Preferred citation: J.A. Van den Akker, C.A. Jentzen and H.L. Spiegelberg. Effects on individual fibres of drying under tension. In **Consolidation of the Paper Web**, *Trans. of the IIIrd Fund. Res. Symp. Cambridge, 1965*, (F. Bolam, ed.), pp 477–506, FRC, Manchester, 2018. DOI: 10.15376/frc.1965.1.477.

EFFECTS ON INDIVIDUAL FIBRES OF DRYING UNDER TENSION

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Synopsis—Following a review of the effects of machine- and cross-direction forces in the web during drying on the stress/strain properties of the finished paper, the nature of the axial forces in the individual fibres during tension drying is discussed in the light of the theory of the structure. The effects on the mechanical properties and structure of individual holocellulose pulp fibres of tension drying have been carefully investigated. An unusual extensional behaviour was observed at the onset of drying. It was found that tension during drying promoted substantial increments in tensile strength, Young's modulus and crystallite orientation; generally, the springwood fibres underwent larger changes than the summerwood: ultimate elongation was reduced and crystallinity remained unchanged.

Partial removal of the hemicelluloses resulted in large decrements in tensile strength and Young's modulus, a phenomenon not attributable to degradation of the fibre or to such side effects as swelling; the levels of these mechanical properties were reduced to those of ordinary pulp and cotton fibres. The relative enhancement of tensile strength and Young's modulus in the extracted fibres caused by tension drying was much greater than that observed in the holocellulose pulp fibres, the latter property rising almost to that of the holocellulose fibres dried under load as the drying load was increased. The crystallinity of the extracted fibres (as determined by the method of half-width of a diffraction peak) was higher than that of the original holocellulose pulp, suggesting enhanced cellulose/cellulose bonding within the fibre, which, in turn, seems to account for the tension drying behaviour.

Theory and experimental data relating to the possible effects of tension drying on the zero-span tensile strength of machine-made paper are presented. It is indicated that more work needs to be done in this area and, more generally, on

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the effect of tension drying of individual fibres on all the mechanical properties of paper.

Introduction

THE JOINT action of the Campbell effect[1] and pressing is to promote fibre-to-fibre bonding. Because of the great importance of bonding in paper, much attention has understandably been directed to the effects of *z*-direction compacting stresses,* but the mechanical effects of forces *in the plane of the paper web* during forming, pressing and drying are also very striking; yet relatively little work has been done on these effects and the published literature presents little more than conjecture on how tension during drying produces such pronounced changes in the tensile properties of the finished paper.

In independent experimental studies, Edge[2-4] and Sapp & Gillespie[5] have demonstrated the very appreciable effects of tension during drying on the tensile properties of machine-made paper. In particular, Edge's work has shown that the strong asymmetry in the tensile strength of machine-made paper is attributable to the tension in the web during water removal and drying rather than to the anisotropic angular distribution of fibres in the sheet. The effects of tension on related physical properties and hygroexpansivity have been investigated by Brecht & Pothmann[6] and Hudson[7] and Schulz[8] has conducted a very thorough study of the effects of wet straining on the viscoelastic properties of paper.

A phase of our work on the properties of individual fibres has been designed to develop a better understanding of the forces in paper under tension and of the actions of tensile and compressive forces in the fibres while the latter are in the wet or damp condition. There are, in principle, two major effects of tension during drying.

The first of these acts upon the *whole assemblage or structure* of fibres; while the fibres and bonds are in the plastic state, tension in the structure will cause local yielding in most fibres and bonds in such manner as to dispose those fibres and bonds (of similar orientation) in the dry sheet to share the load more uniformly, thus causing both the modulus of elasticity and the tensile strength of the final sheet to be enhanced for the given direction of tension during drying.[9] Further consideration of the forces in paper, to be elucidated later, shows that the forces in fibres that lie athwart the direction of drying tension undergo axial compressive loading. This should have an effect that is opposite to that above—that is, local buckling should reduce the uniformity of sharing of (compressive) loading in these fibres in subsequent loading of the dry paper in the above-mentioned direction of drying tension.

* In this paper, we adopt the common convention for co-ordinates in a fibrous web. The *x*-axis is taken along the machine-direction, the *y*-axis along the cross-direction and the *z*-direction is accordingly perpendicular to the horizontal web.

Oddly enough, both of these effects co-operate to yield a greater modulus and ultimate strength in the final paper for the direction of drying tension, while producing a reduction in the levels of these properties for the direction perpendicular to that of the drying tension.

The second major effect of tension during the drying of paper is the significant modification of the properties of the individual fibres comprising the sheet. It is with this effect that the present paper is concerned.

Before turning to consideration of the nature of the forces in individual fibres during tension drying of the web, reference should be made to a possible third effect, which relates hypothetically to the prefailure (plastic) regime of the stress/strain relationship and, possibly, to the tensile failing stress of the paper. This is the probable anisotropy in the strength of a fibre-to-fibre bond, owing to actions described by Steenberg in a discussion of Edge's work.[4]

Forces in individual fibres during tension drying of paper

THE THEORY presented by one of us at the 1961 Oxford symposium has been used in the present study to estimate the forces in the fibres.[10] According to that theory, all the fibre segments lying at angles within $\pm \cot^{-1}\sqrt{\nu_{xy}}$ of the direction of sheet tension (x-direction, say) are under axial tension, whereas the remaining segments, lying at angles within $\pm \tan^{-1}\sqrt{\nu_{xy}}$ of the y-direction, are under axial compression (ν_{xy} is the Poisson ratio for the sheet for stress in the x-direction). A graphical representation of the dependence of the axial tension (or compression) on the angular orientation of the fibre, computed from the theoretical expression for the axial force T in the segment [from equations (*1*) and (*4*) of the Oxford paper[10]], is presented in Fig. 1. For the purposes of this illustrative case, we have assigned the following numerical values—

> Sheet strain 0.01; fibre cross-section 240μ^2; Young's modulus of elasticity of the fibre 3 000 dyn/cm^2 (dry, not wet fibre); Poisson's ratio of sheet 0.3

A sheet having random orientation of the fibre segments was assumed.

The pictorial representation given in Fig. 1 can be understood more clearly when it is recalled that the orientation of a fibre segment is completely specified when the angle θ between the axis of the segment and the y-axis is assigned a value between 0 and 180°—that is, only the first and second quadrants are needed for specification of orientation. It is seen, then, that the running of the polar diagram into the third and fourth quadrants signifies a change in algebraic sign of the axial force. For example, whereas the radius vector for a segment at 80° denotes an axial force of +6 900 dyn, which means a *tension* at this numerical level, the radius vector for a segment at 10° is displayed as running from the curve toward the origin, denoting an axial

force of −1 800 dyn—that is, a *compressive* force in the segment. For the illustrative case shown in Fig. 1, the axial forces in all the fibre segments

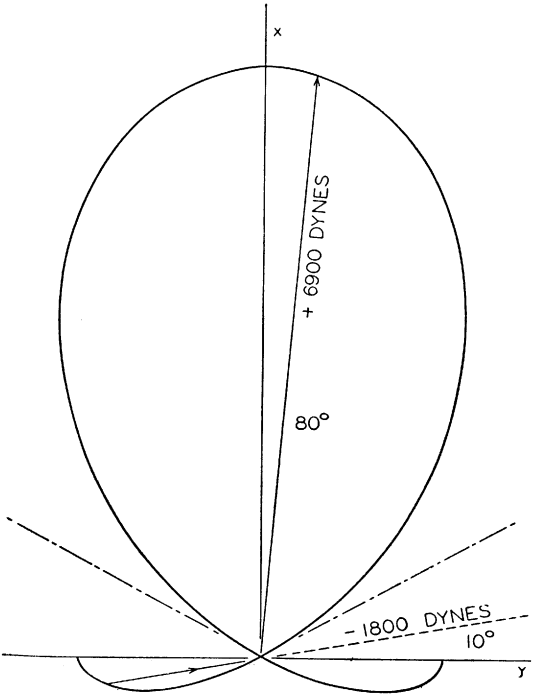

Fig. 1—Polar representation of the tension (first and second quadrants) and axial compression (third and fourth quadrants) in the fibres in a sheet under uni-directional loading (in the *x*-direction); the third and fourth quadrants are used to denote 'negative tension'

lying between 29° and 151° are tensional, with the maximum in the direction of sheet straining at +7 200 dyn. At the foregoing limiting angles, the axial forces are nil; for segments lying between 0–29° and 151–180°, the axial forces are compressive, with the maximum at −2 170 dyn in segments aligned with the *y*-axis.

A similar polar graph would represent the forces in fibres in a wet or damp sheet strained to a similar level, except, of course, that the magnitudes of the forces would be reduced. Acknowledging this, important questions arise. Firstly, are the forces sufficiently large during drying of the web to cause

changes of practical importance in the properties of the individual fibres? Secondly, what is the nature of changes in the mechanical and structural properties of woodpulp fibres induced by drying under tension?

