BONDING IN PAPER SHEETS

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Summary

The bond strength has been defined as the energy required to break the bonds in a bonded area of unit size. A determination of the bond strength thus involves measurements of energy as well as of surface areas. Several methods for measuring the bonded area are reviewed and their limitations are discussed. For investigations carried out in the Finnish Pulp and Paper Research Institute, the optical method based on the Kubelka-Munk theory was employed. Following the concept that micro-breaks occur in a test strip during loading, the increase in the scattering coefficient of a sample subjected to a tensile test is believed to be caused by the breaking of bonds. A number of qualitative tests revealed a strong similarity between bond breakage and stress/strain behaviour of the test strip. Quantitatively, the bond strength was determined from the slope of the line depicting the relationship between the increase in scattering coefficient and the irrecoverable energy loss in a straining/ destraining cycle. The bond strength was found to be dependent on pulp quality. The values for the bond strength thus obtained agree as to the order of magnitude with other values reported in publications.

THE rupture strength of paper, as assessed by a conventional strength test such as a tensile test, is believed to depend on a number of factors, among which the following appear to be the most important. Since the fibres in a paper form a certain three-dimensional network in which the fibres are attached to one other, it seems logical to attribute the strength of the structure partly to the strength of the building elements or fibres and partly to the strength of the joints between the elements. As is the case in any joint, the latter property is, again, dependent on the area of contact and on the quality of the glue or, if

one employs papermaking vocabulary, on the bonded area and the strength of the bonds. When one considers that the strength of the paper is measured as rupture strength, which is essentially an average figure of the strength of weak spots that by chance fall within the area of the test strip, the fourth factor in the strength of the paper is the distribution of weak spots — in other words, the formation of the paper. This paper is in the main going to be concerned with the strength of the bonds and the way in which they break. Attention must be paid, however, to the extent of bonding and to the distribution of bonded areas, too.

The strength of a bond can be expressed as the energy required to break the bond, that is to say, the bond dissociation energy. When trying to determine the strength of the bonds in paper, it is of course impossible to separate and test single bonds: all measurements have to be carried out for the bulk material. In this case, it seems to be most useful to define the strength of the bonds in conformity with the definition of the strength of the single bonds, now taking the unit to be not one single bond, but a unit of bonded area. The strength of the bonds would thus be the energy required to disrupt all the bonds existing in an area of one unit. If the number of bonds per unit of bonded area is known, the average strength of a single bond can of course be calculated.

Part of the problem of measuring the bond strength is thus the question of measuring bonded areas or, in general, fibre areas. Bonded areas are usually expressed as a difference between total area and unbonded area and, consequently, there are two types of measurements to be considered — measurements of the total area of the pulp available for bonding in the papermaking process and, secondly, measurements carried out on the finished sheet to ascertain the unbonded area. In Parsons'[1] pioneering investigation, the specific external surface area of the fibres in a pulp suspension was determined according to a silvering method developed by Clark[2] and, following modifications, now accepted as TAPPI method T 225 m – 55. This method has been seriously criticised, for example, by Emerton,[3] on the grounds that one of the steps in the testing procedure (the silvering of the fibres) changes the property under test in such a way that the thin silver film covers crevices and envelops fine loosened fibre fragments and fibrils in a continuous silver layer, the surface area of which is smaller than the true existing area of the fibres. As a more suitable method for the determination of fibre area, Emerton suggested the water permeability method used by Robertson and Mason.[4] On these grounds, the specific areas obtained by Parsons are probably too small, at least so far as the more beaten pulp samples are concerned. Other methods

used for the measurement of specific external surface area of completely un-bonded fibres are the air permeability method used by Brown,[5] the dye absorption method used by Thode[6] and the nitrogen adsorption method used by Haselton.[7]

To measure the unbonded area in the paper sheet, Parsons used an optical method originally developed by Kubelka and Munk[8] and modified for paper by Steele[9] and Judd.[10] The Kubelka-Munk theory has subsequently been the subject of several articles, notably by Kubelka,[11] Van den Akker[12] and Stenius.[13]

Working on the assumption that only free surfaces scatter light, Parsons measured the scattering coefficient of the paper sheets and in this way obtained a measurement that was considered proportional to the unbonded surface area. In order to convert this measurement to units which were the same as those employed to measure the total external surface area of the pulp, Parsons made virtually unbonded sheets by forming them in butanol. The scattering coefficient of these unbonded sheets, in which the total surface area contributed to the scattering, was thus directly comparable to the surface area figures obtained in the silvering tests. A plot of scattering coefficient of unbonded butanol sheets taken against the specific external surface area of the fibres in water suspension thus offered a possibility of graphically converting the optically measured areas into 'silvered areas' and Parsons concluded that this relationship should be essentially linear, as is shown in Fig. 1. The same diagram shows the results of a similar test carried out in our institute.[15] As can be seen, the results agree reasonably well and are also in agreement with results reported by Ratliff.[14] As a comparison, the results taken from Haselton's investigations[7] also show a linear trend between optically measured surface area and surface area measured by the nitrogen adsorption technique. In this case, the slope is of another magnitude, due no doubt to the different capacities of the silvering technique and the gas adsorption technique to detect details in the surface structure; but it might also depend on the fact that Haselton's scattering coefficient figures are determined for water-dried sheets and not for butanol-dried sheets.

It cannot be taken for granted that optical contact always involves mechanical contact. It could thus be assumed that the optical method is not capable of detecting fibre surfaces as free surfaces, if they are separated by a distance smaller than a certain fraction of the wavelength of light. On the other hand, a wavelength of light is incomparably larger than the span of the bonds regardless of the type of bond.

