

RELATIONSHIPS BETWEEN MECHANICAL AND OPTICAL PROPERTIES OF PAPER AFFECTED BY WEB CONSOLIDATION

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Synopsis—The relationships between bonding strength and web consolidation as affected by beating and wet pressing have been investigated. The effect of both the forces of external pressure and surface tension on the structure and on single fibre elements and crossings is discussed in the light of relevant publications. Wet pressing can exercise both direct effects and effects attributable to the induced liquid flow in the sheet. Various types of bonding strength measurement have been covered and attention has been devoted to the question whether data on the magnitude of the bonded area can be derived from scattering measurements. On introducing variations in the bonded area by means of variation in the wet pressure, investigations have shown that, for a given increase in bonded area, beating is more effective than wet pressing in increasing the rupture strength.

In the present investigation, use has been made of a method developed previously to relate irreversibly expended work to bond breakage with a view to assessing the effect of beating and wet pressing on the bonding strength value. These tests indicate that, for some pulp qualities with a high hemicellulose content, the bonding strength rises with increases in the degree of beating and falls on the application of higher wet pressure. For bleached and unbleached pulp with a low hemicellulose content, the bonding strength is (as has been found earlier) virtually independent of both beating and wet pressing. The possible reasons for the beating and wet pressing effects are discussed and some alternatives proposed. Although no satisfactory explanation can be found, it is believed that beating increases the possibilities of intimate contact between the surfaces and gives rise to a structure that has larger radii of curvature between the building elements. On the other hand, wet pressing may permanently damage the cell walls and result in less entangled contact zones and a structure of more angular configuration.

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Introduction

ALL investigations of the mechanical properties of paper are concerned with a material, the properties of which have been influenced by a sequence of factors acting one after the other and during which the effect of each stage in the process may not be additive. It is evident, for instance, that the effects on the mechanical properties of paper brought about by beating are influenced by the sheet formation, wet pressing and drying, each step of which is in turn influenced by the preceding ones.

The relationship between the factors mostly responsible for the consolidation of the web—beating and wet pressing—also the bonding strength measured for the final product, have quite naturally been the objects of particular interest. Whereas some results reported in the literature indicate that the specific bonding strength is independent of these two steps in production, other information tends to show that this is not the case. In our efforts to clarify this point, we have additionally tried to extract from the literature information on the possible effects of beating and wet pressing not only as they appear in the results for the finished sheet, but also with respect to the possible effects in the earlier stages of paper manufacture.

Effects caused on the wet web

THE consolidation of the wet web can be depicted as a gradual removal of water followed by a progressive formation of bonds, but it is well known that water removal and bond formation follow different paths dependent upon the conditions under which the water is removed. Density and opacity are indicative of the degree of bonding in the sheet. A relationship exists therefore between density and opacity, but this is not unique. If the pressing is carried out in two steps with change of blotters, instead of in one single step, the opacity is lower at each value of density for the two-stage wet pressing.⁽¹⁾ If, on the other hand, the opacity is compared with the amount of water remaining in the sheet after pressing, it is found that in the region where the curves overlap at a given moisture content two-stage pressing gives a higher opacity. A similar observation has been made by Villars⁽²⁾ for tensile strength, which is of course also related to bonding. It was found that the number of changes of blotters has more effect on the dryness of laboratory sheets than has an increase in the pressure, all calculated on the basis of an equal increase in tensile strength. A circumstance that may confuse the relationships between wet pressing and the properties of the sheets is the fact that some of the effects on the wet fibre mat are reversible. Since the drying stage is preceded by recovery of the paper web, it is fully possible that no unique relationship exists between the removal of water and the formation of bonds, in spite of the fact that the bond formation is most closely associated with water

removal, as is apparent in the Campbell effect. On this occasion, there is no reason to go into the question of the Campbell effect, which has been adequately explained and generally accepted as the mechanism that brings the fibre surfaces in to such proximity with each other that bonds can be formed. Beating enhances the effect, partly by reason of the increased flexibility imparted to the fibres, partly because of fibrillation, which aids in forming networks with initially short distances between fibre surface elements. In this connection, however, it should be mentioned that fibrils and exfoliated material formed during beating do not necessarily contribute to bond formation between fibres, but may equally well—and with a high degree of probability—rebound to the fibres from which they originate.

McKenzie & Higgins⁽³⁾ have drawn attention to the lateral conformability of the fibre surface as a contributory factor to the closeness of fibre contact, which increases with beating. Drying of the sheets causes not only fibre bonding, but also fibre collapse. This may occur even if no external pressure is applied, as has been shown by Washburn & Buchanan⁽⁴⁾ in a series of excellent scanning electron micrographs. Nevertheless, if normal drying is replaced by freeze drying, collapse can be observed only after pressing. By application of the freeze drying technique, it was also possible to show that drying from 8 per cent to 29 per cent solids content involved the removal of free water from the surface, whereby fibrils and lamellae were rebonded.

If pressure is imposed on the wet web, regardless of whether this is done in a plate press or dynamically in a nip between a cylinder surface and a felt, it involves a combination of mechanical compression of the web and a flow of water through and out of the sheet. The ratio between the two pressure effects depends on the degree of saturation of the web and the rate at which pressure is applied.