Effects produced in individual fibres by tension drying

IN THE first of a current series of three dissertations designed to study these and related questions, Jentzen has conducted a thorough investigation of the mechanical and structural changes produced by tension during drying in the springwood and summerwood fibres of longleaf pine holocellulose pulp.[11,12] Jentzen obtained estimates of the forces in fibres during drying through consideration of the experimental data of Brecht & Pothmann[6] and of Schultz,[8] utilising equation (*13*) and other pertinent relationships of the Oxford paper.[10] Taking into account the known cross-sectional areas of the fibres employed in his study, he chose the following fibre loadings for his work—

For springwood fibres, 1 and 3 g; for summerwood fibres, 1, 3 and 5 g.

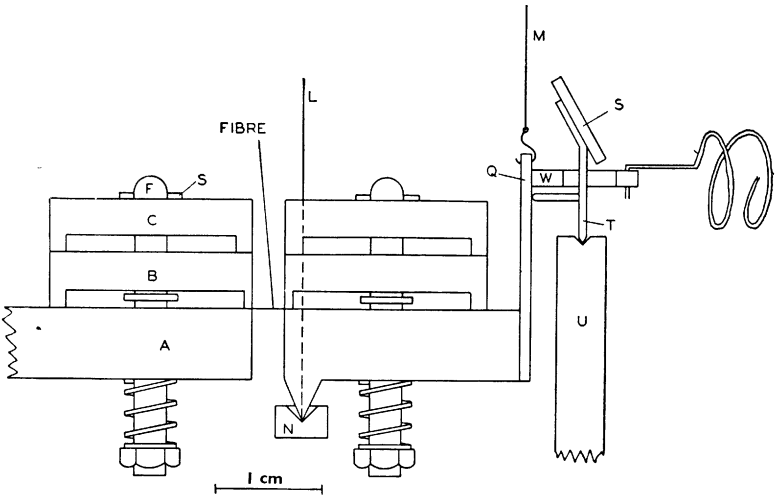

Fig. 2—Schematic diagram of apparatus for drying fibres under load and observing extensional behaviour

A schematic diagram of the heart of Jentzen's apparatus for observing load/elongation data for a single fibre while drying under load is given in Fig. 2. A never-dried fibre, kept under water, is mounted at one end in fixed jaws (*A*,*B*) and at the other end in movable jaws that are supported by three fine jeweller's chains. Two of these (at *L*) support an agate knife edge system; the third (at *M*) is linked to the optical lever plate (*Q*). An optical lever, which rests at *T* and bears against the plate *Q*, reflects a beam of light from its

mirror *S* to a remote scale. A horizontal load of desired magnitude is provided by a carefully calibrated helical spring (calibrated in the horizontal position). A photograph of the apparatus (exclusive of the optical lever system) is given

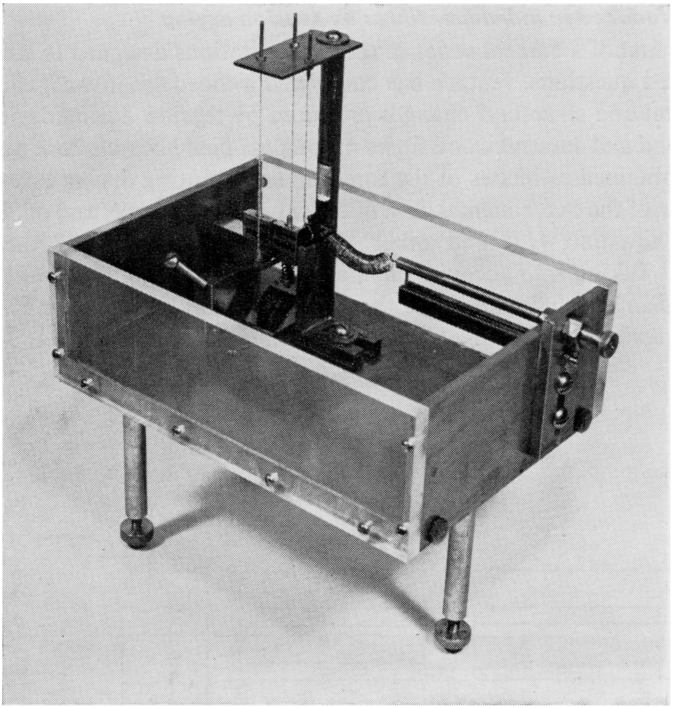

Fig. 3—Photograph of fibre-drying apparatus, exclusive of lamp and scale of optical lever system

in Fig. 3. Initially, the well is filled with water to a level above the fibre. At zero time, the well is drained and clinging droplets are quickly removed from the fixed clamp area with slivers of blotting paper; residual water in the bottom of the well is removed by vacuum. The movable clamp cannot be touched, but residual water there is kept to a minimum by filling the space between the clamping plate and beam with paraffin wax. The initial mechanical condition in all runs is a loading of 1 g (to which the aforementioned loadings are added) and all elongations are relative to the span (nominally 3 mm) under the 1 g load.

Chemical properties of the first pulp studied

Because it has a long average fibre length and large growth rings, longleaf (*Pinus palustris*) was chosen for this study. The wood, in the form of wedge-shaped pieces 2 cm thick, was pulped by a modification of a holocellulose

procedure developed by Thompson & Kaustinen.[13] The 23rd growth ring of a 31 year old tree was used and fibres lying between the springwood and summerwood zones were discarded. The chemical properties of the two classes of fibres are presented in Table 1.

TABLE 1—CHEMICAL PROPERTIES OF LONGLEAF PINE HOLOCELLULOSE PULP
Extractives and moisture 46.4 per cent yield 56 per cent

Extractives	*Summerwood per cent*	*Springwood per cent*
Klason lignin	0.3	0.4
Total sugars	90.6	91.6
Glucan	70.5	71.8
Xylan	5.98	6.46
Mannan	12.20	10.90
Araban	1.12	1.42
Galactan	0.79	1.04

Procedures for determining the physical properties of the individual fibres

The mean cross-sectional area of each fibre studied was determined by taking the quotient of the mass per unit length of that portion of the fibre that was in the tested span and the pycnometric density, which was 1.55 g/cm^3, very nearly. The mass per unit length was determined by an adaptation of the anthrone method,[12] which, for the removed 2 mm portion of the fibre, was found to be adequately accurate.

Load/elongation recordings for the individual fibres, after drying and removal from the apparatus, were obtained with the IPC fibre load/elongation recorder[16] at 73°F and 50 per cent rh. The fibres were glued to the pins employed in this method by first tacking them in position with ethyl-hydroxyethyl cellulose, an aligning manoeuvre, then more firmly adhering them with Epon 907. The nominal span was 2 mm and the actual span was determined with an eyepiece micrometer. Rates of loading of 1.40 and 2.00 g/sec were used to test, respectively, the springwood and summerwood fibres.

By means of an especially designed vacuum camera employed with an X-ray unit using copper $K\alpha$ radiation, Laue X-ray diffraction patterns were taken of single fibres. The crystallinity was estimated by both the crystallinity index proposed by Segal *et al.*[14] and by the integral half-width of the (002) lattice diffraction proposed by Gjonnes *et al.*[15]

The crystallite orientation was measured by fitting the circumferential intensity curve of the (002) lattice diffraction to a normal curve. The standard deviation of the normal curve was used as a measure of crystallite orientation. Only the accumulative probability values between 15 and 85 per cent were

used, because the tails of the intensity curve deviated widely from the fitted normal curve. This method does not give the fibre angle, but it is good for comparative purposes.

Results for the first holocellulose pulp

The elongation behaviour (relative to the span at the base load of 1 g) for springwood and summerwood fibres is presented in Fig. 4. The initial

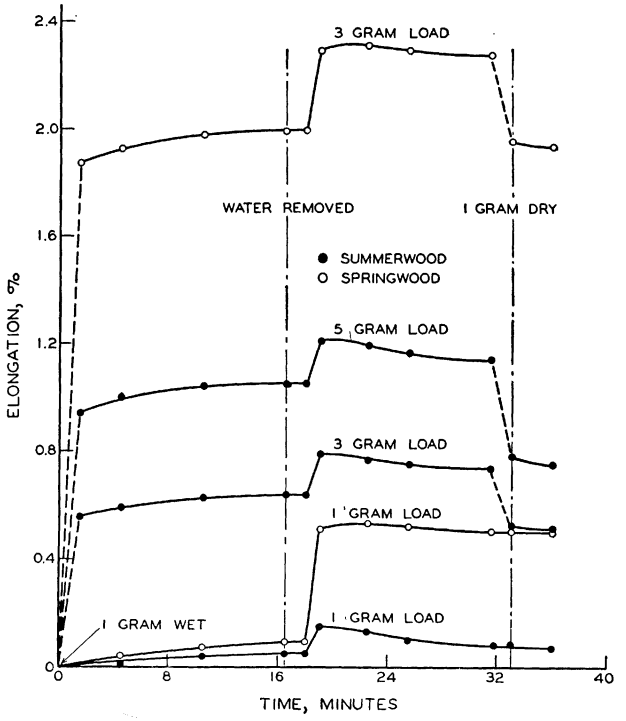

Fig. 4—Elongation behaviour of fibres during drying

extension of a fibre (the magnitude of which is inversely related to the relatively low Young's modulus of the wet fibre) is followed by an interval of creep. The suggestion of fairly long relaxation times is noteworthy. Following water removal, the fibre *suddenly extends* as it dries, then undergoes the expected shrinkage. This is not an apparatus effect; microscopic observation of a fibre during the drying shows that, as long as droplets cling to the fibre, no extension takes place, but that the sudden extension is correlated with the visual disappearance of the last traces of excess water. This sudden extension is roughly independent of the drying load and is about twice as large for the

springwood as for the summerwood fibres. It is significant that the fibres were left with a permanent set or extension that is related to the drying load.

