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# Prepared contributions

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IN RECENT years, there has been so much research work on bonding that it has been necessary to consider paper at times as bonds held together by fibres rather than fibres held together by bonds. Fibres have, however, never been forgotten and an immense amount of scientific evidence on them has been built up. The suggestion by Kallmes & Perez that the idea that mechanical properties of paper depend more than is generally realised on fibre properties forms a new concept seems a strange statement.

Creep properties of individual cotton fibres were studied by Collins<sup>(1)</sup> under wet conditions and there have been many stress/strain studies on textiles and textile fibres. Perhaps, the most important was by Leaderman;<sup>(2)</sup> this was heavily drawn on by the earlier workers on paper rheology.

Any theory should always fit all the known facts, and even before any scientific measurements were done at all, it must have been obvious to users of cloth that individual fibres creep under stress, particularly under hot wet conditions. Cotton cloth, for example, is not bonded to any serious degree. Interfibre bonds do not come into any argument about it and its properties, so easily demonstrated by comparing the effects of different ways of ironing it, must be explained in terms of molecular rearrangement inside the fibres.

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# Cross-linking in cellulose products at elevated temperatures— E. L. Back, Central Laboratory, Swedish Fibre Building Board Industry, Stockholm

THE primary effect of heat treatment on paper products in a low moisture atmosphere is a swelling restriction, indicated by wet strength, wet stiffness, dimensional stability and reduced water sorption isotherms. Furthermore, an increased dry stiffness appears as well. Covalent interfibre and intrafibre crosslinks explain these effects adequately and chemical model experiments support this explanation. The possibility of simultaneous partial recrystallisation cannot be eliminated as part of the explanation.



Fig. 1—Arrhenius plot of the initial velocity of wet tensile strength and wet breaking elongation produced on heat treatment (data refer to sulphate woodpulp papers with and without additional catalyst)

The regularity of the cross-linking reaction appears from Arrhenius plots of the logarithm of the initial velocity in the paper property changes against the reciprocal of the Kelvin temperature. As an example, Fig. 1 shows such a plot of the additional wet breaking elongation and wet strength per minute of heat treatment over the temperature range  $70-350^{\circ}$ C, in the upper region of which 40 per cent wet strength can be produced in a second. Data are given for two sulphate woodpulp papers, copper nitrate being used as catalyst in

one of them. The activation energies are equal, as indicated by parallel curves. Fig. 2 for the last-mentioned paper shows the Arrhenius plot for the relative change in three different dimensional ranges in the cross-direction. Fig. 3 shows a plot of stiffness increase, measured as elongation decrease at 4 kgf/cm strip width in a stress/strain operation.

Simultaneously with the cross-linking, there is a reaction that splits the cellulose chain, this being measurable, for instance, by the increase in water extractable material.<sup>(1)</sup> Finally, if resinous material is present, the fibres are rendered hydrophobic, which can be explained as a reorganisation of the resin particles and partial sublimation to cover a larger surface area.<sup>(1)</sup>



Fig. 2—Arrhenius plot of the initial velocity of dimensional stabilisation on heat treatment given as percentage reduction of dimensional change: the three-dimensional ranges refer to a humidity cycle between 33 and 87 per cent rh; 33 and 100 per cent rh (as total water immersion); and between this 100 per cent rh and a subsequent reconditioning at 65 per cent rh

Arrhenius plots for all these measurable properties show activation energies between 20 and 28 kcal/mole. At 100°C, the velocity of cross-linking is high enough to explain the rather small swelling restrictions appearing during pulp drying.

The cross-linking velocity in the paper product partially depends on the acidity. Fig. 4 shows the initial velocity of wet strength formation at 190°C plotted against the hot extract pH value of the paper (6 min heat treatment). Paper products had been impregnated with various inorganic salts before

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heat treatment. Solid dots refer to salts, the cations of which have redox potentials. Apparently, these salts have an additional catalysing effect. This finding supports the conclusion that the cross-linking is a formation of hemiacetal linkages, subsequent to the formation of carbonyl groups in the polysaccharides by autoxidation. The catalytic effect of the salts with redox potential then is a specific autoxidation to reactive carbonyls; after that, the actual cross-linking is promoted by acidity.

Accordingly, the pretreatment of the paper product or pulp by sodium periodate, producing dialdehyde groups in the polysaccharides, increases the velocity of wet strength formation in dry heat treatment significantly. This is



*Fig.* 3—Arrhenius plot of the initial velocity of stiffness produced on heat treatment, evaluated as the elongation decrease at a loading of 4 kgf/cm strip width

exemplified in Fig. 5—compare with wet strengthening by dialdehyde starches.<sup>(2)</sup> Furthermore, pretreatment of the pulp or paper with sodium borohydride reduces existing carbonyl groups and decreases the velocity of cross-linking. Fig. 5 also illustrates how a high acidity in the paper (for example, with aluminium sulphate), although increasing the initial cross-

linking velocity, increases the velocity of the degradation reaction as well, the effect being more pronounced on prolonged treatment.