The average pressure to act over the surface of the sheet is probably not indicative of the local pressures that may arise in fibre crossings, particularly if several fibres happen to cross in the same area. Evidence for this can be found from the previously mentioned micrographs obtained by Washburn & Buchanan, in which a crossing fibre had made a permanent mark on its neighbour, as could be seen after the fibres had separated upon release of the pressure. This indicates that plastic flow has taken place in the fibre surfaces. Another indication of the mechanical effect of the pressure is observable in the fact that ridges along collapsed fibres are pressed down and that their disappearance will probably allow fibres to come into closer mutual contact.

As was briefly mentioned above, there is a springing back of the fibres upon release of the pressure. This has been demonstrated both by Van den Akker⁽⁵⁾ and by Washburn & Buchanan.⁽⁴⁾ Seborg, Simmonds & Baird,⁽⁶⁾ in their studies of the influence of wet pressing, found that, whereas the compression

of the fibre mat depends very little upon beating, the recovery upon release of the pressure is highly dependent upon the degree of beating. Beating decreases spring-back and the same effect is discoverable in pulps with a high content of fines, a high content of springwood fibres and for soft pulps generally.

A very interesting observation related to the mechanical compression of the fibres was made by Annergren.^(7,8) Laboratory sheets made from pulp beaten to different degrees of beating and wet pressed at different pressures were subjected to a swelling test in 18 per cent sodium hydroxide solution. The swellability of the paper (expressed by its caustic pick-up) was plotted against the beating separately for each wet pressure. Contrary to what was expected, caustic pick-up did not diminish immediately on beating, but showed a slight increase, after which it started to fall. In a critical region of beating, however, the swelling increased, passed through a new maximum value, then fell off markedly. For sheets subjected to higher wet pressures in the sheet-making, the swelling curves were on a higher level and the maximum swelling appeared at a lower degree of beating. The picture was essentially the same for different types of pulp. Annergren's explanation was that the swelling is a phenomenon partly in the interfibre, partly in the intrafibre capillaries. Beating reduces the capillary volume, but at the same time damages the primary wall. This exposes the secondary wall, which starts to swell. An increase in pressure thus exercises an effect parallel to that of the beating, in that it brings about disruption of the fibre wall. The influence of wet pressure is non-existent outside a critical beating region, probably because there beating may already have exposed the inner fibre layers. It is believed that the damaging effect on the surface layers is caused not by the pressure itself, but by the release of the pressure, whereby water that has been forced into the fibre structure and is under a hydrostatic pressure, rapidly explodes the fibre surface. Experiments actually showed that a gradual pressure release had a diminishing effect on the fibre swellability in alkali.

The second effect of wet pressure—an initiator of liquid flow in the mat—can exercise an influence on both the web structure and the surface properties of the fibres. Yih & MacNamara⁽⁹⁾ showed that compression causes a lateral flow of water, the rate of flow being dependent on both the rate of application of the compression and on the rate at which water can be expelled from the compression system. A sufficiently high rate of compression can, by drag on the fibres, bring about a stretching of the system locally. This is observable as the phenomenon known as crushing of the sheet. It seems that the same effect, on a microscale, can affect fine material present between fibres. In narrow capillaries, high rates of flow can evidently occur, which may align fibrils along the fibre surface and thus make them susceptible to re-bonding, as well as remove fibre debris and highly swollen elements from the

probable future bonding sites. This same highly swollen material may of course again move into a bonding area with the receding meniscus of water during drying.

Different measurements of bonding

VERY thorough investigations into the relationship that exists between sheet properties and fibre properties have been made by Doughty,⁽¹⁰⁾ in which the density of the sheets, expressed by the solid fraction, was related to the tensile strength. The changes in solids fraction were induced by changes in the wet pressing. For each degree of beating, the tensile strength rises with an increase in solids fraction. Beating raises the level of this curve.

As a rule, there is rather close agreement between the scattering coefficient and the density of a sheet. Accordingly, it is not surprising that later investigations to relate tensile strength to scattering coefficient give results that are analogous to those of Doughty. Before study of the investigations performed along these lines, however, some general words should be said about evaluation of the bonding strength and estimation of the bonded area between fibres. Unfortunately, no direct method is available for measurement of the bonded area, which consequently must always be calculated as a difference between the surface area of the fibres before bonding and the remaining surface area after bonding. During past years, many difficulties have been experienced in finding suitable methods for the determination of surface areas of pulp fibres and of paper in comparable units. Various methods make it possible to measure surfaces of different degrees of fineness. Some methods are used for wet pulp and others for dried pulp; here, of course, the drying procedure has its own influence on the degree of swelling of the fibres, as well as on the fine structure of the surface.