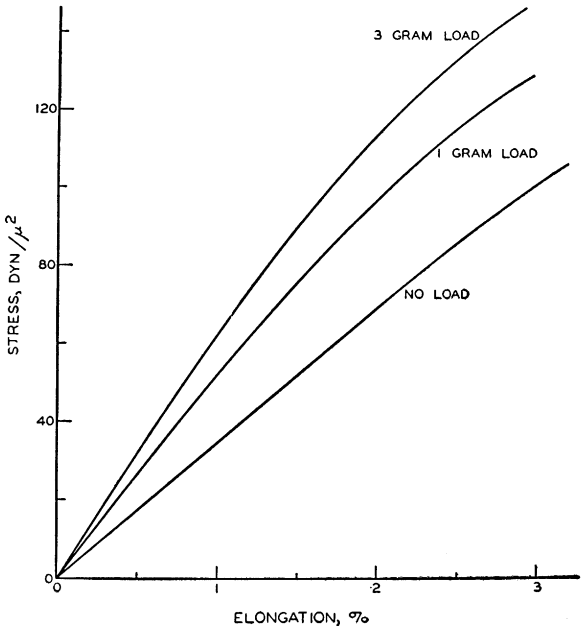

Fig. 5—Average stress/strain curves for summerwood fibres, showing the influence of tension drying

The effects on the mechanical properties of summerwood fibres dried under loads ranging 0–5 g are presented in Table 2. Tensile strength and Young's modulus both display large increments resulting from tension drying, the latter being substantially the larger, with optimum drying loads being in the vicinity of 3 g. It is significant that the standard deviation (S.D.) for all the observations decreases with tension drying, which suggests that drying under load reduces the variance in a set of fibres.

The data presented in the penultimate column of Table 2 show that re-wetting a fibre once-dried under load tends to restore the fibre to its initial state. A fibre once-dried under no load can be rewet and dried under load to yield elevated breaking load, breaking stress and Young's modulus as shown by the data of the last column of Table 2.

Of special interest is the influence of drying under tension on the load/elongation characteristic of the fibre. Typical recordings made on the IPC load/elongation recorder[16] are presented in Fig. 5. Two modifications are

TABLE 2—MECHANICAL PROPERTIES OF SUMMERWOOD FIBRES DRIED UNDER LOAD

Property tested		*No load*	*1 g load*	*3 g load*	*5 g load*	*5 g* load rewet*	*5 g† load dried*
Cross-sectional area, μ^2	Average	395	417	396	427	425	397
	S.D., per cent	15.7	12.2	10.0	14.1	13.0	11.6
Breaking load	Average	42.4	54.6	58.2	58.9	46.1	57.2
	S.D., per cent	25.9	17.2	13.1	19.9	20.0	14.6
Tensile strength, dyn/μ^2	Average	106.1	129.3	145.1	135.4	107.0	141.5
	S.D., per cent	24.4	18.4	13.2	16.2	18.2	11.6
	Change, per cent	0.0	+21.8	+36.8	+27.6	+0.8	+33.3
Ultimate elongation, per cent	Average	3.22	2.98	2.90	3.00	2.81	2.78
	S.D., per cent	23.6	15.0	14.7	17.2	19.3	12.7
	Change, per cent	0.0	−7.5	−9.9	−6.8	−12.7	−13.7
Initial slope of load/elongation curve, kilodynes	Average	1 360	2 230	2 500	2 400	1 770	2 470
	S.D., per cent	27.4	13.0	11.5	14.4	22.0	11.9
Young's modulus, dyn/μ^2	Average	3 470	5 370	6 370	5 630	4 160	6 220
	S.D. per cent	25.7	12.6	7.5	7.7	18.3	6.8
	Change, per cent	0.0	+54.8	+82.2	+62.3	+19.9	+79.3
Area under load/elongation curve, dyn μ/μ	Average	680	852	908	968	675	856
	S.D., per cent	34.1	28.8	23.9	33.2	34.8	24.8
Work-to-rupture, dyn μ/μ^3	Average	1.74	2.06	2.32	2.27	1.60	2.16
	S.D., per cent	34.5	30.9	25.1	32.3	35.0	23.6
	Change, per cent	0.0	+18.4	+33.4	+30.4	−8.0	+24.2
Number of fibres tested		73	40	36	36	30	41

* These fibres were dried under a 5 g load, rewet and dried under no load
† These fibres were dried under no load, rewet and dried under a 5 g load

TABLE 3—MECHANICAL PROPERTIES OF SPRINGWOOD FIBRES DRIED UNDER LOAD

Property tested		*No load*	*1 g load*	*3 g load*
Cross-sectional area, μ^2	Average	289	282	272
	S.D., per cent	19.6	15.1	16.7
Breaking load, g	Average	17.5	26.1	30.4
	S.D., per cent	42.8	21.5	21.6
Tensile strength, dyn/μ^2	Average	59.4	91.0	109.8
	S.D., per cent	33.8	16.9	13.4
	Change, per cent	0.0	+53.3	+84.9
Ultimate elongation, per cent	Average	4.46	2.70	2.83
	S.D., per cent	39.4	19.5	12.0
	Change, per cent	0.0	−39.5	−36.6
Initial slope of load/elongation curve, kilodynes	Average	525	1 337	1 499
	S.D., per cent	64.0	16.6	19.9
Young's modulus, dyn/μ^2	Average	1 770	4 750	5 510
	S.D., per cent	54.8	9.5	10.9
	Change, per cent	0.0	+168	+212
Area under load/elongation curve, dyn μ/μ	Average	359	401	486
	S.D., per cent	39.4	34.8	26.0
Work-to-rupture, dyn μ/μ^3	Average	1.29	1.43	1.79
	S.D., per cent	43.8	33.8	21.6
	Change, per cent	0.0	+10.4	+38.8
Number of fibres tested		36	39	41

noteworthy. Firstly, as noted in Table 2, Young's modulus is significantly enhanced. Secondly, the load/elongation characteristic for the fibres dried under no load is *more linear* than that for fibres that have undergone tension drying. Mechanical cycling studies have shown clearly that two major effects occur during the straining of the dry fibre. In the case of the fibre dried without load, strain hardening—that is, continuous increase of the modulus during straining—is quite substantial and this effect happens almost to balance that of creep (which alone would tend to produce curvature towards the strain axis). The strain hardening effect in fibres dried under load is much reduced (the enhancement of modulus attributed to structural modification has *already* occurred), so that the curvature assignable to creep becomes the governing factor. It is to be noted that the enhancement in Young's modulus because of dry straining in a fibre that has been dried without load is far less than that caused by tension drying from the wet state.

The mechanical properties of springwood fibres dried under 0–3 g loads are presented in Table 3. Even larger changes in tensile strength and Young's

modulus resulting from tension drying were observed, the percentage increments in the latter for one and three grams loading being 168 per cent for 1 g load, 212 per cent for 3 g load.

Information from the X-ray diffraction data on the crystallinity and crystallite orientation for both classes of fibres is presented in Table 4. Although all the results show increments in crystallinity and axial orientation, the changes in crystallinity are not statistically significant in either class of fibre. The change in crystallite orientation for the summerwood fibres is significant within 88 per cent confidence limits, whereas that for the springwood fibres induced by a drying load of only 1 g is quite large. It is noteworthy that the orientation of the springwood fibres dried under no load is far inferior to that of the summerwood fibres dried without tension, but that the change promoted in springwood fibres by tension drying is so large that the orientations in the two classes after tension drying are comparable.

Discussion of results for the first holocellulose pulp

The observations on the sudden extension of fibres during the first phase of drying and on permanent set are of great importance to our knowledge on intrafibre phenomena and behaviour. Both of these phenomena are consistent with a fibre model in which the prominent feature is a helical set of fibrils.[11,12]

Our principal concern here is in the mechanical properties of the tension-dried fibres. The changes in these properties occasioned by tension drying are attributed to two mechanisms. In its highly plastic state, the fibre should undergo an internal reorganisation while drying under tension, the chief features of which (for our present interest) are local sliding of microfibrils over one another in the S2 layer—not on a gross scale, but on the somewhat more subtle level of load equalisation among fibrils of like orientation. This phenomenon should occur in the S1 and S3 layers also, in spite of the less-ordered nature of the fibrils in those layers. As a result of this internal reorganisation, the dry fibre should be disposed to resist extension with greater stress. This mechanism parallels that given in the third paragraph of this paper for the increased modulus and strength of the whole sheet as a result of drying under tension. It may be reasoned, of course, that what we have just set forth as an intrafibre mechanism may itself be expected to play a role in the equalisation of forces in the whole assemblage of fibres in the sheet. In other words, the fibre behaviour that we are attempting to understand is involved in *both* of the sheet mechanisms presented in the third and fourth paragraphs of the introductory section.