The change in dry strength properties is the net effect of cross-linking and of chain breaking. With non-acidic catalysts, the dry tensile strength and breaking elongation of sulphate woodpulp papers can actually be improved, but with an increase of the modulus of elasticity. Fig. 6 gives the tensile strength of the heat-treated papers of Fig. 4 as a function of the dimensional stability produced, evaluated here as thickness swelling on water immersion. Each curve connects periods of treatment at 190°C, the solid dots referring to 3 min treatment. High acidity gives rapid dimensional stabilisation as in the





lower curves, but only at the cost of high tensile strength losses. Some catalysts at a slower speed of dimensional stabilisation produce an actual gain or only a slight reduction in tensile strength.

Cross-linking stresses are developed in the paper on reconditioning, which are of opposite direction to the well-known drying stresses.<sup>(3, 4)</sup>

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Thus, swelling restrictions produced in pulp, paper or single cellulose fibres on heating and drying should be imagined primarily as interfibre and intrafibre cross-links.



**Fig. 5**—The wet strength of several treated papers plotted against the time of treatment at 190°C: pretreatment in the periodate solution was sufficient to insert dialdehyde groups in 10 per cent of the monosaccharide units of the paper



## ring to 3 min

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# Discussion

**Chairman**—Van den Akker and his co-workers have shown a considerable change to occur in the property of the fibres when they are alkali-extracted, which they attribute to decrease in hemicellulose content. If you treat a fibre with 8 per cent potassium hydroxide, is not a considerable proportion of the native cellulose converted to cellulose II? Could not the onset of mercerisation be more responsible for the effect than that portions of hemicellulose are extracted?

Dr J. A. Van den Akker—Spiegelberg observed that the 002 diffraction peak was not disturbed by treatment with 8 per cent potash solution, thus showing that the cellulose remained cellulose I. He was very concerned, of course, with both this and the problem of degradation, which he handled as described in the paper.

It is difficult to resolve the differences between the data of Duncker, Hartler & Samuelsson and ours (as someone has asked), because the bases were different. In the Swedish work, the fibre was quickly extended a fixed distance, whereas in our laboratory the fibre was subjected to a fixed load and so permitted to extend. When a fibre of helical structure is dried under constant load and is free to extend, the structure after drying is different from that of a fibre dried under fixed strain and would have different properties. Without a doubt, a complete resolution of the two sets of results must await more information on the visco-elastic properties of wet and dry fibres.

**Chairman**—Indeed, the trouble is that we do not understand the background of visco-elastic properties of any material, whatever it is, so the problem is really of quite a magnitude.

**Dr B. Leopold**—Van den Akker referred to the work that McIntosh and I have done as being along the same lines as his own. What I have to say refers to the Chairman's question on the effect of alkali extraction. Our results show that the most drastic effect of extraction on fibre strength occurs at the lower end of the concentration range; in other words, long before cellulose II has

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a chance to appear. We observe no change once the concentration range is reached when mercerisation is likely to occur, which I think supports what Van den Akker said. We have been bolder than he in trying to attribute the changes to specific fractions of the hemicellulose and think that the removal of xylan is mainly responsible for the fall in fibre strength.

Dr C. A. Jentzen—Referring first to the Chairman's question, after extracting cotton fibres with the same treatments used for the pulps, an increase in the modulus occurred, whereas extraction of the pulp caused a decrease in modulus. Then, additional experiments were run to confirm the results of sudden extension at the start of drying. Measurements taken at several span lengths gave the same percentage elongation, which indicated no fibre slippage in the clamping jaws. The exact time of extension and its amount were predictable and reproducible.

**Prof. H. W. Giertz**—We have to keep in mind that the hemicellulose, which is supposed to be located between the microfibrils, is plastic when wet, but stiff when dried. Thus, the dried fibre is composed of two solid phases—the aniso-tropic microfibrils (which are extremely strong in their length direction) and the more or less isotropic hemicellulose. When the fibre is loaded, the micro-compressed areas will elongate and the hemicellulose in these parts will be broken down. This flow elongation will proceed until the microfibrils are straightened. With this approach, the flow properties of paper should be referred to the irreversible microcracking of the interfibrillar hemicellulose material.

*Mr D. H. Page*—Had Giertz not commented as he did a few minutes ago, I would probably have said exactly the same thing, except that I would have left out the word hemicellulose.