In order to avoid all these difficulties in some earlier investigations performed at our Institute,⁽¹¹⁾ it was decided completely to ignore the surface area of the fibres before bonding and to concentrate on the free surface area remaining in the sheet. If the same pulp was used in all experiments, the surface area naturally stayed constant; thus, all the changes that could be made to the bonded area were quantitatively reflected in the free surface area of the papers. As a relative measurement of the free surface area, use was made of the scattering coefficient calculated according to the Kubelka-Munk equation from reflectance measurements. As a means of changing the size of the bonded area in the different sets of sheets made from the same beaten pulp, the sheets were subjected to different degrees of wet pressure in the sheetmaking procedure. This enabled the acquirement of relative measurements of the variation in the bonded area. Different pulps were subjected to beating and, for each beating point, sheets were prepared by the application

of different pressures in the wet pressing stage. Tensile strength values were plotted against the scattering coefficient. For each beating point separately, the figures obtained fell on a straight line; the slope of this line was considered to be a relative measurement of bonding strength. The straightline portions were parallel, which indicates that beating does not materially influence the bonding strength determined in this way. No attempt was made to extrapolate the lines to zero strength to obtain a scattering coefficient value for unbonded fibres.

Ingmanson & Thode,⁽¹²⁾ as well as Swanson & Steber,⁽¹³⁾ utilised the same technique, with sheets subjected to various wet pressures in the formation stage. A composite extrapolation curve was formed for all the test data and extrapolated to zero strength. The conclusion was that the total dried surface area was independent of the degree of beating. The surface area in the wet swollen state increases with beating, but it becomes evident that most of this increase is reversible upon drying—for example, by the rebonding of fibrils and lamellae to the main body of fibre. When the extrapolated scattering coefficient value was taken as the total area and the scattering coefficient for the sheets as an indication of the free surface area, it was possible to calculate the bonded area. When tensile strength was plotted against bonded area, Swanson & Steber found that each beating point formed its own curve.

With the aim of obtaining a value for the dried total specific surface area expressed in optical units, Kärnä⁽¹⁴⁾ tried out several extrapolation parameters; apart from breaking length, he used the modulus of elasticity and the breaking energy. A power function was employed for the mathematical extrapolation. Furthermore, an attempt was made to use the apparent density of the sheets as the extrapolation parameter. As in this case zero density has no physical significance, extrapolations were made to a limiting apparent density, arbitrarily chosen as 0.150 g/cm³. For some pulps, beating resulted in an increase in the extrapolated surface area of dry unbonded fibres, whereas in other cases a distinct fall in this property was experienced. The explanation that beating diminishes intrafibre scattering does not seem to account for this surprising result. It appears that the use of the power function for extrapolation may be erroneous, the choice of constants being too dependent on the results relating to the lowest wet pressure.

The common conclusions to be drawn from the four investigations in which essentially the same technique was utilised is that, if a definite change in the bonded area results from changing the pressure, the change in strength induced is less than if the bonded area is correspondingly changed by beating.

Opacity considerations

THE question of whether scattering coefficient values can be considered

representative of the surface area that is not in mechanical contact has been discussed in detail in many connections. The general belief, based on various correlations between scattering values and surface area values determined by other methods, particularly on those relating scattering to nitrogen adsorption, clearly indicate a linear relationship. These methods measure distances of quite different orders of magnitude. It has been held that the correlation found depends on fibre surfaces brought within a distance shorter than the limiting wavelength of scattering measurements being automatically drawn together by the surface tension forces into the regime of mechanical bonding. This means that fibre surfaces are either bonded to each other or are so greatly separated that they are distinguishable by optical means and that the intermediate distances form a negligible part of the total free surface area. An indication that this is true is afforded by the very few interference fringes found by Page⁽¹⁵⁾ around optical bonds. The fact that the relative bonded area as calculated by Ingmanson & Thode⁽¹²⁾ is virtually independent of the wavelength of light used for scattering measurements is also considered to support this. It is a controversial point whether the proportionality factor between area measurements and scattering coefficient measurements is a constant for different types of pulp. Although Swanson & Steber⁽¹³⁾ maintain that the relationship between the BET* area and scattering approaches a common value when the optical measurements are made by means of longer wavelengths of light, Stone⁽¹⁶⁾ found that a comparatively high variability evidently exists in the proportionality factor. According to Arnold,⁽¹⁷⁾ the governing factor is constituted by the size and shape of the fibres.

It was mentioned that the relative bonded area determined optically in Swanson & Steber's investigations was very little changed by varying the wavelength for the optical measurements. Although the relative bonded area seems to be fairly constant, there is a very distinct difference in the scattering coefficient when different wavelengths are employed for the measurements. For all bleached pulps, there appears to be within the visual part of the spectrum a drop in the scattering coefficient when moving from blue light to longer wavelengths (Fig. 1). When dyeing a bleached pulp with a neutral grey dye that has almost a constant absorption over the whole wavelength range, the scattering coefficient curve is displaced towards lower values, but continues to show a form that is the same as for the undyed bleached pulp (Fig. 2). If the pulp is dyed with a dyestuff with a specific absorption in a certain wavelength range, however, the scattering coefficient value diminishes over the same wavelength range (Fig. 3). These experiments indicate that the presence of colouring (that is, absorbing) matter causes a diminution in the

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scattering coefficient value over the same range in which the absorption coefficient is high. In view of this, it seems improbable that the drop in the scattering coefficient curve when moving toward higher wavelengths could in any way be caused by absorption effects and that the inability of the Kubelka-Munk equations to distinguish between absorption and scattering effects cannot account for the high scattering values in the blue, short wave region.