The second mechanism involved in the fibre strength enhancement caused by tension drying is the improved alignment of crystallites. Although this is

TABLE 4—CRYSTALLINITY AND CRYSTALLITE ORIENTATION

Data reading	*Drying load, g*	*Average*	*Standard deviation*	*Fibres tested*	*Drying load, g*	*Average*	*Standard deviation*	*Fibres tested*
		Summerwood				**Springwood**		
Width at half height of (002) diffraction arc	0	4.24°	0.47°	5	0	5.38°	1.65°	5
	5	3.95°	0.31°	5	3	4.52°	0.34°	5
Crystallinity index	0	61.6	6.3	5	0	50.5	12.4	5
	5	64.4	4.4	5	3	57.0	4.6	5
Orientation as standard deviation of circumferential arc	0	7.92°	1.71°	5	0	14.13°	4.55°	10
	5	6.33°	1.09°	5	1	7.30°	0.75°	10
					3	7.10°	0.50°	10

Fig. 6—Dependence of Young's modulus and tensile strength of individual fibres on drying stress

presented on the basis of physical principles, it is of interest to note that the information from X-ray diffraction (Table 4) is consistent with the hypothesis that reduction in angle between the axes of the crystallites and the fibre occasioned by tension drying should tend to enhance Young's modulus and the tensile strength, but to diminish the ultimate strain. In particular, the large increments in the modulus and strength of the springwood fibres correlate with the (relatively) large enhancement of crystallite orientation observed for that class of fibres.

It is of interest to compare the values of Young's modulus and tensile strength of springwood and summerwood fibres for the same drying stresses, a comparison that can be readily made by inspection of Fig. 6. As the drying stress increases, the modulus and ultimate tensile stress of the springwood fibres approach the levels observed in the summerwood fibres and, concomitantly, the crystallite orientation in the springwood fibres approaches that of the summerwood fibres; it may be that stress equalisation in the springwood fibres also undergoes a relatively larger increment, but a measure of this is not at hand. The modulus and tensile strength are, very probably, dependent almost wholly on the highly oriented S2 layer and it should be recalled that summerwood fibres have a substantially higher mass percentage of the S2 layer than have springwood fibres. Using data published by Jayme & Hunger and assuming that the thicknesses of the P, S1 and S3 layers are the same in both classes of fibre, one finds that the S2 layer constitutes 87.5 per cent of the summerwood cross-section and 78.5 per cent of the springwood wall. Working with maximum values and assuming that the modulus is dependent only upon the S2 layer, it is calculated that the Young's moduli for the summerwood and springwood fibres are, respectively, 72×10^{10} and 70×10^{10} dyn/cm^2. The agreement to within experimental error lends support to the assumption that the S2 layer governs Young's modulus. In this connection, there is a good chance that the orientation of the S2 fibrils in the two classes of fibre is similar, a possibility in view of the fact that the X-ray data include the influence of the more random fibril arrangements in the P, S1 and S3 layers, which, in turn, are relatively more abundant in the springwood fibres. The maximum tensile strengths (stresses) in the two classes of fibre cannot similarly be brought together on the basis of S2 content, a fact that might be attributable to a higher occurrence of discontinuities and imperfections (causing stress concentrations) in the springwood fibres.

The foregoing maximum values of Young's modulus, based on the S2 layer, are about 20 per cent less than the theoretical value of 90×10^{10} dyn/cm^2 calculated by Meyer & Lotmar[17] for perfectly oriented crystalline cellulose, taking into account bond distance elongations and valency angle distortions. If it is assumed that the hemicelluloses, being less-ordered

than the cellulose, do not contribute significantly to the modulus, correction based on the hemicellulose content (Table 1) leads to close agreement between the adjusted and theoretical values of Young's modulus.

The role of hemicellulose in the effects of tension drying

IN A SECOND dissertation on the topic of this paper, Spiegelberg[18] has conducted a study of the effects of systematically reducing the hemicelluloses in holocellulose fibres. In this work, the apparatus and techniques of Jentzen[11,12] were employed with relatively minor modifications. The summerwood fibres from the 27th and 28th growth rings of a 49 year old longleaf pine tree were used in this phase of the study. Jentzen's apparatus for observing extension/load data for individual fibres was used with the following modifications in technique. The test fibre was dried in a slowly moving stream of conditioned air; the wet creep time was reduced from 15 to 6 min; the drying time was reduced from 15 to 9 min; the fibre span was reduced from 3 to 2 mm. Stress/strain data observed for the dry fibre after removal from the Jentzen apparatus utilised the same recording and ancillary equipment, with the following modifications. The test span was reduced from 2 to 1.03 mm and the cross-sectional area of the test fibre was determined by means of the relatively new IPC fibre dimension apparatus,[19] which enables one to determine, with considerable accuracy, the compacted double-wall thickness and fibre width.

Extraction procedures and sugar analysis

In addition to the holocellulose pulp, the samples prepared for this phase of the programme were obtained by means of four extraction solutions. Following each treatment with an extraction solution there was of course a thorough washing. The extractions were as follows—

1. 0.1N potassium hydroxide solution (potash): for partial removal of pectins, arabinose and galactose.
2. 2 per cent potash, washing, 9 per cent potash, washing, 9 per cent potash, washing; for partial removal of xylans. This followed step *1*.
3. Two extractions with 9 per cent potash and 3 per cent boric acid: for partial removal of glucomannans. This followed steps *1* and *2*.

The sugar analyses for the pulps are presented in Table 5.

Crystallinity

The X-ray diffraction equipment employed by Jentzen was used here, except that diffraction patterns were obtained for 0.5 g discs of dry pulp fibres, formed by 15 sec compaction under a compressive loading of 20 000 lb/in^2: crystallinity was then determined by measurement of the width at half-height of the 002 diffraction peak. This technique was used to lessen the

TABLE 5—CHEMICAL CONTENT OF LONGLEAF PINE SUMMERWOOD HOLOCELLULOSE PULPS*

Sample	*Yield,† per cent*	*Glucan, per cent*	*Xylan, per cent*	*Mannan, per cent*	*Araban, per cent*	*Galactan, per cent*
Unextracted holocellulose pulp‡	72	55.5	6.68	15.6	1.29	1.82
Holocellulose pulp extracted with 0.1N potash	62	56.0	5.52	15.2	0.86	1.13
Holocellulose pulp extracted with 0.1N potash + 2 per cent potash + 9 per cent potash	54	53.0	1.35	11.9	—	0.86
Holocellulose pulp extracted with 0.1N potash + 2 per cent potash + 9 per cent potash/3 per cent boric acid	50	51.5	1.28	7.8	—	0.78

* Method of Saeman *et al.*
† Based on extractive-free and moisture-free wood
‡ Klason lignin 0.45 per cent

uncertainty arising, in the comparison of different pulps, in the different levels of hemicelluloses. The observations are given in Table 6, in which it will be seen (through interpretation) that extraction caused increases in average crystallite size and crystallinity, the effects being small in the first extraction and larger in the second and third extractions. It seems likely that, at least in the second and third extractions, removal of hemicelluloses was accompanied by increments in cellulose-cellulose bonding.

Investigation of side effects

The several extraction solutions might have caused changes in fibre properties other than those directly associated with hemicellulose removal. One

TABLE 6—X-RAY CRYSTALLINITY VALUES OF HOLOCELLULOSE PULPS AS A FUNCTION OF HEMICELLULOSE CONTENT

Reading	*Non-extracted holocellulose fibres*	0.1N *potash extracted*	9 *per cent potash extracted*	9 *per cent potash and* 3 *per cent boric acid extracted*
Width at half-height, degrees	2.87	2.82	2.73	2.57

of the first of the possible modifications that comes to mind is that of alkaline degradation. To minimise this, the extractions were carried out under nitrogen for short times. Viscosity tests revealed no degradation.

There was no possibility of mercerisation of the cellulose, as the maximum potash concentrations employed were below the mercerisation level. Even so, the possible existence of mercerisation was investigated by means of X-ray diffraction; this showed that the structure of the cellulose in all the samples was that of cellulose I.

Chemically induced swelling might have produced changes in the mechanical properties of the fibres. Although such modifications could not be observed directly (or inferred from the data), a special series of determinations was made with cotton fibres, which approximate the final condition of a series of hemicellulose extractions of a holocellulose pulp. Load/elongation recordings were run on single cotton fibres from treated and untreated samples, in a series in which the alkaline extraction solutions were applied to specially purified cotton in a manner simulating the extraction treatments of the holocellulose pulp. The stress/strain data showed that both the breaking stress and Young's modulus increased slightly with increasing potash concentration of the extraction solutions. As can be seen from the data to be presented later, this result is the opposite of that observed in the holocellulose series. This strongly indicates that the data for the holocellulose series are governed by the removal of the hemicelluloses.