Nevertheless, the linear relationship between scattering coefficient and surface area shown in Fig. 1 and particularly the results published by Haselton very strongly suggest that the scattering coefficient is a function of the free surface area.
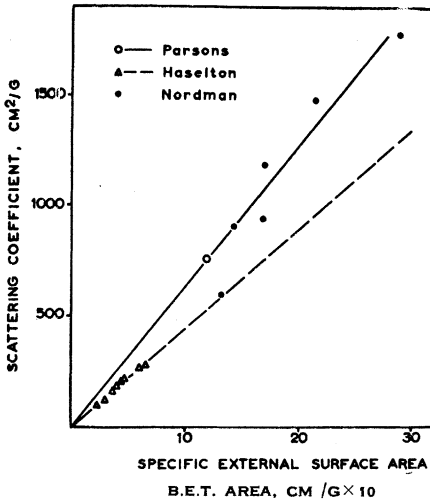

Fig. 1—Relationship between scattering coefficient and surface area, as obtained by the silvering technique (Parsons, Nordman) and the nitrogen adsorption technique (Haselton)
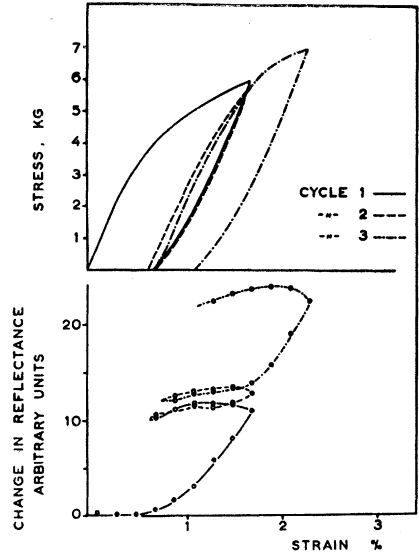
Fig. 2—Comparison between a stress/ strain curve and the corresponding curve, showing the change in reflectance

Another observation which supports the assumption that the optical method is able to measure free surfaces is the commonly known fact that the scattering coefficient of a sheet is virtually independent of the degree of static compression of the sample in the dry state. Dry compression is not believed to increase mechanical contact and neither does it, at least at moderate pressures, increase strength. On the other hand, it must be assumed that, since the fibres are brought closer to each other, some of the fibre surfaces, which prior to the compression were separated just enough to cause scattering, after compression must have approached one another so as to have passed the assumed limit of no scattering. As, however, the scattering does not decrease, it must be assumed that either the limiting distance is much closer to the distance of bond separation or that the distribution of distances between

fibres is such that there is an extremely low proportion of distances which fall within the bond separation/wavelength of light range. Even a comparatively extensive compacting of the sheet in the latter case will not bring appreciable fibre areas into such proximity as will prevent scattering.

It is true that the evidence in favour of the scattering coefficient being a measurement of unbonded surface area is only circumstantial. On the other hand, no evidence has as yet been brought forward to prove beyond any reasonable doubt that it is not. In this, as well as in many other investigations, the optical method has accordingly been employed as a useful means of measuring what is believed to be the unbonded fibre area. Other methods have also been employed, as for example the air permeability method, but the most interesting development is that recently described by Haselton,[7] the application of the nitrogen adsorption method to paper. This method appears to give new possibilities of determining the actual size of the bonded area and there are in Haselton's article some estimates of the bonded area, which substantiate the assumption by Nordman and Gustafsson[16] that the difference between the total area measured when the fibres are in a wet and highly fibrillated state and the unbonded area in a dried paper yields a value of the bonded area, which includes areas not effective from the point of view of strength. In other words, the total surface area of a pulp exposed in a water suspension and the surface area of butanol-formed sheets are both too high; this is not necessarily so because of experimental errors, but because part of this highly fibrillated surface will form bonds, which will not be engaged in carrying stresses in a strength test. The surface area from which to subtract the unbonded area, so that one may obtain the true bonded area should consequently be the external area of dried, unbonded fibres. Haselton tried to measure this area by carrying out nitrogen adsorption tests on spray-dried fibres, but concluded that this area was, by reason of fibre losses and some bonding, probably too small. Nevertheless, the results made it possible to estimate a range within which the dried external surface area would fall. As a correction factor to be used in order to calculate the dried external area from the area obtained by the silvering method or to calculate the scattering coefficient of dried unbonded fibres from the scattering coefficient of butanol-dried sheets, Haselton suggested a value of 0.67 – 0.68. This is fairly close to the value of 0.59 obtained by Leech.[17]

In order to avoid the still existing uncertainties involved in the measurement of bonded areas, the present approach to calculation of the strength of the bonds does not depend on an exact figure for the bonded area, but takes into account only those changes in the bonded area of a given paper that

occur when bonds are broken. Before proceeding to discuss this method and the results in detail, it is necessary to consider at some length the use of rupture strength measurements in connection with determinations of the bond strength. In accordance with the definition of bond strength, this should be given in terms of energy and not in terms of force. We were therefore of the opinion that all treatments involving rupture strength determinations, useful as they are from a practical point of view, do little to bring much further forward the question of the bond strength.

There are, however, reasons to avoid a rupture strength value other than that set by the definition. If it is intended that the strength of the bonds be measured, no other effects should be allowed to influence the measured value. It has however been found by Graham[18] that an appreciable number of fibres are broken in the zone of rupture when the tensile strength of paper is being tested. Fracture of the test strip is therefore not only associated with the breaking of bonds, but also with the breaking of fibres, which in this connection is certainly not a desirable feature.

Our approach towards investigation of the strength of the bonds in a paper therefore rests on two principles. Firstly, the strength should be measured in terms of energy and, secondly, only such bonded areas as are actually broken up should be considered. As it was found that the scattering coefficient, measured for a paper strip which had been subjected to a tensile test, was higher subsequent to the tensile test than before it and since an increase in scattering coefficient or free surface area is equivalent to a corresponding decrease in the bonded area, it was assumed that bonds were broken in the test strip. If the testing procedure could be arranged in such a way that the energy required to break a certain number of bonds could be measured, this would afford a means of calculating the strength of the bonds.

Before discussion of the quantitative determination of the bond strength, a few qualitative relationships between bond breaking, as assessed by the decrease in bonded area and the stress/strain behaviour of paper, should be demonstrated.[19] If a test strip, while mounted directly over the aperture of a reflection meter, be subjected to a stress/strain test involving cycling, it is discovered, as in Fig. 2, that the stress/strain curve and the curve showing the changes in R_o are very similar in nature. The scattering commences to increase at about the same strain value as that at which the stress starts markedly to fall off from the tangent of the first almost straightline portion of the stress/strain curve — that is to say, in the region where the irrecoverable portion of the energy imparted to the strip starts to grow at an increasing rate. The scattering rapidly increases until the direction of straining is reversed.

When destraining the strip, the scattering continues to increase, although at a slower rate and, finally, when the stress/strain cycle is nearly complete, it begins to decrease slightly. When repeating the cycle to the same percentage of strain, the increase in scattering is small, as is the energy loss in the strip. In a successive cycle to a higher strain value, a considerable increase in scattering is again noted.