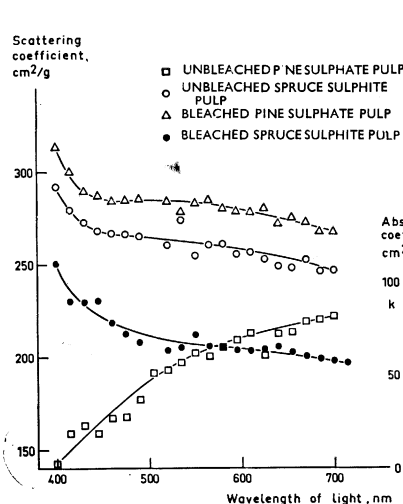


Fig. 1—Scattering coefficient of sheets made from various pulp qualities presented as a function of the wavelength of light used for the measurements

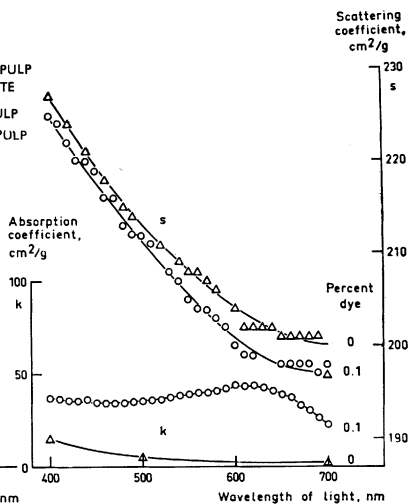


Fig. 2—Absorption and scattering coefficients of sheets made from an undyed and a grey-dyed pulp presented as a function of the wavelength of light used for the measurements

Unbleached pulp, kraft pulp in particular, has a very high absorption in the short wavelengths; this causes the curve of the scattering coefficient plotted against the wavelength to assume a slope quite different from those obtained for bleached pulps (Fig. 1). For unbleached sulphate pulp, there is a steady increase in the scattering coefficient value when moving from 400 nm to higher wavelengths. That this is an effect attributable to the colouring matter was shown qualitatively by dyeing a bleached sulphate pulp to give a complete match for the unbleached pulp. By this means, the typical curve for the bleached pulp was reversed into a curve that displayed an increase with increasing wavelength of light.

It is therefore believed that pulp in general, if there is no influence from colouring matter, would have a higher scattering coefficient in the blue

wavelengths. Both beating and wet pressing influence the curve of the scattering coefficient plotted against wavelength. It is common knowledge that beating reduces the scattering coefficient, but this does not take place uniformly over the whole wavelength region: the changes are more pronounced in the short wavelength range. Similarly, wet pressing has a tendency to diminish the scattering coefficient, but this effect also is more clearly seen in the short wavelength range. A particularly pronounced dependence on wavelength is observable in a lightly beaten, lightly pressed sheet; whereas, for a

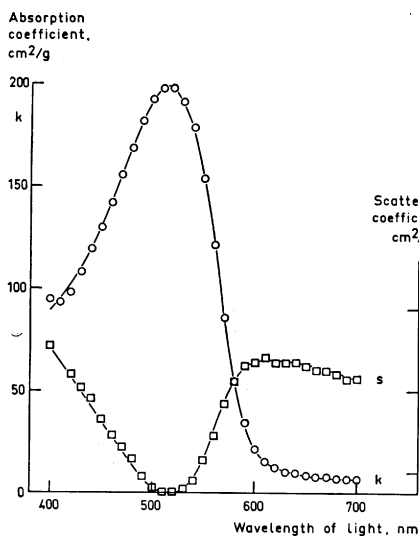


Fig. 3—Absorption and scattering coefficients of a sheet made from a pulp dyed red presented as a function of the wavelength of light used for the measurements

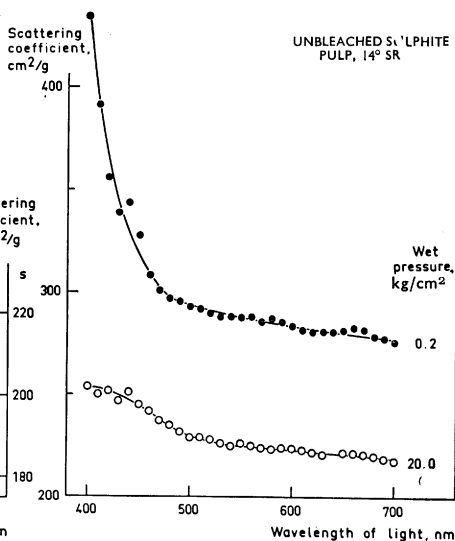


Fig. 4—Scattering coefficient of sheets made from a lightly beaten pulp and subjected to low and high wet pressures presented as a function of the wavelength of light used for the measurements

highly beaten, highly pressed sheet, there is virtually no effect exerted by the wavelength used for the measurements (Fig. 4 and 5). These observations indicate that structural factors are responsible for the dependence of the scattering coefficient on wavelength. The inference is that, in a lightly pressed sheet, a certain number of fibre surfaces exist that are separated by quite small distances. As a consequence, these surfaces are seen with a blue light of 400 nm, whereas they are beyond the resolving power of longer wavelengths. The effect of wet pressure would then be to cause fibre surfaces separated by short distances to form bonds. The very slight influence of wet pressure on the

slope of the scattering curve for the highly beaten sheets is in agreement with the generally observed slight effect of wet pressing on sheets from highly beaten stock. Owing to the flexibility and fibrillation of beaten pulp fibres, surface tension forces develop, with no assistance from wet pressure, to a degree sufficient to bring about efficient bonding.