I would like to refer to Fig. 4C of the paper on load elongation properties of fibres by Kallmes & Perez and to the comment on it in the text—'Quite frequently, fibres picked from handsheets underwent a small plastic deformation somewhere in the middle of the curve (Fig. 4C). This may have been caused by a removal of microcompressions or straightening of the fibres . . .' Now, if we have a fibre with a microcompression in it and it gives under test a stress/strain curve like that of Fig. 4C, this implies that the stress/strain curve of the microcompressed region of the fibre would be quite similar to the curve for paper, having an initial elastic region followed by an appreciable plastic region. There would seem to be a case for the view that we expressed at Oxford that the whole stress/strain curve of a paper containing appreciable microcompressions can be explained by the stress/strain curve of microcompressed fibres and that the random structure of paper merely acts to produce an averaging effect.

Mr J. A. S. Newman—In the investigation of the stress/strain characteristics of fibres, we appear to be at the same point we were ten years ago in the investigation of the stress/strain characteristics of paper. The explanation of paper strength properties is not being validly based on the statistical geometry of the fibre network. Equally, I believe that the theory of the strength properties of fibres should be based on the concept of the statistical geometry of a network of fibres or of microfibrils inside the fibre itself, which are crosslinked or bonded together at discrete points.

Mr P. A. Tydeman—I do not want to appear ungracious after the extensive reference to microcompression made by Kallmes & Perez, but I have one comment to make on the cross-direction or transverse modulus of fibres, which has obvious importance. I think that there is an anomaly. The argument is that, by bonding other fibres at random to your tensile test fibre, its modulus is doubled. The implication that at least as much fibrous material again is bonded to the test fibre seems unlikely upon consideration of your method. Can this apparent anomaly be explained?

**Prof. B. G. Rånby**—May I first refer to the question of visco-elasticity. I am not as pessimistic as the Chairman about the state of knowledge of visco-elasticity in polymer systems: I think the theory is in good shape for amorphous polymers. For partly crystalline polymers, the interpretation is more difficult. For papermaking fibres, the problems are even more difficult, because the virgin wet fibres are thixotropic.

I would like to make one remark about the properties of papermaking fibres by referring to the *Summing up* at the Oxford symposium in 1961 published, but not much observed. There is accumulating evidence that the hemicelluloses are fairly well ordered, in the native fibres, although they are *not* X-ray crystalline. It can be shown that the hemicelluloses carry part of the load when the pulp fibres from wood are stretched or dried under tension. There are close relationships between the cellulose microfibrils and the hemicelluloses—for example, well-ordered hydrogen bonds. Our recent NMR data gives support to this concept and they will be published elsewhere.

Dr O. J. Kallmes—First Tydeman's comments. The measurements consisted of taking a small section out of a thin sheet, then one fibre from the

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sheet, with numerous fibres bonded to it, was strained to a point below failure and relaxed. All the fibres were carefully pulled off and its stress/strain curve measured. The fibre was not completely bonded, but there were several fibres almost parallel to that being strained. This showed whether or not this technique would be sensitive to fibres bonded to it.

In reply to Hudson's comment, fibre properties varied throughout the sheet to a far greater extent than is generally realised. This is what I was referring to.

The curves referred to by Page are purely speculative so far as curves in paper go. We have never measured stress/strain curves of fibres in paper, though we have developed a technique of measuring the size of strains in paper and found the variation of strain along a fibre to be very marked. Some stretch tremendously, some parts do not stretch at all, so it is from this idea that I drew this curve. There are many ways you could draw the curve and Fig. 4C was purely speculative. These are the only two that have been measured and they were measured on fibres in air.

It is going rather far to say that microcompression explains the stress/strain behaviour of paper. This picture does not take into account, for example, bond failure, nor does it take into account the parts of the fibre that are stiff and straight. In other words, in a sheet dried under tension in this direction, fibres lying in this direction did not shrink and there are no microcompressions.

**Chairman**—It is easy to speculate. May I remind you that, about 15 years ago, Eyring and a few others were working on stress/strain properties of different fibres. Some types of wool exhibited unusual kinks in their stress/strain curves. Within half a year, Eyring & Halsey produced a beautiful absolute reaction kinetic theory that explained this new feature. It was found that the diameter of this specific form of wool fibre was not uniform.

We are dealing with natural fibres, which are very complicated in their build-up; when we measure stress and strain on single fibres, we are dealing with something that is rather poorly defined material geometrically. It is probably easier to make theories than to make observations. We have many new observations today and I think the future will bring more.

Mr L. G. Samuelsson—In preparing our specimens for fibre stiffness measurements, thin, wet paper sheets were dried in a desiccator to different solids contents by varying the time. It is important to remember this, because no conditioning of the specimens occurs under these circumstances. The drying conditions could rather be compared with those present on the papermachine. Since we cannot expect an even moisture content in the fibre material, the outer fibre surface, which is most efficiently exposed to the drying

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medium, can very well have a high solids content, even if the inner parts of the fibre are still wet. We believe, therefore, that the increase in fibre stiffness during drying can occur within the range 15-35 per cent solids content, since it is the outer layer of the fibre that most probably determines the stiffness of the fibre.