Results and discussion

The drying phenomena observed by Jentzen were found also for all the fibres in the partially extracted holocellulose pulps, namely, the creep in the first period, followed by the rapid extension of the fibre in the first stage of drying, followed by a slow shrinkage, then, on removal of load, a small elastic contraction in span length to a residual permanent set of appreciable magnitude.

Detailed results computed from observations on fibres after removal from the Jentzen apparatus are presented in Table 7. The rupture stress and Young's modulus data presented in this table are based on the cellulose cross-sectional areas of the fibres. It is of considerable interest to note that the strongest fibres (at remarkably high rupture stresses) were those of the holocellulose pulp and the pulp after treatment with the 0.1N potash solution. One notes that the increments in tensile strength and Young's modulus produced by drying under tension are pronounced as in the earlier work and that the relative increments are substantially greater in the extracted pulps, the latter tending towards levels at the 3 g and 5 g drying loading comparable with those of the unextracted and 0.1N potash-extracted pulps.

TABLE 7—INDIVIDUAL FIBRE CHARACTERISTICS AS FUNCTIONS OF DRYING LOAD AND HEMICELLULOSE CONTENT

Fibre characteristics		*Non-extracted holocellulose fibres* Drying load, g				*0.1N potash-extracted holocellulose fibres* Drying load, g			
		0	*1*	*3*	*5*	*0*	*1*	*3*	*5*
Breaking load, g	Average	50.1	67.3	59.6	63.8	45.3	52.1	60.5	60.5
	S.D., per cent	32.6	18.9	22.1	25.9	29.8	25.0	23.3	27.1
Tensile strength, dyn/μ^2	Average	222	245	254	267	186	246	254	261
	S.D., per cent	26.7	18.0	15.7	18.8	25.8	28.3	13.1	22.0
Ultimate elongation, per cent	Average	5.44	4.93	4.07	3.99	5.45	4.97	4.11	3.74
	S.D., per cent	27.0	17.8	17.6	16.8	34.1	21.0	19.2	23.2
Young's modulus, dyn/μ^2	Average	5 150	7 180	8 570	8 830	4 640	8 000	8 910	9 700
	S.D., per cent	32.3	15.3	10.7	13.0	31.6	21.5	13.4	16.0
Measured cross-sectional area, μ^2	Average	479	587	495	505	476	418	464	456
Absolute cellulose cross-sectional area, μ^2	Average	221	271	228	233	240	211	234	230
Number of fibres tested		33	16	15	29	31	16	24	26

Fibre characteristics		*9 per cent potash-extracted holocellulose fibres* Drying load, g				*9 per cent potash and 3 per cent boric acid extracted holocellulose fibres* Drying load, g			
		0	*1*	*3*	*5*	*0*	*1*	*3*	*5*
Breaking load, g	Average	23.4	34.6	36.8	41.5	17.4	31.4	35.1	38.9
	S.D., per cent	28.1	17.7	16.7	20.4	32.1	17.8	18.3	18.0
Tensile strength, dyn/μ^2	Average	98.8	146	161	171	77.5	136	157	153
	S.D., per cent	24.0	12.1	17.5	18.2	22.4	21.3	15.1	14.6
Ultimate elongation, per cent	Average	5.30	3.67	2.73	2.56	6.15	3.74	2.66	2.47
	S.D., per cent	26.9	43.2	15.4	15.7	39.1	21.0	14.5	14.8
Young's modulus, dyn/μ^2	Average	2 060	6 180	7 800	8 400	1 080	6 110	7 990	7 980
	S.D., per cent	32.7	18.8	17.3	12.4	38.5	20.9	10.6	12.1
Measured cross-sectional area, μ^2	Average	398	397	389	410	348	376	353	403
Absolute cellulose cross-sectional area, μ^2	Average	234	234	228	240	217	235	220	252
Number of fibres tested		32	16	26	26	27	14	24	25

The decrement in cross-sectional area associated with increasing extraction of the hemicelluloses is associated, of course, with the removal of material from the fibres. It is generally felt that the hemicelluloses do not contribute *directly* to the strength characteristics of woodpulp fibres; accordingly, it is often the practice to compute stresses on the basis of the cross-sectional area of the cellulose—the central idea being that the cellulose fibrils constitute nearly all of the strong core of the structure, the hemicelluloses playing important secondary roles.

For these reasons, we have converted the stress/strain data to the basis of the solid (or cellulosic) cross-section. The latter was determined by plotting the

observed areas against the glucose content and extrapolating the relationship (fortunately, a linear one) to 100 per cent glucose. This yielded a figure of 231μ^2 for the fibre population and this was used, in turn, to convert the stress data for the individual groups to the cellulose base.

The converted data are presented in graphical form in Fig. 7, 8 and 9, which give respectively the breaking stress, ultimate strain and Young's modulus as functions of the drying load. The breaking stresses (Fig. 7) of the holocellulose fibres before and after treatment with 0.1N potash are remarkably high. That of the fibres following the second and third extractions is only *relatively* low, as the strength is quite high when compared with existing data for individual fibres; as already stated, there was no evidence of degradation of the fibres by the extraction treatment. Accordingly, the substantial difference between the strengths of the holocellulose pulp and the more heavily extracted pulps is surprising. As already observed, the relative enhancement of strength caused by drying under tension is greatest in the more heavily extracted pulps. The present work sheds some light on the observations of Leopold & McIntosh.[20]

The results for Young's modulus (Fig. 9) display a more striking dependence on the drying load. The increment for the first two pulps is almost a factor of two, whereas that for the more heavily extracted fibres is a factor of about five. It will be seen, too, that the moduli for the more heavily extracted pulps more closely approach the levels for the first two pulps than is the case for tensile strength. It will be noted that the highest values of the modulus are in agreement with the value of Meyer & Lotmar[17] and that, in the case of the present data, it is not necessary (as was the case earlier) to convert to the basis of cellulose in the S2 layer only.

It is too early, at the time of writing, to draw definite conclusions on the connection between the close grouping of the results for the second and third pulps and the changes in the compositional patterns of the hemicelluloses (Table 5).

Having noted that the partial removal of the hemicelluloses reduces both the breaking stress and Young's modulus, it is interesting to speculate on the possibility that the hemicelluloses, while possibly not contributing directly to the tensile stiffness and strength, do enhance uniformity of stress distribution within the fibre. In fibres of reduced hemicellulose content, it is possible that the more extensive cellulose-cellulose bonding produces a more rigid structure in which the stress cannot be so uniformly distributed. Accordingly, it is understandable that these fibres on drying *without* load should display reduced tensile stiffness and strength. When these fibres (never having been dried) are loaded in the turgid condition, however, internal configurational changes towards a more uniform distribution of stress can occur and large

increments in the tensile stiffness and strength for the final dry condition ensue. There is not yet an explanation at hand for the fact that tension drying of the more heavily extracted fibres produces a much closer approach of tensile stiffness to that of the holocellulose fibres than is the case for tensile strength. It is possible, of course, that local stress concentrations in the fibre

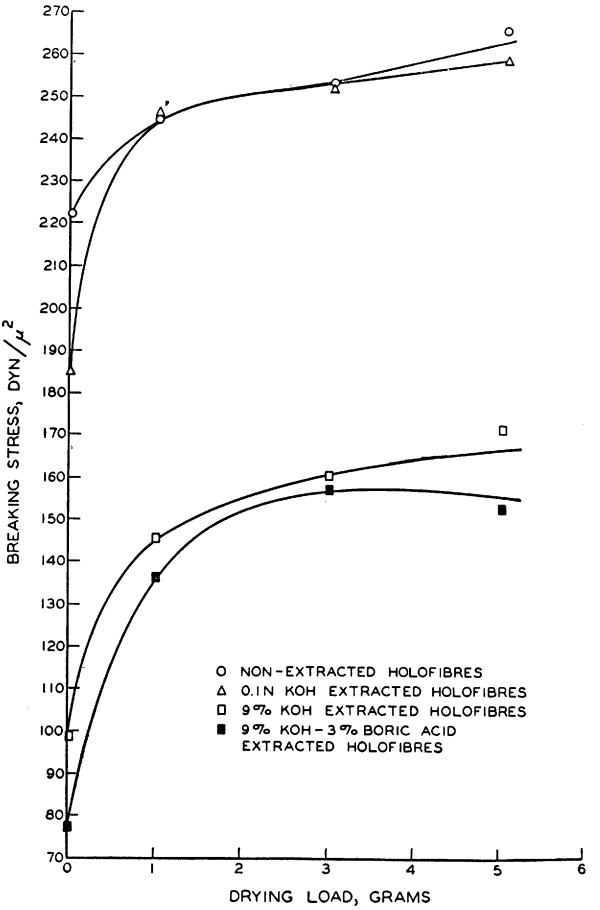

Fig. 7—Tensile strength of individual fibres as a function of drying load for various levels of hemicellulose content

tend to promote early failure in the more rigid structure of the extracted fibres. This is strongly supported by the data presented in Fig. 8, which show that the more heavily extracted fibres dried under load have substantially lower breaking strain—often a symptom of internal stress concentrating effects.