The increase in scattering after the commencement of destraining is very interesting, in that it suggests that bond breakage is time-dependent in the same way as is relaxation under destraining. In another pure relaxation test, at constant strain, the decrease in bonded area was very clearly observed (Fig. 3).
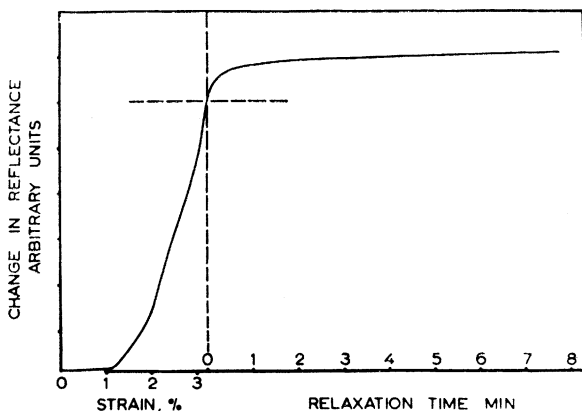

Fig. 3—Change in reflectance caused by straining and subsequent relaxation at constant strain

The cycling tests indicated that, although a slight decrease in scattering was observed toward the end of the destraining, the increase in free area was, on the whole, irrecoverable, which means that the broken bonds did not reform to any appreciable degree. Moreover, it was found that when cycling a strip according to a given programme, the decrease in bonded area, as measured by the increase in scattering after each cycle, was proportional to the energy loss in the cycle in question and, of course, the total decrease in bonded area proportional to the sum of energies lost in different loading/deloading cycles (Fig. 4).[20]

When, as has been described, the paper test strip is subjected to loading over the aperture of the reflection meter, it is of course possible continuously to record the changes in scattering during the whole of the loading or the
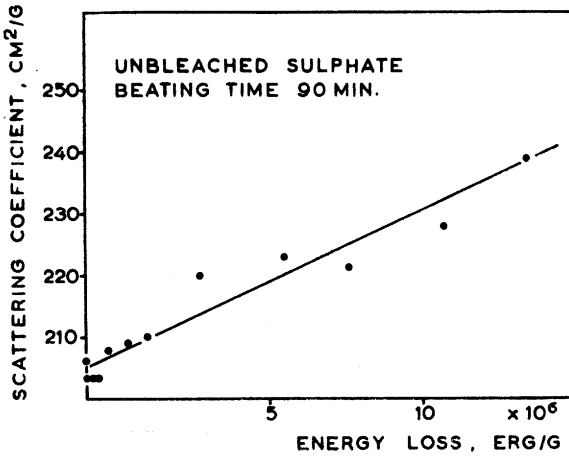
Bonding in paper sheets

Fig. 4—Relationship between scattering coefficient and energy loss when a strip of a laboratory sheet has been subjected to several consecutive straining/destraining cycles
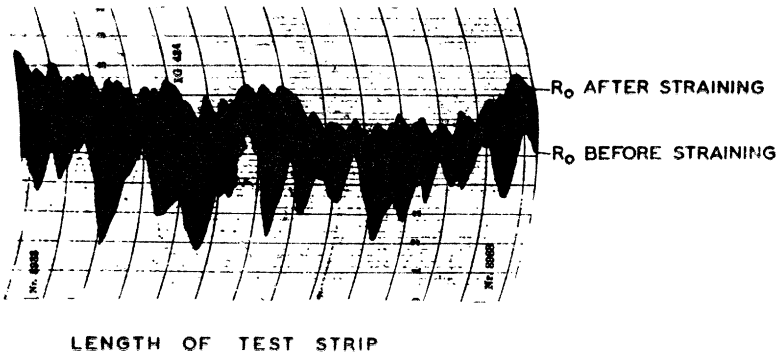

Fig. 5—Recorded reflectance curves, showing the irregular increase in reflectance in different locations of a test strip of bleached sulphite pulp after a straining/destraining cycle very close to final rupture of the strip

deloading process. The bond breakage can thus be followed in detail for the particular part of the strip covered by the aperture of the optical instrument. What happens in other parts of the strip, however, cannot be assessed by this technique. Nevertheless, since the energy is consumed by the whole length of the strip, it is important to have a value for the bond breakage that is representative of what happens in all parts of the sample. The reflection value R_o was therefore recorded for the whole length of the strip and, subsequent to the strip having been subjected to a straining/destraining cycle, the same value was again recorded (Fig. 5).

These two curves, when compared with each other, revealed some important facts. It was found that the increase in R_o, which can be shown to be closely related to the change in scattering, was by no means constant over the length of the specimen. It was normally found that in areas in which the virgin strip had a low R_o value — that is to say, in areas where the strip had a low scattering coefficient — the bond breaking was more extensive than in areas with high R_o values. It is thus evident that bond breakage does not
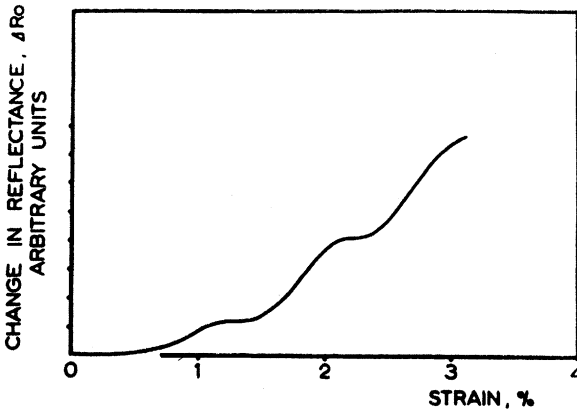

Fig. 6—Irregular increase in reflectance for one particular area
of a test strip subjected to straining

occur uniformly over the whole sample, but that certain areas are more susceptible to loading. If one judges from the low R_o values, these areas are most probably thinner areas than are the surrounding ones. On the other hand, it was sometimes found, when during a period of straining the breaking of bonds was followed for one particular area, that the increase in scattering did not follow a smooth curve, but had a wavy appearance (Fig. 6). It is not believed that this is caused by disturbances in the measuring system, but has

been interpreted in the following way. The test strip consists of a multitude of local areas with different properties in respect of their resistance to straining. Bond breaking in one location immediately changes the stress distribution pattern in surrounding areas. It is therefore conceivable that a period of rapid bond breakage in one area may eventually establish a more favourable structure in that location and, as a consequence, the rate of bond breakage decreases. When this discontinuous bond breakage in a given location is taken in combination with the previous finding that at constant time there is a discontinuity in bond breakage with regard to location, it can be thought that the loading causes a very complex pattern of bond breakage. It is therefore most important to carry out all measurements so that the values of energy and bond breakage are obtained for corresponding sample dimensions and also that they are taken at times which correspond.

