that it would require an energy of  $U_0$  to disrupt  $N_{Avog}$ . such bonds. We can then determine the value and characteristics of this bond from rheological data. If these match up with the value of  $U_0$  and other characteristics of the hydrogen bond, then the union of the structural network theories and that of the molecular approach would be achieved. If they do not match up, we would have at least a better approximation to the molecular approach than we have today.

I suggest that these critical studies could be done along the following line. Let us assume N to be isotropically distributed. It can be shown that, with certain restrictions, this is equivalent to a system of bonds distributed along the three orthogonal axes with n' = N/3 bonds along each axis. Thus, we can deal with a system of n' bonds, of unknown magnitude and nature, along the axis of uni-directional stress in tension or compression. Not all these bonds will be effective in carrying stress, as some will be shielded by microfibrils from

carrying stress. Let the fraction of n' that are effective be n. Since we have assumed isotropic behaviour and uniformity, the cm<sup>3</sup> can be divided into nsmaller cubes with a side l, each containing one bond: l will then be equal to  $n^{-\frac{1}{3}}$ . From here onwards, we can derive expressions for the stress, strain and the modulus of elasticity E in terms of n,  $U_0$  (the unknown energy of rupture of the bond) and the partial lengths of the stressed and unstressed portions of l, respectively, in a manner similar to what I have used in deriving these quantities in terms of the characteristics of the hydrogen bond.\* I would then suggest that, if paper characteristics are studied in terms of these derivations, it will be possible to see whether indeed the bonds between microfibrils are hydrogen bridges or, say, long flexible molecules forming cross-links. I believe such a study will prove not only rewarding, but will become increasingly necessary as we penetrate to deeper levels in our understanding of the network theories of paper.

I would suggest further that time effects may be studied in terms of the kinetics of bond breakage. Thus, stress relaxation may be studied by investigating—

$$\frac{-d(n/n_0)}{dt} = k(n/n_0)^{\alpha}$$

where  $n_0$  is the number of bonds at time zero, *n* the number at time *t*, *k* is a constant and  $\alpha$  is a *co-operative index*, showing how many bonds will have to break simultaneously for a unit jump to be possible. This equation has been elaborated.<sup>†</sup> It yields a spectrum of relaxation parameters that can be checked against observed paper behaviour.

Finally, rupture can be studied also along the weak link theoretical approaches made by Pearce for textiles and Griffiths for glass. Here, one has simply to consider that  $U_0$  is in fact the mean of values with a distribution with, say, standard deviation of  $\pm \Delta U_0$ . Thus, there will be weak bonds of  $(U_0 - \Delta U_0)$  with calculable frequencies of occurrence. With these assumptions, it is possible to obtain descriptive formulae for the changes of breaking length with sample size. These predictions can be again checked against observations made on paper to see whether the bridges between microfibrils are true hydrogen bonds or some other type of link—for example, flexible molecules of, say, hemicelluloses.‡

Thus, in brief, I see the trend towards a reduction in the size of the structural unit to that of the microfibril and of the *bonded area* to that of a few  $Å^2$ , containing most probably a hydrogen bond, possibly a cross-linking molecule. At

<sup>\*</sup> See, for example, Tappi, 1964, 47 (1), 1-6

<sup>†</sup> Nissan, A. H. and Sternstein, S. S., Pure & appl. Chem., 1962, 5, 131-146

<sup>&</sup>lt;sup>‡</sup> See Nissan, A. H., *Trans. Far. Soc.*, 1959, **55**, 2 048–2 053, with erratum, *ibid.*, 1961, **57**, 1 646

the moment, there is no evidence for a chemical branching of the cellulose molecule in paper. So, I myself assume that, even if a molecule acts as a link between the microfibrils, it will do so by means of hydrogen bonds between it and the cellulose, not by covalent or other similarly strong bonds. Thus, I believe that ultimately the two approaches will merge at the molecular level. Even if the equations 'finally' derived will look different from those available today, one factor will emerge—the importance of *n*, the effective number of bonds (hydrogen or other types) per cm<sup>3</sup> taking part in sharing a stress. This number (at present defined by  $E=7600 n^{\frac{1}{3}}$ ) is controlling, I believe, in most aspects of the mechanical properties of paper.\*

**Dr Corte**—May I ask why you chose the Morse function as the particular potential function? Why not use another such as the Lennard-Jones function, which considers both attraction and repulsion forces (which the Morse function does not). Why, indeed, choose any particular function at all, instead of representing the stress/strain curve by a polynomial and fitting the coefficients?

**Dr** Nissan—The most precise function available is the Lippincott and Schroeder function for the hydrogen bond and it consists of a summation of four potentials. It is an empirical function. It suffers from complexity as it has ten parameters to deal with. The Morse function has the virtue of simplicity, needing only one adjustable parameter. Both are equally empirical. There is as yet no rigorous quantum-mechanical function that can be used. A polynomial would fit the curve, but would not link the stress/strain curve to any fundamental molecular or hydrogen bond parameters. Thus, the Morse function appeared to be the best compromise. Those who might wish for greater accuracy should use the Lippincott and Schroeder function.

\* See Nissan, A. H. and Sternstein, S. S., Tappi, 1964, 47(1), 1-6