The earlier reported strain hardening of holocellulose fibres, observed in dry load/elongation cycling, is found also in the extracted fibres, but the effect is much reduced. Evidently, the hemicelluloses enhance the uniformity of stress distribution in dry fibres as they do in wet fibres, although not to as great an extent.

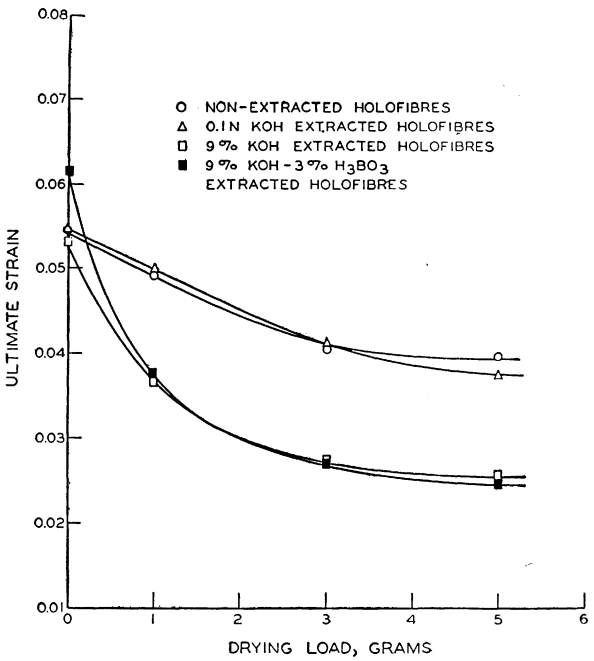

Fig. 8—Ultimate strain of individual fibres as a function of drying load for various levels of hemicellulose content

In view of the lower tensile stiffness and strength of the extracted fibres dried without tension, but of the relatively large enhancement of these properties caused by drying under tension, the effect of drying tension is seen to be of more importance in pulps approximating to commercial types than in holocellulose.

Tension drying and the zero-span technique for determining fibre strength

ON THE BASIS of the work presented in the foregoing sections, it is clear that the effects in individual fibres of tension drying must be taken into consideration in using the zero-span technique for measuring fibre strength. For

example, the most commonly employed techniques for preparing handsheets for pulp characterisation involve drying of the sheets under restraint. The

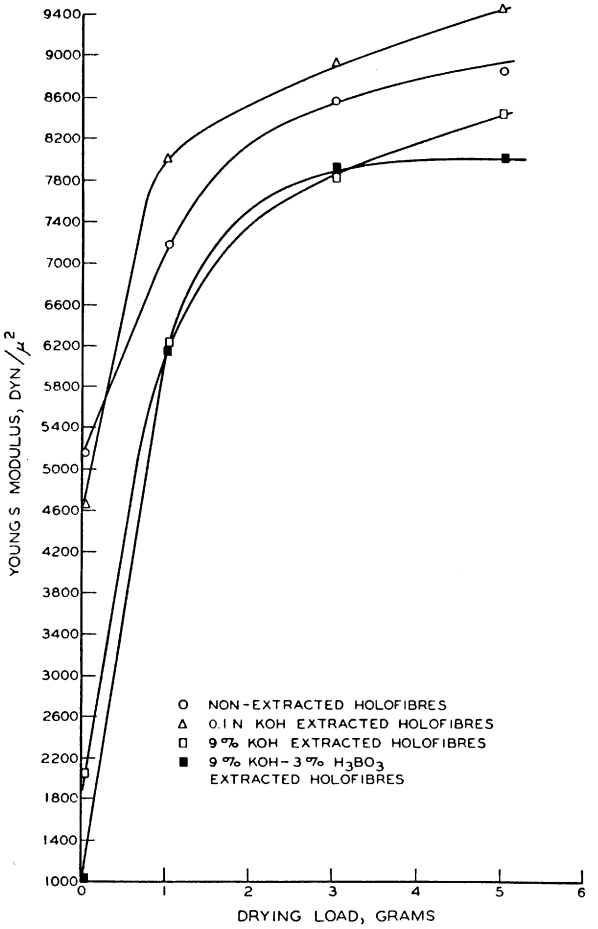

Fig. 9—Young's modulus of individual fibres as a function of drying load for various levels of hemicellulose content

tension developed in such sheets is nominally isotropic, so that all the fibres dry under axial tension. The actual level of the tension depends upon the nature of the fibres, the degree of beating and the wet pressing. Accordingly, the fibre strength measured by the zero-span technique is affected to some extent by the shrinkage characteristics of the handsheet.

This consideration gives insight into an old and puzzling problem. It has long been known that the zero-span tensile strength is an increasing function of the degree of beating, particularly at low levels of beating. It has been commonly supposed that the effect is attributable to the influence of bonding; bonding should enhance the gripping of the fibres and, as is well known, beating promotes bonding. Although this effect may indeed be a significant factor, not all data support this hypothetical mechanism.[21] It is now appreciated that at least a portion of the initial increase in zero-span tensile strength with increasing beating is attributable to the actual enhancement of fibre strength produced by augmented tension in the fibres during drying.

It is obvious that the effect must be taken into account in future work on the determination of fibre strength through zero-span tensile data. This could be effected through development of new methods for preparing handsheets that would permit variation and control of drying stress or strain in the sheet.

One of the planar properties of machine-made paper that would be modified by tension in the web during drying is the zero-span tensile strength. Although the practice is often inadvisable, technical men have for some time measured the zero-span tensile strength of machine-made paper in an effort to determine the strength of fibres as they exist in finished paper. The test has also been made to determine the 'squareness' of paper.

These aims are commendable and the work presented in this section was done in an effort to improve the interpretation of data on and to define the scope of zero-span tensile strength of commercial paper. With regard to the latter, Wink & Van Eperen[22] have shown in a very comprehensive study of the zero-span test that legitimate data may be obtained only when the variables of the equipment and test material fall in certain ranges. Extending from their observations with handsheets, it may be said that valid interpretation of zero-span data for machine-made paper is not to be expected unless the paper is (*a*) uncoated, (*b*) of a substance near optimum for legitimate zero-span testing—that is, in the approximate range 40–80 g/m^2, (*c*) of good formation, (*d*) homogeneous in composition (for example, the furnish is not a mixture of pulp and synthetic fibres) and (*e*) uncreped or flat in the sense that it has not been treated to be unusually extensible. Until the effect of bonding in paper on the zero-span tensile is more completely understood, it would seem that the test should not be made on paper for which the stock has been subjected either to essentially no refining or to intensive beating.[22]

With the possible exception of restriction (*a*) above, it would seem that all of the foregoing conditions should be rigidly adhered to. It is conceivable that, for given grades of paper, empirical relationships might be discovered that would permit one to deviate from conditions (*a*) and (*b*).

Perhaps the most significant problem encountered in the interpretation of

zero-span tensile test data for machine-made paper is that of the anisotropic distribution of fibre elements in the xy-plane of the sheet. One of the aims of the present discussion is the development of theory for the interpretation of zero-span test data in terms of intrinsic fibre strength and sheet asymmetry.

Theory

The theoretical analysis of paper structure presented at the 1961 Oxford symposium, to which reference has already been made,[10] can be extended to yield a relationship between zero-span tensile load and fibre stress in anisotropic paper. For the reasons set forth in the last section of the Oxford paper, *Note on the theory of the zero-span tensile test*, only the second integrals appearing in equations (*13*) and (*14*) of the paper are retained. It may be added that, if the higher state of bonding in commercial paper would seem to render vulnerable the assumption that the first integrals may be dropped, these integrals are always numerically small when the level of refining is moderate and, more important, when rupture is imminent, it must be supposed that bond breaking in the critical zone has proceeded to the point of making s^2 (in h) large enough to justify dropping the first integrals (the terminology of the Oxford paper is retained in the present work).

The paper should be 'flat' and approximate the linear model described in the first paragraph of the Oxford paper under *Model and assumptions for the present work*. In other words, the paper should not be creped or otherwise treated to render it unusually extensible.

The angular distribution function P_θ is nominally symmetrical about the machine-direction; the shake at the wet end of the machine (if in action) can cause a cyclic variation of angle between the axis of symmetry (the x-axis) and the machine-direction. With this in mind, the assumption is made that P_θ is symmetrical about the x-axis. As stated earlier, the angle θ is referred to the y-axis, the range being from zero to π.