The testing procedure that was developed for quantitative determinations of the bond strength was described in detail in a previous paper[21] and consists in determination of the scattering coefficient of a paper strip before and after the strip has been subjected to a straining/destraining cycle. The increase in scattering is plotted against the energy lost in the cycle per gram of paper. This test is repeated with other strips of the same paper, each strip being subjected to a different straining cycle. The line of best fit is calculated and the slope of the line gives the relationship between the bond breakage and the irrecoverable energy loss.

When the strength of the bonds is calculated from the slope of the line, it is believed that there will be eliminated those energy losses which are not associated with bond breakage. In fact, the line intersects the energy axis, indicating a small energy loss of this type.

The strength of the bonds is given in terms of the energy required to decrease the bonded area by one unit of scattering coefficient. Since the energy is expressed in erg/g. and the scattering coefficient is expressed in cm.^{2}/g., the dimension of the bond strength is erg/cm.^{2} However, it should once again be emphasised that cm.^{2} in this case means optically measured surface area and not true surface area. By the introduction of a proportionality factor, the strength of the bonds could also be expressed in terms of true surface area.

One of the results obtained of special interest is that beating does not affect the bond strength, as can be seen from Fig. 7. In this diagram, results are plotted for sheets made after various times of beating of the pulp, sheets of unbeaten pulp being excluded. The reason for omitting the unbeaten sample is a purely practical one; the strength and, correspondingly, the energy loss of such sheets is so low that the change in scattering coefficient is of the

same order of magnitude as the variability of the test. All other points, however, regardless of the degree of beating, fall on a common straight line. It would thus appear that the reason for an increase in tensile strength with beating, for instance, is not a question of increased bond strength, but of increased bonded area and in certain cases of improved formation only.
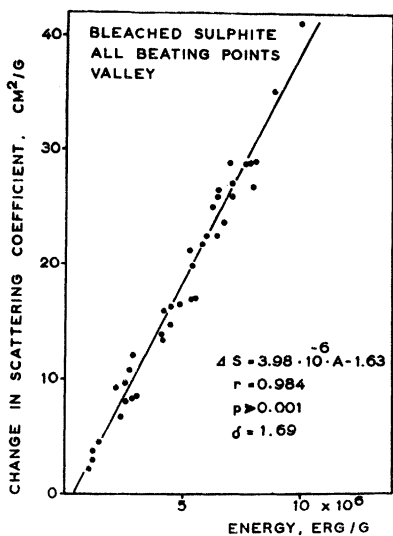

Fig. 7—Quantitative relationship between change in scattering coefficient and energy loss in a straining/destraining cycle: all points, regardless of degree of beating of the pulp, are grouped along the same straight line
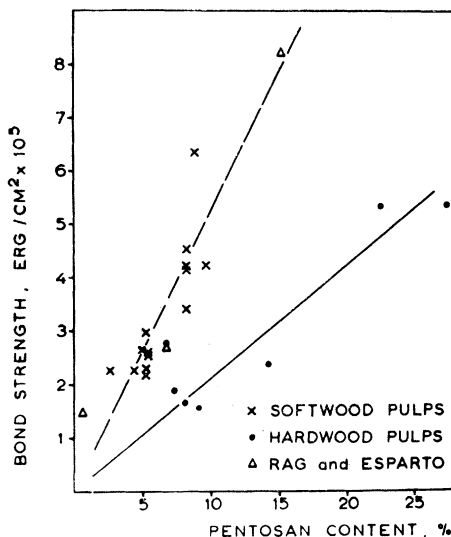
Fig. 8—Relationship between bond strength and pentosan content

Various pulp qualities, nevertheless, gave different results for the strength of the bonds. A fair correlation was found between the strength of the bonds and the pentosan content of the pulp (Fig. 8). The bond strengths of hardwood pulps and softwood pulps, however, form different curves as a function of the pentosan content, the hardwood pulps forming a group below that of the softwood pulps. The results indicate that increasing amounts of hemicellulose increase the strength of the bonds, but that hemicelluloses in hardwood pulp are not as effective as are the same quantities of hemicellulose in softwood pulp.

The strength of paper has generally been attributed to the existence of hydrogen bonds between the fibres and, in this case, it could be expected that

the bond strength should be more uniform than was found to be the case in this investigation. As the bond strength, however, is calculated per unit of bonded area and is in fact a product of the strength of single bonds and their number per unit area, it can be assumed that the number of bonds per unit area differs for different qualities of pulp. One factor affecting the number would thus be the amount of pentosans, the other factor being the quality of the hemicelluloses. In an investigation by Saarnio, Wathén and Gustafsson,[22] it was in fact found that xylan from birchwood pulp is branched, which could perhaps explain the lower number of formed hydrogen bonds for a given quantity of hemicellulose.

The values found for the strength of the bonds fall in the range of $1.6 \times 10^5 - 8.2 \times 10^5$ erg/cm.^{2} In this connection, it is interesting to compare these values with a value for the bond strength reported by Corte.[23] This value was arrived at by the following test procedure. Strips of paper were tested in a recording stress/strain instrument and the rupture energy was calculated from the area under the stress/strain curve. By testing strips of different length and by plotting the energy against the specimen length, Corte could arrive by extrapolation to zero length at an energy value which was considered representative of the zone of rupture. By dividing this value by the weight of the sample in the zone of rupture, which was calculated on the assumption that the zone of rupture was 1.5 times the average fibre length, the strength of the bonds in a paper of medium strength made from a spruce sulphite pulp was found to be 197 cm.kg./g. In order to compare this value with those obtained by the optical method for spruce sulphites, namely, (2.94×10^5), (2.16×10^5) and (2.23×10^5) erg/cm.^{2}, it is necessary to assume a value for the bonded area in optical area units. As the paper was of medium strength, a value of 350 cm.^{2}/g. seems to be a fair assumption. This yields a value of 0.562 cm. kg./cm.^{2} or roughly 5.5×10^5 erg/cm.^{2}, which is only $1.9 - 2.5$ times the bond strength values obtained by the optical method. By the employment of a deuteration technique, Corte found that the production of the paper from the corresponding pulp was associated with a 1.4 per cent. decrease in the number of free hydroxyl groups. The mean energy of the hydrogen bond was calculated from spectroscopic data and found to be 4.5 kcal./mole. This gave a theoretical value for the rupture energy of 49.8 cm. kg./g. If this value is converted to energy per optical bonded area, employing the same assumptions as before, the theoretical value would be 1.4×10^5 erg/cm.^{2}, which is roughly half the experimental value obtained by the optical technique. When one considers the approximations in conversion of the values the agreement is fairly good.