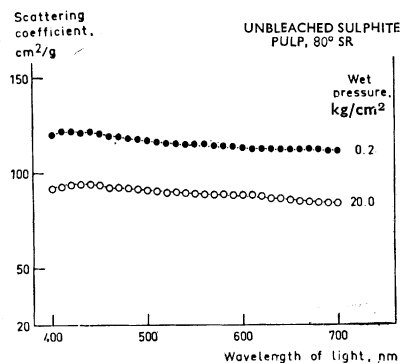


Fig. 5—Scattering coefficient of sheets made from a highly beaten pulp and subjected to low and high wet pressures presented as a function of the wavelength of light used for the measurements

Relationships between bond breakage and light scattering

DETERMINATIONS of bonding strength based on the methods referred to in a previous section are to be regarded with some doubt. This treatment involves an attempt to relate the total amount of bonds formed to the breaking strength with no positive knowledge that the bonds are in reality all simultaneously engaged at the moment of rupture. Another aspect of this problem is that there exists no guarantee that the breaking zone between two fibres will actually follow the bond constituted between them in the bond formation stage. Accordingly, the investigations into the bonding strength made at our Institute soon took as starting point not the bonds formed in making the sheet, but the bonds actually broken in loading the paper. It is evident that, if breakage occurs anywhere in the material, a crack will be formed that is in fact nothing but a fibre/air interface where previously no such discontinuity had been present. On the assumption that light is scattered by fibre surfaces not in mechanical contact and that an increase in the scattering coefficient thus denotes an increase in the unbonded area, it is possible to follow the

changes that occur in paper on loading. The scattering coefficient of a particular strip is measured before and after a loading cycle. The energy absorbed by the strip is then related to the decrease in bonding, as measured by the increase in scattering coefficient experienced. In the early work, it was found for a number of commercial pulp qualities that the bonding strength calculated from the energy absorption and the changes in scattering was essentially independent of beating and wet pressing, but that it varied with different qualities of pulp. Against this, it was found by Kärnä⁽¹⁴⁾ and later also by Göttching & Nordman⁽¹⁸⁾ that there was a rise in the bonding strength value with progressive beating of the pulp, but that it fell on the application of higher wet pressures. In both of these investigations, the pulp qualities tested did not represent the normal range of commercial pulps. It was therefore considered necessary to carry out additional tests to find the reasons for the different results.

For the tests, four different sulphite pulps from spruce were used. Two pulps were unbleached, one of them having a high hemicellulose content, the other a low hemicellulose content. The two remaining pulps were bleached pulps, again representing pulps with high and a low hemicellulose content. Beating was done with a Valley beater and ordinary handsheets were made in accordance with the Finnish method. The widest range of beating and wet pressing conditions was utilised in the case of the unbleached pulp with a high hemicellulose content. The results for the unbleached pulps are given in Fig. 6 and the corresponding results for the bleached pulps in Fig. 7. The bonding strength values have been plotted as a function of the beating time, separately for each wet pressure. For both bleached pulps, it is clearly evident that, except for the very first beating period, the bonding strength is independent of the extent of beating. This can also be found to apply to the unbleached sulphite pulp with a low hemicellulose content. Nevertheless, a very pronounced influence of beating on the bonding strength is experienced for the unbleached pulp with a high hemicellulose content. The influence is more marked when the sheets are subjected to a low than to a high wet pressure. When the results are judged from the point of view of wet pressure, it becomes clear that over the range tested no significant influence was found for the bleached pulp with a low hemicellulose content. With the unbleached pulp of low hemicellulose content, there is some decrease in bonding strength when wet pressure is increased. Once again, the most significant influence is observable for the unbleached pulp with a high hemicellulose content. For low wet pressures, the bonding strength is much greater than when a high wet pressure is applied. There is clearly a limit for the diminution, because the results for 20 and 40 kg/cm² pressures nearly coincide. The fall in bonding strength is again more conspicuous in the higher beating region. When these

results are compared with previous findings, it appears that the dependence both on beating and wet pressing observed for the unbleached pulp with a high hemicellulose content is in close agreement with the results obtained both by Kärnä⁽¹⁵⁾ and by Göttching & Nordman⁽¹⁸⁾ for a series of special hardwood pulps.