Actual angular distribution functions such as those published by Danielsen & Steenberg[23] could, no doubt, be represented with good accuracy by finite series of sinusoidal terms. In view of the $\sin^4\theta$ weighting of P_θ when the external load is in the x-direction (and $\cos^4\theta$ weighting when the load is in the y-direction), it occurs to one that a relatively simple function might suffice for the purposes of zero-span theory. Theoretical trials might be done, for example, with symmetrical functions like $P_\theta = \alpha + \beta \sin^n \theta$, in which α and β are adjustable constants and n is an even number. Three functions of this form have been tried—

$$P_\theta = \alpha + \beta \sin^2 \theta \quad . \quad . \quad . \quad . \quad (1)$$
$$P_\theta = \alpha + \beta \sin^4 \theta \quad . \quad . \quad . \quad . \quad (2)$$
$$P_\theta = \alpha + \beta \sin^6 \theta \quad . \quad . \quad . \quad . \quad (3)$$

Of course, in fitting these functions to experimental data by theory, one finds that α and β take on different values in the three functions. The natures of the functions are depicted in Fig. 10 for a particular ratio of the constants. The perfectly random distribution, for which $\alpha = 1/\pi$ and $\beta = 0$, is shown by the half-circle. For the rather extreme ratio, $\beta/\alpha = 4$, the distribution given in equation (*3*) most closely resembles the experimental distributions published by Danielsen & Steenberg.[23] This particular function then is favoured, although, as shown later, the results obtained by the theoretical interpretation of zero-span tensile data are not sensitive to the choice of function.

For any distribution function, the condition expressed by equation (*4*) must be satisfied—

$$\int_0^{\pi} P_\theta \, d\theta = 1 \qquad . \quad . \quad . \quad . \quad (4)$$

It can be shown from equations (*13*) and (*14*) of the Oxford paper that the zero-span breaking loads per unit width of the sheet in the x- and y-directions are—

$$\mathscr{T}_x/\mathscr{U} = (W/\rho)\sigma^* \int_0^{\pi} \sin^4 \theta \, P_\theta \, d\theta \qquad . \quad . \quad . \quad (5)$$

$$\mathscr{T}_y/\mathscr{U} = (W/\rho)\sigma^* \int_{-\pi/2}^{\pi/2} \cos^4 \theta \, P_\theta \, d\theta \qquad . \quad . \quad (6)$$

in which $\mathscr{T}_x$ and $\mathscr{T}_y$ are the zero-span breaking loads, $\mathscr{U}$ is the width of the zero-span jaws, W is the substance of the sheet, ρ is the mean density of the fibre wall and σ^* is the intrinsic strength or tensile rupture stress of the fibres.

We must now take into account the effect of axial tensile and compressive forces in the individual fibres during drying of the web. This discussion will provide us in essence with an interpretation of σ^* in equations (*5*) and (*6*). Let σ_0^* be the failing stress of a fibre dried without tension and D_θ be so defined that the failing stress of a fibre in which the failing segment is at θ is $\sigma_\theta^* = D_\theta \sigma_0^*$. In view of our earlier discussion of the nature of variation of axial forces in fibre segments in a web dried under tension and of the effects upon fibre strength of tension drying (including the hypothetical decrement in strength caused by axial compressive force), it is seen that D_θ is less than unity for the angular ranges of zero to about 30° and about 150° to 180°; greater than unity for the angular range of about 30° to about 150°, with a maximum at 90°. With reference to equations (*5*) and (*6*), it is seen that a more correct representation of the righthand terms is obtained by introducing the failing stress in the integrands, in the form of $D_\theta \sigma_0^*$. When this is done, it is found that the factor σ^* must be replaced in equation (*5*) with $\sigma_0^* \langle D \rangle_x$ and with $\sigma_0^* \langle D \rangle_y$ in equation (*6*), where—

$$\langle D\rangle_x = \left[\int_0^{\pi} \sin^4\theta\, P_\theta D_\theta\, d\theta\right] \Big/ \left[\int_0^{\pi} \sin^4\theta\, P_\theta\, d\theta\right] \quad . \quad . \quad (7)$$

and

$$\langle D\rangle_y = \left[\int_{-\pi/2}^{\pi/2} \cos^4\theta\, P_\theta D_\theta\, d\theta\right] \Big/ \left[\int_{-\pi/2}^{\pi/2} \cos^4\theta\, P_\theta\, d\theta\right] \quad . \quad (8)$$

In other words, the averages given by equations (*7*) and (*8*) are continuously weighted means, in which the weighting functions are, respectively, $\sin^4\theta\, P_\theta$, with a maximum along the x-direction, the x-direction being the centre of the range of averaging and $\cos^4\theta\, P_\theta$, with a maximum along the y-direction, the y-direction being the centre of the range of averaging. In view of the consideration that D_θ runs from a maximum that is greater than unity in the x-direction to a minimum that is less than unity in the y-direction, *equations* (*7*) *and* (*8*) *show that* $\langle D\rangle_x$ *is greater than unity and* $\langle D\rangle_y$ *is less than unity.*

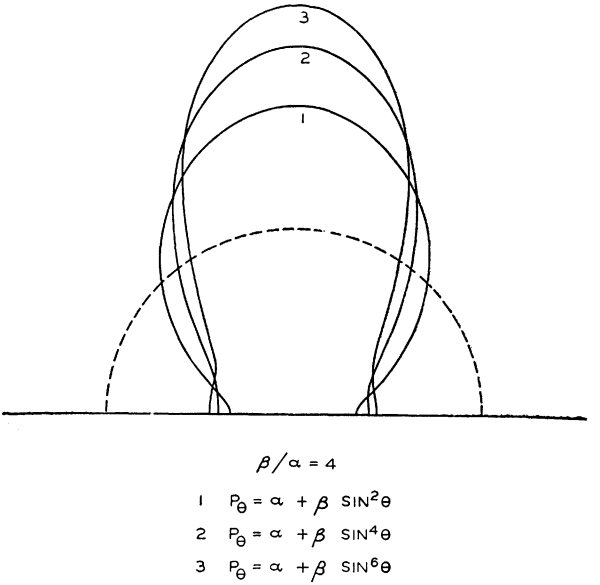

Fig. 10—Distribution functions P_θ for fibre segments employed in the theoretical treatment of zero-span tensile strength of machine-made paper

When the distribution functions of equations (*1*), (*2*) and (*3*) are substituted into the foregoing expressions [utilising equations (*4–8*)], the sets of expressions given below [equations (*10–21*)] are obtained for the quantities of interest. The quantity Q in these expressions is given by—

$$Q = (\mathcal{T}_x/\mathcal{T}_y)(\langle D\rangle_y/\langle D\rangle_x) \quad . \quad . \quad . \quad (9)$$

The first factor on the right side of equation (*9*) is the ratio of the machine-direction zero-span tensile strength to the cross-direction strength and is generally greater than unity; the second factor, for the reasons given immediately above, is less than unity. Until more is known about the second factor, it is impossible to estimate its value, but the second equation in each of the three sets of expressions below implies that Q is greater than unity (in view of the consideration that β is a positive number). Considerable interest is found in β/α, as this may be taken as a measure of the asymmetry of the paper with regard to fibre orientation. Of course, the quantity of $\sigma_0^*\langle D\rangle_x$, given in the fourth of each of the three sets of equations, is of importance, because it is the mean breaking stress appropriate to the x-direction zero-span tensile strength.

Distribution of equation (*1*)

$$\alpha = (1/\pi)(5-Q)/(2Q+2) \quad . \quad . \quad . \quad . \quad (10)$$

$$\beta = (3/\pi)(Q-1)/(Q+1) \quad . \quad . \quad . \quad . \quad (11)$$

$$\beta/\alpha = 6(Q-1)/(5-Q) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\sigma_0^*\langle D\rangle_x = (\rho/W)(8/3)[(Q+1)/2Q](\mathscr{T}_x/\mathscr{U}) \quad . \quad . \quad (13)$$

Distribution of equation (*2*)

$$\alpha = (1/\pi)(35-3Q)/(15Q+17) \quad . \quad . \quad . \quad (14)$$

$$\beta = (48/\pi)(Q-1)/(15Q+17) \quad . \quad . \quad . \quad (15)$$

$$\beta/\alpha = 48(Q-1)/(35-3Q) \quad . \quad . \quad . \quad . \quad (16)$$

$$\sigma_0^*\langle D\rangle_x = (\rho/W)(8/3)[(15Q+17)/32Q](\mathscr{T}_x/\mathscr{U}) \quad . \quad . \quad (17)$$

Distribution of equation (*3*)

$$\alpha = (1/\pi)(21-Q)/(9Q+11) \quad . \quad . \quad . \quad . \quad (18)$$

$$\beta = (32/\pi)(Q-1)/(9Q+11) \quad . \quad . \quad . \quad . \quad (19)$$

$$\beta/\alpha = 32(Q-1)/(21-Q) \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$\sigma_0^*\langle D\rangle_x = (\rho/W)(8/3)[(9Q+11)/20Q](\mathscr{T}_x/\mathscr{U}) \quad . \quad . \quad (21)$$

The square-bracketed quantity in each of equations (*13*), (*17*) and (*21*), which we shall designate B, is unity for the isotropic distribution (for example, ideal handsheets) and diminishes as the asymmetry increases. This quantity is shown for four typical levels of Q, for each of the three distributions, as follows—

		$Q = 1.0$	$Q = 1.3$	$Q = 1.6$	$Q = 2.0$
Distribution 1	$B =$	1	0.885	0.813	0.750
Distribution 2	$B =$	1	0.878	0.802	0.735
Distribution 3	$B =$	1	0.873	0.793	0.725
Distribution 1	$\beta/\alpha =$	0	0.49	1.06	2.00
Distribution 2	$\beta/\alpha =$	0	0.46	0.95	1.66
Distribution 3	$\beta/\alpha =$	0	0.49	0.99	1.68

Fortunately, B is very insensitive to the choice of the distribution and,

accordingly, the computed value of the fibre rupture stress does not depend importantly on which of the three distribution functions is chosen. At $Q=1.3$, the whole range is 1.4 per cent; when $Q=1.6$, the range is 2.5 per cent and, even when $Q=2.0$, the range is only 3.4 per cent, which is of the order of uncertainty of the experimental data. For the reason given earlier, the third distribution given by equation (*3*) is preferred.