Another very interesting possiblity of comparing the optically measured bond strength with the energy of the hydrogen bond will be discussed. Nissan [24] has derived an equation for the stress/strain curve when a hydrogen bonded material is subjected to strain. Young's modulus E, as well as a secondary elasticity coefficient K appearing in the empirical equation are both given in terms of hydrogen bond parameters. From the value of Young's modulus for a given sample, there can be calculated the number of hydrogen bonds per cm.³ being subjected to stress. The use of this equation was suggested by Nissan [25] in order to check whether the number of stress-carrying hydrogen bonds decreased at the same rate as the bonded area decreased when cycling a paper sample in a stress/strain instrument. It was, however, impossible to take graphically from the stress/strain curves the appropriate values with the accuracy required to detect the small changes in the number of bonds. On the other hand, there could be satisfactorily determined an estimate of the order of magnitude of the number of hydrogen bonds engaged. For a special set of laboratory sheets, made from a bleached spruce sulphite pulp and beaten in a Valley beater to various degrees of wetness, the bond strength was determined in the usual way and it was found to be 2.6×10^5 erg/cm.² A similar set of sheets was also made from birch sulphite pulp and the bond strength was found to be 1.9×10^5 erg/cm.² In addition to the normal water-formed sheets used for the determination of the bond strength and for calculation of the number of hydrogen bonds according to Nissan, sets of sheets were formed in benzene with the purpose of determining the bonded area expressed in optical units.

For the calculation of the bonded area, the previously mentioned correction factor of 0.67 given by Haselton was used to convert the scattering coefficient for the benzene-formed sheets into a value applying to unbonded dried fibres.

If we suppose that all bonds are of uniform energy and that they are equal to the value 4.5 kcal./mole the number of bonds per sq. cm. of bonded area can be obtained by dividing the bond strength value by the energy of a single bond. With the knowledge of the bonded area per gram and the specific gravity of the sample, this value can be converted to correspond to the number of bonds per volume, which again can be directly compared with the number of bonds obtained by Nissan's method.

These values, plotted against each other in Fig. 9, show a remarkable correspondence and, even if the exactitude naturally depends on the choice of the factor for converting the scattering coefficient of benzene-formed

sheets to that of unbonded dried fibres, a change in this factor could never change the order of magnitude of the number of bonds.

Another observation which can be made is that the number of bonds per volume increases with beating, due in part to the fact that the bonded area increases partly because of the increase in weight of cellulose within a given volume of paper. This is, of course, one reason for the increase in rupture strength when the beating time is increased.
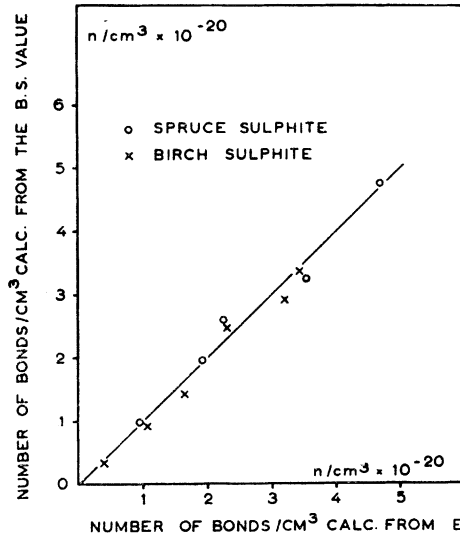

Fig. 9—The calculated number of bonds per c.c. in sets of sheets made from bleached birch sulphite and bleached spruce sulphite beaten to various degrees of wetness

Prerupture behaviour of paper under stress has been explained by Rance[26] as being dependent on a disruption of bonds in the structure of the paper and the same line of thought is the basis for the mathematical treatment by Nissan[24] who postulated that the different phases of the rheology of hydrogen-bonded materials can be explained by changes in the number of hydrogen bonds undergoing strain. The investigations of the optical changes in a paper under stress have, as a result, yielded the fact that a number of phenomena in the stress/strain behaviour of paper are parallelled by similar phenomena in the scattering properties of the paper.

Since a change in the scattering coefficient indicates a contrary change in the bonded area, these tests seem to corroborate the theoretical investigations.

The optical method has also been useful for a quantitative estimation of the bond strength expressed in terms of energy per bonded area and the values obtained appear to be in reasonable agreement with other calculations of this very important property of a pulp.

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DISCUSSION

DR. J. A. VAN DEN AKKER: In my opinion, the work of Mr. Nordman and Dr. Gustafsson and their colleagues during the last several years has been outstandingly good and of great significance, certainly of interest to everyone working in the field of mechanical properties. Of great significance, because, until we know the importance of interfibre bonding and the breaking of bonds between fibres, we cannot even begin to create a theory concerning the mechanical properties of paper.

Mr. Nordman, I think, has used the breaking of bonds in a rather general sense, but my feeling is that the specific reference was to the breaking of bonds between the fibres. From our point of view, there are various interpretations that can be placed on observations of the sort Mr. Nordman has presented to us today and published with his associates in the past. The first is that there can be interfibre bond breaking. The second, a suggestion made by Dr. Valley of the Eastman Kodak Co. in Rochester, is the possibility that, as a sheet is stressed, unbonded fibre elements that happen to be close enough to each other to give rise to what we call optical contact may be further separated, thus causing an increment in the scattering coefficient. Incidentally, we have some information to the effect that the thickness of a sheet increases rather than decreases when the sheet is stressed. This could be a sign of bond breaking between the fibres; also of simple separation between the fibres without the breaking of bonds.

The third possibility is that the individual fibres exhibit an increase in light scattering when stressed. We do not yet have much evidence for this. During his thesis work, Howard Leech made the interesting observation that fibres dried by the solvent exchange process scattered much more light (magnification $\times$ 200 with dark field illumination) than water-dried fibres. This shows that the expanded system of a fibre can scatter light, presumably because of the rupture of intrafibre bonds. Now, when a fibre is stressed, we may open up the structure of the fibre sufficiently to cause some change in the amount of light scattered by the fibre. I think that, tentatively, we have to admit all these possibilities; then it is just a question of the relative importance of the several mechanisms in particular cases. Obviously, if one has a poorly bonded sheet, there will be extensive bond breaking. If one is dealing with a sheet prepared from well-beaten pulp, the amount of interfibre bond breaking would be much less and possibly the amount of intrafibre bond breaking much more.

We are at present working on the scattering of light from individual fibres that are under stress, but do not have enough data yet to report. It has been quite a job, as you might imagine, to arrange apparatus sufficiently steady and sensitive to do this. This involves a photomultiplier tube and an optical system that enables one to see where the fibre is in relation to the zone of illumination. In our earlier apparatus, the fibre moved relatively to the illuminated zone and we got changes in the amount of light scattered that were clearly spurious. We hope to complete these and other refinements and be in a position in another year or so to report some data.