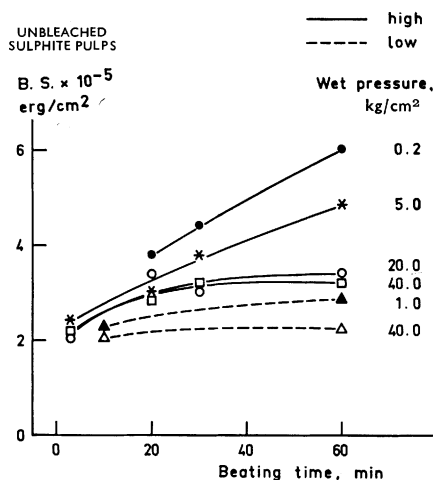


Fig. 6—Bonding strength values obtained for sheets made from unbleached sulphite pulps as a function of the beating time and the degree of wet pressure

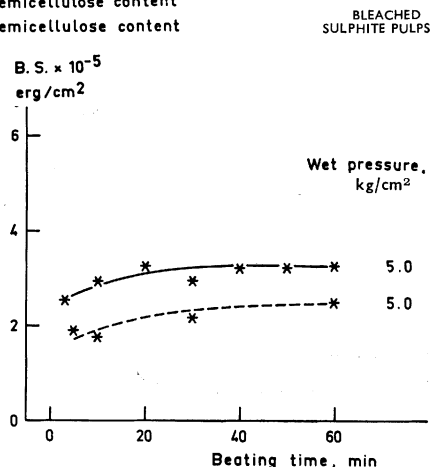


Fig. 7—Bonding strength values obtained for sheets made from bleached sulphite pulps as a function of the beating time

The present results can be summarised as follows. For the very lightly or almost unbeaten pulp, the differences between different pulp qualities and different wet pressures are slight and all of the points nearly coincide around a value of 2×10^5 erg/cm². For high wet pressures—and, in some cases, for moderate wet pressure—no effect of beating is discernible. If the wet pressing is non-existent or light, however, beating seems to increase the bonding strength value considerably for a pulp with a high hemicellulose content. This effect is more pronounced for the unbleached pulp. In most cases, an increase in the wet pressure up to a certain limit reduces the bonding strength value.

Discussion

IN the search for an explanation, some possibilities are worth discussion. The obvious explanation is that the relationship between the surface area in

mechanical contact and that in optical contact is dependent on beating and wet pressing. This point has been discussed previously and, as was evident, both these factors were utilised in establishing a linear relationship between nitrogen adsorption values and scattering values. The possibility remains that some areas inaccessible to nitrogen could exist in a bond between two crossing fibres, which could have been bonded at one stage, but have been disrupted at a later state of the drying, say, when the shrinkage and microcompression postulated by Page⁽¹⁹⁾ occur. Yet it is difficult to see why a bond that has been subjected to a more pronounced wet pressure should be more susceptible to partial bond breaking during drying.

Another possibility is that, as work-consuming processes other than bond breakage must occur simultaneously, the relationship between these processes and bond breakage would change by reason of beating and wet pressing, respectively. Increased beating would thus augment other work expenditures, whereas wet pressing would reduce them; but, as both beating and wet pressing change the structure of the paper more or less in the same direction, this explanation seems less probable. In this connection, a point previously referred to only in passing should be mentioned. When bonding strength values are determined by plotting the change in scattering against irreversible work, the straight lines of which the slope determines the bonding strength value do not pass through the origin, but intersect the work axis at a positive value. Testing points in this region are not very reliable, since the optical changes are extremely small. Nevertheless, in some cases, we have been able to obtain points that come very close to the origin and it can then be seen that there is a curved part of the plot in proximity to the origin. Of course, the results indicate that, when stretching a sample in the first part of the stress/strain curve, most of the irreversibly lost work is lost in processes other than breaking of the bonds. It has also been found that beating transfers the extrapolated crossing point of the straightline portion of the change in scattering coefficient against reversible work curve towards higher work values. For pulp beaten to a higher degree, therefore, more work is expended without the breakage of bonds. The effect of wet pressure is not equally well documented, although the trend is in the same direction. Consequently, if a relationship between change in scattering and irreversible work is calculated before the straightline portion is arrived at, there might of course be differences in the relationship between breaking and other work expenditures; since this is not the case and since the bonding strength is determined later, well in the post-yield region, this is not believed to be a factor in the variability of the bonding strength values.

As has been pointed out by Asunmaa & Steenberg,⁽²⁰⁾ the beating has an effect on the morphology of the fibres. After long periods of beating, the S1

layer may be partially or completely removed. It is thus possible in the sheet to find S1—S1, S1—S2 and S2—S2 contacts between the fibres, with the S2—S2 bonds dominating in the highly beaten samples. As a result, an increase in bonding strength may be explained as a transition from S1—S1 contacts to S2—S2 contacts. This naturally presupposes that contacts between S1 surfaces are inferior to contacts between S2 surfaces. A high wet pressure almost neutralises this effect, which would indicate that some of the surfaces broken in a heavily wet pressed sheet have been of even lower bonding strength than that of the unbeaten fibre. Some bonding in the lumen might have this effect.

In conclusion, there is a chance that the high pressure exerted locally on fibre-to-fibre crossings may exert a damaging effect on the bonding strength. Some of the effects discussed in the first part of the paper are of this nature. Washing out or aligning fibrils and highly swollen material in the high shear fields in the water pressed out from gaps between fibres may influence the degree of intimacy of the bonds. The damaging of the fibre wall, found by Annergren^(7,8) in the increased swellability, may have some effect and, finally, a phenomenon observed in electron micrographs that fibres that have been pressed against each other are permanently compressed may be a reason for stress concentration around the periphery of the bond. Evidence of some kind of real damage occasioned to the bonds by the application of greater pressures is found in the very interesting investigations carried out by Schniewind, Nemeth & Brink.⁽²¹⁾ In their experiments, pairs of fibres were bonded together under pressure and the shear strength in the joint was measured directly in an Instron tester. These authors found that increased pressure on the fibre crossing during drying reduced the shear stress. Their explanation was that the water squeezed from the area of overlap interferes with the formation of hydrogen bonding as drying takes place.