It will be seen also that the measure of asymmetry β/α is less insensitive to the choice of distribution function. There is not, however, an appreciable difference between the calculated values for the second and third distributions.

Illustrative treatment of zero-span data

The foregoing theoretical treatment has been applied (within the limitations of our present state of ignorance) to zero-span data for twelve samples of 50 lb kraft sack paper ('flat'), all made on Fourdrinier machines. In the absence of information on the ratio of the means of D for the x- and y-directions, this ratio was equated as an experimental trial to unity, so that Q becomes simply the ratio of the machine-direction to cross-direction zero-span tensile strengths. The data together with calculations are presented in Table 8. The rupture stress calculations presented in the last three columns are based, respectively, on the distributions of equations (*1*), (*2*) and (*3*). For the purposes of these calculations, it was assumed that the fibre wall density was 1.55 g/cm^3. The third distribution function was used for calculating the asymmetry factor given in the sixth column of Table 8.

Although the asymmetry factor varied through a wide range (ratio of maximum to minimum values was equal to 7.6), the calculated fibre rupture stress varied only 53–60 kg/mm^2. It seems quite obvious that the fibre strength of sample 1 was the lowest by a wide margin; overlooking the data for this sample, all of the computed fibre rupture stresses lay within 55–60 kg/mm^2, a spread of only ± 4.3 per cent. This result is remarkable when it is considered that it includes variance of sheet and fibre properties in eleven machine-made papers, rather remarkable differences in the assumed fibre distribution functions and all sources of experimental error. Additionally, the mean fibre rupture stress for samples 2–12 is 57 kg/mm^2, which compares well with laboratory data[24] observed for unclassified kraft pulp—namely, about 54 kg/mm^2 for southern pine and 69 kg/mm^2 for Douglas fir (after making a 10 per cent correction for zero-span jaw improvement since 1954, when the zero-span tensile strength data for handsheets were obtained).

It is tempting to conclude that, for the twelve samples of machine-made paper involved in this work, D_θ was fairly isotropic, but trial calculations showed that $\langle D\rangle_y/\langle D\rangle_x$ can be appreciably less than unity without modifying the constancy of $\sigma_0{}^*\langle D\rangle_x$ computed on the basis of the three distribution

functions. As one would expect, this value increases with reduction in the foregoing ratio.

In future work, it will be of interest to fit observed data on P_θ with, for example, the distribution of equation (*3*). Then, on the basis of the observed ratio of x- and y-direction zero-span strengths and equations (*18–20*), the asymmetry in D [the last factor in equation (*9*)] could be determined. This kind of information would be of interest in studying, for example, the importance of tension drying in commercial pulp fibres in the normal production of paper.

TABLE 8—CALCULATION OF FIBRE RUPTURE STRESS FROM ZERO-SPAN DATA

Sample number	*W*, g/m^2	*Machine-direction zero-span*, *kg/cm*	*Cross-direction zero-span*, *kg/cm*	*Q**	β/α	*Fibre rupture stress*, kg/mm^2		
						(1)	(2)	(3)
1	82.0	10.78	10.16	1.060	0.096	53	53	53
2	81.0	12.80	10.58	1.210	0.34	60	59	59
3	83.3	13.00	10.21	1.273	0.44	58	57	57
4	83.5	12.30	9.98	1.233	0.38	55	55	55
5	84.6	12.91	10.56	1.223	0.36	58	57	57
6	81.3	13.00	9.15	1.421	0.69	57	56	55
7	82.6	14.22	9.83	1.446	0.73	60	60	59
8	83.0	12.60	9.80	1.286	0.46	56	55	55
9	80.7	12.20	10.47	1.165	0.27	58	58	58
10	84.6	12.95	10.03	1.291	0.47	56	56	55
11	84.3	12.68	10.73	1.182	0.29	57	57	57
12	82.3	13.27	10.70	1.240	0.39	60	60	60

*With the ratio of the means of D for the x- and y-directions equated to unity

Concluding remarks

EVEN THOUGH an application of theory and of experimental findings to improve our understanding of the zero-span test of fibre strength is of current importance, the larger problem of improving our knowledge of the connections between paper properties and fibre behaviour should receive more attention. Through theory and the findings reported herein on the effects of tension drying of fibres, one can hope to develop a much better understanding and working knowledge of the effects on web properties of tension in the draws, cross-direction tension on the dryers, of the actions of bowed rolls and the like.

The effects of hemicelluloses on the mechanical properties of sheets are well known. Reference is often made to the probable contributions of these substances in fibre-to-fibre bonding. The present work strongly indicates that, in addition to their role in fibre bonding, the hemicelluloses promote greatly

enhanced fibre strength and Young's modulus, both of which properties are significantly increased by drying of the fibre under tension; these actions should, of course, be reflected in the properties of the paper.

Acknowledgements

The authors wish to express their appreciation of the care of Mr W. A. Wink and his associates in the determinations of zero-span tensile strength. We wish also to thank the sponsors of a programme on pulp characterisation for their kindness in releasing work that forms a portion of this paper.

References

1. Campbell, W. B., *Canada Dept. Interior, Forest Service Bull. No. 84* (1933)
2. Edge, S. R. H., *Proc. Tech. Sect. P.M.A.*, 1944, **25**, 210–215
3. Edge, S. R. H., *Proc. Tech. Sect. P.M.A.*, 1945, **26**, 425–431
4. Edge, S. R. H., *Chem. & Ind.*, 1948, **67** (51), 803–807
5. Sapp, J. E. and Gillespie, W. F., *Paper Trade J.*, 1947, **124** (9), 120, 122, 124, 126
6. Brecht, W. and Pothmann, D., *Das Papier*, 1955, **9** (13/14), 304–311
7. Hudson, F. L., *Svensk Papperstidn.*, 1963, **66** (3), 60–63
8. Schulz, J. H., *Tappi*, 1961, **44** (10), 736–744
9. Van den Akker, J. A., *Tappi*, 1950, **33** (8), 398–402
10. Van den Akker, J. A., *Formation and Structure of Paper*, Ed. F. Bolam (Technical Section, B.P. & B.M.A., London, 1962), 205–241
11. Jentzen, C. A., *Doctor's Dissertation* (The Institute of Paper Chemistry, Appleton, 1964)
12. Jentzen, C. A., *Tappi*, 1964, **47** (7), 412–418
13. Thompson, N. S. and Kaustinen, O. A., *Tappi*, 1964, **47** (3), 157–162
14. Segal, L., Creely, J. J., Martin, A. E. and Conrad, C. M., *Textile Research J.*, 1959, **29** (10), 786–794
15. Gjonnes, J., Norman, N. and Viervol, H., *Acta Chem. Scand.*, 1958, **12** (3), 489–494
16. Hardacker, K. W., *Tappi*, 1962, **45** (3), 237–246
17. Meyer, K. H. and Lotmar, W., *Helv. Chim. Acta*, 1936, **19** (1), 69–86
18. Spiegelberg, H. L., *Doctor's Dissertation*, in preparation (The Institute of Paper Chemistry, Appleton)
19. Hardacker, K. W., Work to be published
20. Leopold, B. and McIntosh, D., *Tappi*, 1961, **44** (3), 235–240
21. Wink, W. A., Unpublished work
22. Wink, W. A. and Van Eperen, R. H., *Tappi*, 1962, **45** (1), 10–24
23. Danielsen, R. and Steenberg, B., *Svensk Papperstidn.*, 1947, **50** (13), 301–305
24. Van den Akker, J. A., Lathrop, A. L., Voelker, M. H. and Dearth, L. R., *Tappi*, 1958, **41** (8), 416–425

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

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 anisotropic microfibrils (which are extremely strong in their length direction) and the more or less isotropic hemicellulose. When the fibre is loaded, the microcompressed 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 cross-linked 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

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 paper-machine. Since we cannot expect an even moisture content in the fibre material, the outer fibre surface, which is most efficiently exposed to the drying

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.