MR. J. BOS: In Mr. Nordman's paper is given a detailed survey of the significance of the scattering coefficient of normal and butanol-formed sheets for the determination of the unbonded and the total surface of fibres in paper. He mentioned also uncertainties involved in the underlying assumptions, especially raised by the work of Haselton.

Recently, we experimented with butanol sheets and this may give further justification of and reasons for the correction factor applied on the *s* values of butanol sheets by Haselton, Leech and Nordman.

The experiments were performed on a bleached softwood sulphate pulp, beaten to 26° S.R. The scattering coefficient of the normal sheets is 210 cm.²/g.; for the butanol sheets it is 930 cm.²/g. We calendered the butanol sheets in a laboratory calender and to our surprise the *s* value decreased considerably, depending on the pressure applied, until a value of 400 cm.²/g. was reached. Calendering of the normal sheets gave only an insignificant fall in scattering coefficient, down to 200 cm.²/g.

Influence of calendering on sheets formed in different media

Medium	Scattering coefficient, cm.²/g.		Burst factor		Relative pressure applied in calendering
	O	*C*	*O*	*C*	
Water	210	200	48	50	1
Acetone/water (1 : 1)	270	250	37	42	1
Acetone/water (3 : 1)	370	350	21	22	1
Butanol	930	400	(6)	12	1
		470		11.5	$\frac{3}{4}$
		690		8.5	$\frac{1}{2}$
		780		7.5	$\frac{1}{4}$

O = original   C = calendered

The explanation of this decrease in the *s* value of the butanol sheets could, to our knowledge, only be that the bonded surface area of the fibres had increased considerably and, therefore, also the strength of the sheets.

Determination of the bursting strength gave the values in the following table. The decrease in scattering coefficient of the butanol sheets through calendering is not accompanied by a corresponding increase in bursting strength.

To get some intermediate values, we made sheets in acetone/water mixtures (1 : 1 and 3 : 1). With these sheets, there is only the same slight effect of the calendering on the values of the scattering coefficient and the burst factor (*see* table opposite).

By plotting the scattering coefficient against the burst factor, all measurements (except those made on the original butanol sheets) fall on a straight line, which gives the real change in bonded surface area with strength. Through extrapolation to zero burst factor, we get about 500 cm.²/g. for the *s* value of the unbonded sheets (*see* Fig. **R**). The *s* value of the butanol sheets was 930 cm.²/g. The ratio of these two values is again this correction factor, in this case 0.55, which is about the same as that given by Haselton and Leech. More experiments should be performed to obtain a reliable value.
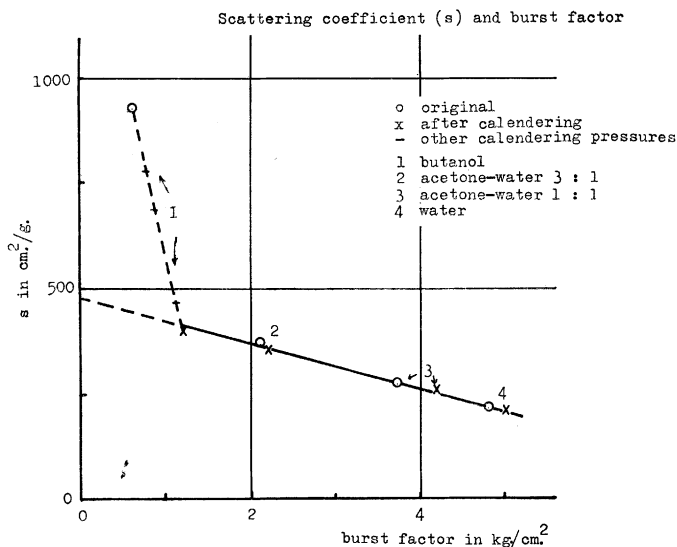
Fig. R

One thing has still to be explained — what is happening in calendering a butanol sheet. Here, water again comes into play — a substance we always need in our bondmaking activities. Evidence of this was obtained from our last experiment. We dried regular butanol sheets in an ordinary drying oven at 100°C and calendered the sheets immediately on leaving the oven. Now the scattering coefficient decreased only to about 650 cm.^{2}/g. and the burst factor increased to 8.

Our conclusions on this subject are that the correction factor, first applied by Haselton and later by Leech and Nordman, is no longer a suspect figure to multiply the *s* values of butanol sheets. In calendering butanol sheets, the amount of water present in the air-dry condition is sufficient to close the light-scattering surfaces produced by internal fibrillation. These surfaces do not contribute to paper strength.

MR. L. NORDMAN: I think this is perhaps a very good explanation. The butanol sheets are very porous in structure and very heterogeneous. We have, in some other cases, observed that when we compress such a sheet (putting the same material in a smaller volume), then the scattering coefficient can change, even if nothing else happens to the structure. For instance, we have observed this, even for water-dried sheets, provided the pulp is unbeaten and very weak (for example, an unbleached aspen sulphite pulp). There was first a slight increase in the scattering coefficient upon calendering; after that, a decrease without changing the other properties of the sheet at all.

MR. O. ANDERSSON: What we have here, including Mr. Nordman's paper, will convince us that measurement of light scattering is a good tool for understanding something about the internal structure of an assemblage of cellulose fibres.

In this paper, I have found quite a few so-called Brask scraps. The author states that the evidence in favour of the light scattering coefficient being a measure of the unbonded area is only circumstantial. I would like to call it ambiguous, although it is not easy either to prove or disprove the statement. What is critical in changing the light scattering properties is the intrafacial distance. The critical distance will have an order of half or quarter of a light wavelength. As soon as an intrafacial distance passes this critical value, a change in light scattering will occur. Now, this distance is of the order 1 000 — 2 000 Å, but the critical distance in forming hydrogen bonds (which I think we will agree is the pertinent type of bond here) is of the order of $\frac{1}{100}$ — $\frac{1}{500}$ of that. That there is a change in light scattering — that is, an intrafacial distance passes its critical value — does not necessarily

mean that a bond is broken. The two occurrences might, of course, be proportional to one another.

In considering the diagrams that are put forward here, I have tried to find out whether I could become convinced that the change in light scattering during straining is proportional to strain or to energy. If we compare Fig. 4 and 7, we have the relationship between scattering coefficient and energy lost. In one case, scattering is plotted against energy and, in the other case, against strain. To me, the comparison of these two pictures is by no means exclusive on the question of linearity with energy or strain.