Other indications that an increase in bonding caused by wet pressing is less effective than a corresponding increase caused by beating has been found in many of the investigations discussed above. When bonds are formed between fibres, additional contact surface is provided by fine material moving into the receding water menisci, finally drying and increasing the radii of curvature in the bonds. This phenomenon, which was illustrated in some pictures given by Kärnä,⁽¹⁴⁾ does not occur of course when the surface of contact is increased by wet pressing. The possibility of crack formation starting from an angular rather than from a curved structure may thus provide an explanation of the difference in bonding strength between the wet pressed and beaten fibres. One final factor worthy of mention is that, in determination of the bonding strength for equal amounts of irreversible work, the sheet that has been subjected to greater pressure displays a higher maximum stress. It is possible

then that the local stress on the bondings that are stretched may be higher in the case of higher wet pressure. In this connection, a reference to the following statement by Campbell⁽²²⁾ may be of use—the energy per unit surface has little to do with the force required to separate them: this depends on how many bonds must be broken simultaneously. This statement could be reversed, which would mean that, if a few bonds are subjected to high stress, comparable energy consumption may not be observed for the whole strip.

An attempt has been made to analyse the value of bonding strength under various conditions, all of which lead to consolidation of the paper web. Although some of the results do not contradict previous findings that the bonding strength as measured by optical means is independent of beating and wet pressing, some important and significant exceptions have been found for certain types of pulp. No final explanations can be given, but it seems that both previous experience as reported in literature and the results of our own investigations appear to indicate that the way in which the bonded surface area is created has a definite influence on the strength of the structure. This applies both to the rupture strength and to the strength of the bonds between the fibres.

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ADDENDUM

IN ORDER to obtain a more detailed picture of the influence of beating and wet pressing on the breaking of bonds in paper subjected to loading and in particular on the local distribution of bond breakage in the test strip, a series of tests was performed.

By means of a scanning device with a small aperture, 3 mm × 5 mm, the reflection with a black background R_o along a strip of paper can be obtained. A certain wavy curve results, which by using the beta-radiography method of Tydeman⁽¹⁾ can be shown as very nearly depicting the mass distribution or formation of the strip (Fig. 8). If the scanning of the strip is continued also when the strip is stretched, a series of scans that gradually move toward higher R_o values will be obtained (Fig. 9). For a laboratory test strip made from a slightly beaten pulp, the increase in R_o is nearly uniform along the whole strip. If the strip is cut from a sheet made from a highly beaten pulp, however, the situation is very different. As can be seen from Fig. 10, the changes brought about by loading the strip are concentrated in those regions

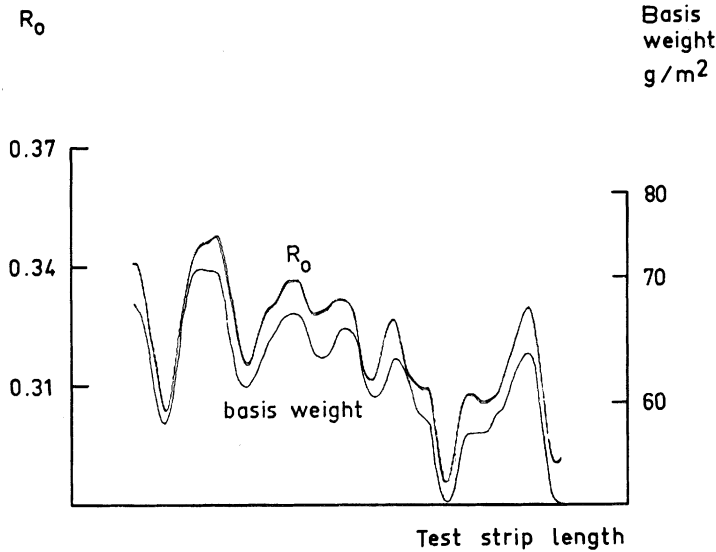


Fig. 8—Reflection curve and substance curve along a test strip

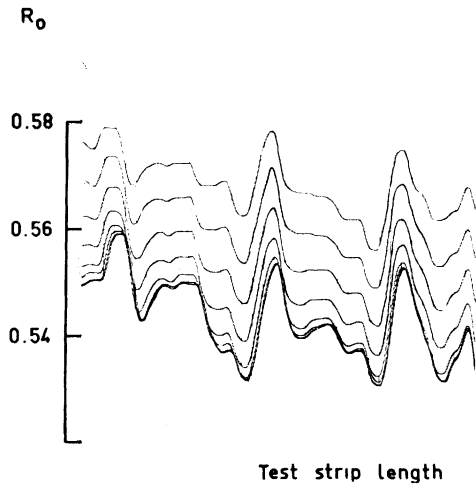


Fig. 9—Uniform increase in reflection along a test strip made from slightly beaten pulp when the strip is subjected to loading

of it at which the original R_0 value is low. A distinct levelling-off of the curve upon loading is clearly apparent. Similar experiments were then made with laboratory sheets that had been given a striped appearance by subjecting the wet sheets locally to high pressures with a grooved pressing plate (Fig. 11). This uneven wet pressure results in a definite pattern being superimposed upon the naturally occurring reflection curve. When these sheets are loaded and

