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Prepared contributions

Effect of filler on the structure of paper—R. R. Davidson, Welwyn Hall Research Association, Herts.

SCHWALBE⁽¹⁾ has discussed the loss of strength and gain in scattering coefficient on addition of filler to paper, also some effects of fibre unbonding by filler, but he supports Steele's assessment of the scattering coefficient of a paper filler as the difference between the scattering coefficients of the paper with and without filler. This assumes that the contributions of scatter provided by the fibre and filler are additive. Giertz⁽²⁾ also assumes this additivity.

This may be approximately true for titanium dioxide and pulp for which the pigment is in a reasonably deflocculated state. If it is not, the reduction of light scattering by the crowding together of the titanium dioxide particles will be the major effect controlling opacity.



For fillers with refractive indices close to that of the pulp, the assumption of additivity of the scattering coefficients is unlikely to be even approximately correct for a normally beaten chemical woodpulp. For loaded papers sized with ketene dimer with a polyelectrolyte retention ais, the scattering coefficient of sheets was non-linear with percentage filler content (Fig. 1).

If the scattering coefficients of pulp and fibre had been additive, this would

have been linear, but linearity was obtained when the scattering coefficient per unit *pulp* rather than paper substance was plotted (Fig. 2). This could satisfactorily be explained⁽³⁾ only if it is assumed that in these papers the direct contribution of the filler to opacity was quite small and that the important effect was an increase in the light scattering of the fibre due to the unbonding effect of the filler.



Fig. 2—Experimental paper: scattering coefficient s' per unit fibre and percentage of filler



This was suggested by the knowledge that the opacifying power of clay and carbonate fillers is indeed very small when the particles are surrounded by cellulose material of similar refractive index. It was confirmed by removal of filler from sheets loaded with natural chalk whiting by dissolving it out with hydrochloric acid in butanol. The opacity was little decreased and was notably greater than that of the unloaded sheet. In addition, the increase of scatter per unit filler addition was not constant, but increased with the degree of beating of the pulp.

Furthermore, a linear relationship was found between the scattering coefficient and the breaking length of sheets as the filler content was varied, other things being maintained constant (Fig. 3). This would be expected of the change in opacity is mainly due to fibre unbonding by the filler. The changes in the properties (scatter and strength) caused by comparable additions of different low refractive index fillers were very different, but, when plotted in this way, all the important fillers gave results almost lying on the one line. This



Fig. 4—Drying a single beaten fibre without and with filler

meant that paper with scatter and strength properties represented by any point on the line could be obtained by an appropriate addition of any filler. For equal cost fillers, therefore, the most economical in use will be what is *least* effective in altering the scatter and strength properties. Since low refractive index fillers are the cheapest components of paper, the more filler that can be included in a sheet of required opacity and strength properties, the cheaper the paper will be.

The model derived from the above and from the work of Kärnä⁽⁴⁾ is shown in Fig. 4. Evidence of fibre unbonding by filler particles and of a resulting increase in light scattering is shown on a photomicrograph taken by Page (Fig. 5 and 6).



Prepared contributions

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Dr D. L. Taylor, Monsanto Co., St Louis, U.S.A.

IT APPEARS to me that an important aspect of the long-standing question of optical versus mechanical contact of paper fibres has not received full consideration (page 914). What I refer to is the possibility that there exist, in paper, surfaces that are not in molecular contact, yet are nevertheless inaccessible to nitrogen molecules and do not scatter light. Nordman mentions this possibility in his discussion (pages 920–923).

At a level of resolution of, say, tens of Ångströms, the surface of a natural cellulose fibre is almost certainly quite rough. The discrete, microfibrillar structure of cellulose would seem to demand this. When two such rough surfaces are brought into contact by the acting surface tension faces, true molecular contact would exist only where microfibrils cross. Inaccessible 'pockets' or voids would thus be created within the region of 'optical bonding'. Mechanical refining of woodpulp with a high hemicellulose content might produce a redistribution of the hemicellulose that would result in a greater real molecular area of contact in the optically bonded zone.

Bearing on this problem are the microscopic observations of bond rupture presented by Jayme & Hunger at the 1961 symposium and the findings of Kallmes & Eckert on the relationship of geometric to nitrogen adsorption areas referred to by Algar (page 824).

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

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 cm²/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 cm²/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 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 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.

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[†] 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	1.4×10^{4}	30	3×10^{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 cm²/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 cm³ 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 cm³ 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 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 $Å^2$, 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**, 2048–2053, with erratum, *ibid.*, 1961, **57**, 1646

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 cm³ 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