Fig. 2 also relates scattering to strain. This certainly does not suggest a linear relationship between the two quantities at a first glance, but, if we disregard all contraction branches and only consider the main strain branches, I think the linear approach is justifiable.

We must remember that, as soon as we commence cycling, relaxation phenomena, time delay functions, etc. will occur in the structure. These might well explain the deviation of the general linear relationship between strain and optical properties. The author has obtained a straight line by plotting energy instead of strain; but, in Fig. 3, the first branch suggests a fairly linear relationship between light scattering and strain. On the right, where the horizontal axis represents time — this is a relaxation procedure — there is a change in light scattering, although no energy change in the previous sense is involved, because of constant strain.

I would also like to comment on the agreement between measurements of the number of bonds per unit volume according to the theory put forward by Nissan and according to the present light scattering hypothesis. The agreement shown in Fig. 9 is far too good to be true, especially when considering all the hypothetical assumptions made. The Nissan theory implies that the bond density is proportional to the third power of the elastic modulus. If the method of calculation described in the present paper is written mathematically in terms of the variables involved and these variables are expressed in terms of elastic modulus, the result is a third power law of elastic modulus. The agreement may therefore only be ostensible.

MR. NORDMAN: I will answer the last question first. I have never tried to relate quantitatively the increasing scattering to anything but energy. The fact that I have produced curves showing the qualitative relationship between scattering and strain is because the experimental design could not give the energy value: I only got the scattering as a function of the strain.

In that connection, I should answer also the question about Fig. 3. There are no missing points, because there are no points; it is a curve obtained on a recorder.

I think I have already answered the question about Fig. 4 and 7. Their relationship is between scattering and energy, not between scattering and strain. The fact that we have produced curves relating scattering to strain is merely because we could follow the increasing scattering as a function of time with our recorder.

In Fig. 2, we have again produced the same type of curve. In this case, too, I believe the increasing scattering is related to the energy and not to the strain.

MR. C. R. G. MAYNARD: Work started sometime ago in our Glory Mill laboratory and carried on in one of our other laboratories may be of interest in connection with Fig. 5 and 6 in Mr. Nordman's paper. It concerns the variation in opacity produced along a strip when the strip is under strain. If a strip of transparent paper (or opaque paper that has been transparentised with a solvent or wax) is strained, two systems of opaque parallel lines that form a criss-cross pattern appear. The angles between the two systems and the strip direction depend on the angle of the strip to the grain of the paper and the type of paper. We believe that these lines are caused by higher strains occurring at these opaque parts.

A weak spot in the material causes strains beyond the 'yield point' and consequent opacity from bond breaking. The strain occurs in a line across the strip and the angle of this line is determined by the mechanical constants of the material. The severity of this opacifying effect varies over the strip and increases first in one place and then in another. This would seem to have some bearing on Fig. 6.

MR. NORDMAN: I have no comments, Mr. Chairman.

DR. I. JULLANDER: In Fig. 8 of his paper, Mr. Nordman shows that there is a difference between hardwood and softwood pulps in the relationship of bond strength and pentosan content. Which types of hardwood pulps are represented in the diagram?

I do not think the difference in specific bond strength between softwoods and hardwoods must necessarily be explained as a consequence of the chemical composition of the hemicelluloses. In paper manufacture, different carbohydrates and carbohydrate derivatives can often replace each other. It is, for instance, known that starch and carboxymethylcellulose can both be used in the manufacture of coated paper by means of a size press. The

difference in chemical structure between starch and carboxymethylcellulose must be much larger than can be expected between two types of hemicellulose.

Recalling Dr. Lange's paper yesterday, there is another possible explanation. At the same average hemicellulose (pentosan) content, the distribution across the secondary wall might be different for softwoods and hardwoods. There is no proof for this assumption in Dr. Lange's paper, however: it seems to me that his studies show us the only way to connect physics and chemistry in the study of fibre bonding in paper. I would like to ask if we can expect more results along these lines either from Dr. Lange himself or from somebody else who has taken up this type of research.

DR. P. W. LANGE: In answer to Dr. Jullander, most of my earlier work was done on spruce and, since during that time we had difficulty in collecting a sufficient amount of data, I have no detailed information about the hemicellulose distribution in different types of birch pulp. Therefore, it is not so easy to compare the two types, birch and spruce. In addition, absolute distribution curves for pulps of different wood origin are very difficult to compare, but I have a feeling that on the surface of birch fibres there is relatively more hemicellulose than on the surface of spruce fibres. Concerning the future, I hope that, with the new type of interference microscopy and with new data-collecting methods, I will be able to answer your question better the next time you ask it.

MR. NORDMAN: The woodpulps we used are all commercial pulps and, among the hardwood pulps, we used aspen pulp and birch pulp. The pulps are sulphite or sulphate or unbleached. That proves that the material is not very homogeneous and other effects can, of course, be possible.

DR. VAN DEN AKKER: In Mr. Andersson's criticism connected with Fig. 3 of Mr. Nordman's paper, he pointed out that for the relaxation portion of the figure there was no energy expenditure. This is true, there is no energy expended by the apparatus; however, if I understand the experiment, the strip of paper possessed strain energy at zero time and it seems to me quite likely that some of the strain energy was transferred to bond breaking — if, indeed, there was bond breaking in the process. In other words, I do not think we can necessarily conclude that there is a mystery about this part of the figure.

MR. NORDMAN: That is so.

DR. F. MULLER: I should like to say something about the question already touched upon by Dr. Jullander.

Mr. Nordman states in his paper (page 343) —

"The bond strengths of hardwood pulps and softwood pulps, however, form different curves as a function of the pentosan content, the hardwood pulps forming a group below that of the softwood pulps. The results indicate that increasing amounts of hemicellulose increase the strength of the bonds, but that hemicelluloses in hardwood pulp are not as effective as are the same quantities of hemicellulose in softwood pulp."

I should like to point out that pentosans constitute the majority of the hemicellulose in hardwood pulps; they constitute less than half in softwood pulps. It is clear to me that, when you correlate bond strength with pentosan content, you get a different curve with softwood pulps than with hardwood pulps. The bulk of the hemicellulose in softwoods consists of glucomannan, which will contribute equally or even more than pentosan to bond strength.

PROF. H. W. GIERTZ: The discussion of Mr. Nordman's paper has brought out the very important question of the correlation between paper strength and opacity. Every maker of fine paper has been forced to realise that any way of increasing strength involves a reduction in opacity at the same time.