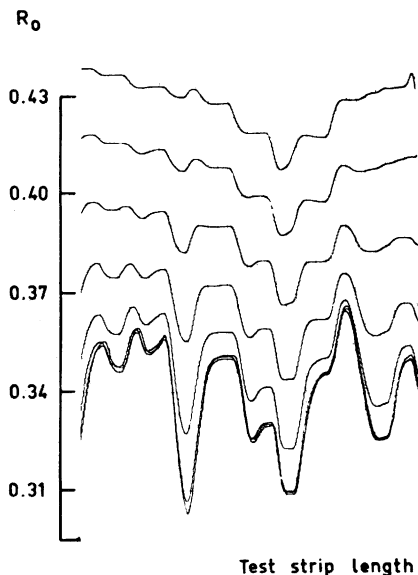


Fig. 10—Non-uniform increase in reflection along a test strip made from well-beaten pulp, when the strip is subjected to loading

scanned, it is discernible that the breaking of the bonds, as shown by the increase in scattering, is now concentrated in the highly wet pressed zones of the strip. These tests thus confirmed that bonds are more apt to break when a higher wet pressure is applied in sheetmaking. As in the quantitative investigations referred to in the main paper, it is possible in this instance, too, that the effect is more pronounced for highly beaten pulps than for those subjected to less beating. From these sheets, deliberately non-uniform in their wet pressing, it can be inferred that unintentional concentrations of wet pressure in certain parts of the sheet will cause the concentration of bond breakage in these same areas.

High rates of bond breaking are thus observed both in light substance regions of highly beaten sheets as in highly wet pressed regions. In both instances, local stress concentrations can be anticipated. For the highly wet pressed zones, the stress concentrations are mainly a consequence of the higher degree of bonding, which leads to a more unyielding structure and

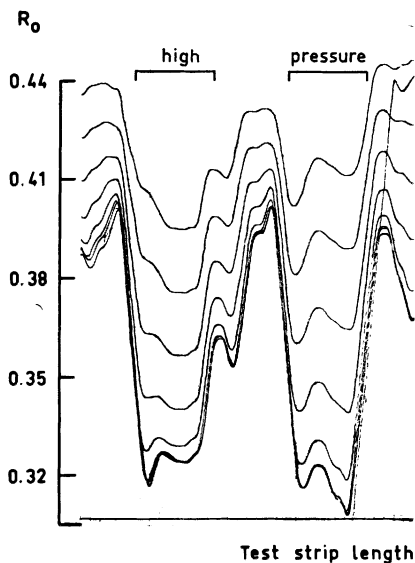


Fig. 11—The increase in reflection caused by loading is concentrated to the highly pressed zones of a test strip made from well-beaten pulp

fewer possibilities of stress relief on loading. For paper made from lightly beaten pulp, the bond breakage is more uniform with less influence exercised by local heterogeneities. Investigations are in progress in order to determine the conditions under which bond breakage changes from random to a more concentrated breakage at certain zones.

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Transcription of Discussion

Discussion

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

* 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

Discussion

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 $200 \text{ cm}^2/\text{g}$, 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 $200 \text{ cm}^2/\text{g}$.

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

* See also Foote, W. J., *Paper Trade J.*, 1939, **109** (25), 31–38

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 inter-fibre 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 cm²/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.

Discussion

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 absence 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† 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 $15\,000\text{ cm}^2$ and 10^7 fibres per gram, 1 per cent of retained loading gives the following results—

	<i>Titanium dioxide</i>	<i>Chalk</i>	<i>Precipitated 'chalk'</i>
Diameter	0.3	3.0	0.3
No. particles/fibre	1.4×10^4	30	3×10^4
Projected area of particles on a fibre/fibre area	1/40	1/170	1/17
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 $1\text{ cm}^2/\text{g}$; if 100 g/m^2 , it will be $100\text{ cm}^2/\text{g}$. 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^2/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

Discussion

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 whittings, 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

Discussion

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 \AA , 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 $35 \text{ \AA} \times 35 \text{ \AA} \times (200\text{--}400 \text{ \AA})$ 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^3 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

Discussion

carrying stress. Let the fraction of n' that are effective be n . Since we have assumed isotropic behaviour and uniformity, the cm^3 can be divided into n smaller cubes with a side l , each containing one bond: l will then be equal to $n^{-1/3}$. 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 α 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.† 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 \AA^2 , containing most probably a hydrogen bond, possibly a cross-linking molecule. At

* See, for example, *Tappi*, 1964, **47** (1), 1–6

† Nissan, A. H. and Sternstein, S. S., *Pure & appl. Chem.*, 1962, **5**, 131–146

‡ 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^3 taking part in sharing a stress. This number (at present defined by $E = 7\,600\, n^{\frac{1}{3}}$) 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