When saying strength, I mean fibre-to-fibre bonds, which, in my opinion, are best measured by tensile or bursting strengths. To increase such strength,
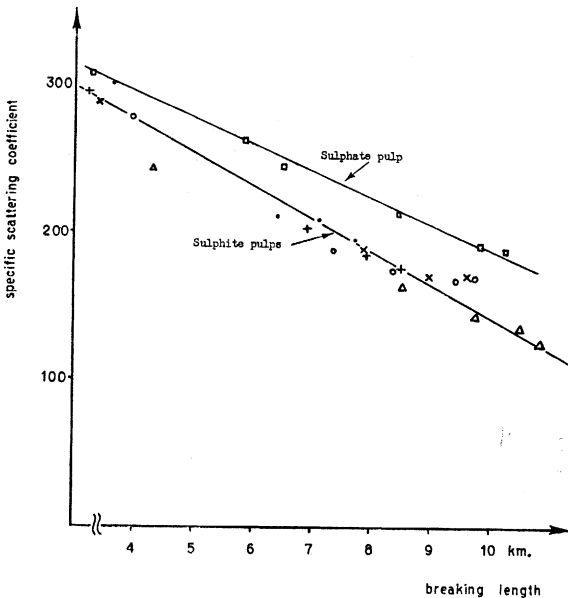

Fig. S — The relationship between specific scattering coefficient (opacity) and breaking length

we have to create contacts between the fibres and, in doing so, we lose the optical surfaces that scatter the light, thus decreasing opacity.

This correlation between breaking length (obtained by beating) and opacity (the specific scattering coefficient, *s*) is shown in Fig. S for different sulphite pulps and one sulphate pulp, all bleached and prepared from spruce. The sulphite pulps are of quite different quality, ranging from extra strong pulps (yield 55 per cent.) through ordinary pulps to rayon grade pulps and one extra soft pulp (yield 39 per cent.) Nevertheless, there is a very close relationship between strength and opacity: the coefficient of correlation is 0.99. The same relationship holds for the sulphate pulp, though the opacity in this case is on a higher level and the drop in opacity is not so serious. For the sulphite pulps, an increase of 1 000 m. in the breaking length corresponds to a decrease of 30 units in the *s* value; for the sulphate pulp, however, this decrease is only 21 units. Obviously, when trying to combine strength with opacity, it is better to use bleached sulphate pulps than sulphite pulps.

THE CHAIRMAN: I have felt for a long time that this work by our Finnish colleagues, however controversial it may be, is one of the most significant lines of work that has been carried out for many years and the discussion this afternoon has shown that other people may have that point of view, even if they disagree with the particular interpretations that have been put forward.

MR. D. S. BELFORD: I was very interested to hear Prof. Centola's references to the action of aqueous solutions of various salts on cellulose fibres. In the Biophysics Department at Leeds University, we have recently been carrying out some work on the location of water soluble preservatives introduced into timber by pressure treatments. During this work, we have used the technique of transmission electron diffraction in the electron microscope. We have, for instance, treated Douglas fir shavings with an aqueous 4 per cent. copper sulphate solution, allowed them to dry at room temperature and subsequently blended them for examination in the electron microscope.

Untreated wood particles do not give an electron diffraction diagram of cellulose under these conditions, because of the relatively low lattice perfection of the crystalline component of wood cellulose mentioned earlier by Dr. Rånby. Certain particles from the copper sulphate treated wood, on the other hand, give quite characteristic oriented electron diffraction diagrams.

The spacings calculated from the electron diffraction diagram oriented with respect to the direction of the cellulose microfibrils do not correspond with any known copper salt listed in the ASTM Crystallographic Index.

Similar patterns were obtained from cotton cellulose and from wood treated with aqueous solutions of zinc sulphate, ferric sulphate, cobalt sulphate and potassium dichromate. The pattern shows a tendency to fade, owing to the effects of the electron beam, which is fairly characteristic of organic rather than of inorganic substances.

I would emphasise here that we have so far been working with this material purely from the point of view of preserving wood and not from a fundamental point of view.

More work is needed before a clear explanation of these results can be made, but we suggest that the electron diffraction diagram may be given by a metallo-cellulose complex. It is inconceivable that any modification takes place of the crystalline component of cellulose, since water is known not to penetrate within these regions and the X-ray diffraction diagram remains unchanged after treatment. It may be that the copper, for example, is involved in a cross-linking between adjacent cellulose molecules in those amorphous regions of the microfibril where the molecules of cellulose are parallel, but not evenly spaced. This is supported, to some extent, by the fact that we have been unable to detect the complex in *Valonia* cellulose.

I am not suggesting that this sort of thing takes place on a large scale, since this work is not quantitative and is still in the preliminary stages. It may suggest, however, that there may be a specific action under certain conditions between aqueous solutions of various salts, on the one hand and wood fibres, on the other. At present, we have insufficient evidence to be too definite about the mechanism of the process, but I thought this work might be of general interest.

Whether these remarks have any significance in connection with the beating rate is, of course, another matter.

DR. JULLANDER: Some years ago, we made experiments having a bearing on what Prof. Centola and his co-workers have told us today. In their first investigations, published 1940, a thickening effect was observed upon addition of some substantive dyes to methylcellulose solutions. We have followed up this idea by investigating the thickening effect on aqueous ethylhydroxyethylcellulose solutions of different types of substantive dyes. More than 50 different dyes were tested, only comparatively few of them gave a positive effect. The dyestuffs with known structure giving a thickening effect all had two azo groups and at least two sulphonic acid groups. From this and from spectrophotometric studies, we have concluded that the thickening is the result of a loose cross-linking between the macromolecules by means of the dyestuff molecules.

I should like to ask if any investigations have been made of the constitution of those dyestuffs that are able to give the effect in the beating process just described. It could be that cross-linking effects in this case are quite unnecessary or even unwanted and, consequently, the requirements on the constitution of the dyestuff different

PROF. G. CENTOLA: In the second table of our paper, we have presented the effect of many dyes on beating and we have seen that Congo Red (the molecule has two sulphonic acid groups) was the most active among them. Many years ago, I observed a similar trend when I measured the changes of specific viscosity for a methylcellulose following addition of a series of substantive dyes to its water solutions. The maximum increase of specific viscosity of the methylcellulose solutions was caused by those dyes that have on the one side of the molecule amino groups symmetrically distributed and on the other side some lyophilic groups, as is the case for Congo Red and Benzopurpurine. Less activity was observed for the dyestuffs that have either more than two sulphonic acid groups present in the molecule or hydroxyl groups instead of amino groups or an asymmetrical distribution of the hydroxyl, amino and sulphonic acid groups in the molecule.