

THE INFLUENCE OF ELECTROLYTES AND CERTAIN SUBSTANTIVE AZO-DYES ON THE RATE OF BEATING

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Summary

From the results of beating experiments on several pulps in the presence of electrolytes and water soluble substantive azo-dyes, it has been possible to draw the following conclusions —

- 1. Generally speaking, the presence of various electrolytes causes a decrease of the beating rate of the cellulose fibres in comparison with beating in distilled water. In some few instances, there has been noted a slight increase of the beating rate. This fact could be explained on the basis that the additive acts as a sequestrant of the cations present in water. In fact, this seems to be more realistic than the hypothesis of specific action of the electrolytes on the fibre during the beating process.*
- 2. Some substantive azo-dyes belonging to the benzidine class cause outstanding acceleration in beating, together with a remarkable improvement in the mechanical characteristics of the corresponding paper sheets.*

3. *When the same dyes are added to beaten pulp, an increase of beating degree ($^{\circ}$ S.R.) is obtained without any remarkable change in the strength.*

4. *When the dye is extracted from the beaten pulp, a decrease of beating degree ($^{\circ}$ S.R.) is observed. If compared with paper sheets prepared from unextracted pulps, those prepared from the extracted pulps show an increased folding endurance. The other strength characteristics do not present any noticeable variation.*

The results of these experiments are discussed on the hypothesis of the lamellar cleavage of cellulose fibres during beating and the interaction between dye molecules and cellulose macromolecules.

Foreword

WE had already noticed for some time that certain direct dyes added to aqueous solutions of hydrolysed polymers (methylcellulose) induce a considerable increase in viscosity.

This phenomenon, which was stressed in a brief paper, ⁽¹⁾ was later the subject of recent publications ^(2, 3) aiming to show the nature of interactions between dyes and dissolved macromolecules. Owing to certain phenomena not fully explained during this research work, the publication of results and pertinent observations was made a long time after the beginning of the research.

It was possible to observe in the meantime that addition of dyes involves an increase in the hydration of the pulp macromolecules and our attention was therefore drawn to the examination of the action that dyes may have on the beating of papermaking pulps.

The results of these tests have for the greater part been given in two papers ^(4, 5) already published and, in addition, a partial interpretation of their nature was given in other later papers. ^(6, 7)

How electrolytes affect beating

It is a known fact that the presence of certain substances in a suspension of pulp fibres in water may somewhat affect the beating rate. We have confined ourselves to the examination of the action brought about by various electrolytes. Some research on this subject was carried out by Cohen *et al.*, ^(8, 9) who also quoted an extensive bibliography on the subject. Based on the results achieved, these authors observed ⁽⁸⁾ that the beating rate of pulp and the physico-mechanical properties of paper processed in the presence of various cations, added as chlorides, decrease in proportion to the concentration and cation valency.

At the time when these papers became known, similar experiments carried out on different pulps beaten in distilled water, in tap water (18° French total hardness, 5° French permanent hardness), in softened water, in sodium bicarbonate solutions (pH 8), in alum (pH 5) and in tap water acidified with hydrochloric acid to pH 6, were being made at this institute.

The results, which were not published because they were superseded by the publication of more extensive and detailed results obtained in the Australian laboratories, agreed with the latter.

It is to be noted that, when referring to the behaviour of pulp and to the properties of paper processed in distilled water, sodium ions added as chlorides had no noticeable effect, whereas those added as bicarbonates had a slightly favourable action both on the rate of beating and on the paper properties. A similar behaviour was observed in the presence of tap water in which calcium and magnesium ions were replaced by sodium ions by ion exchange.

The presence of bivalent ions (Ca, Mg) — that is, processing with fairly hard tap water or with calcium bicarbonate solutions — is notoriously unfavourable; whereas, when acidifying hard water with hydrochloric acid to pH 6, in order to change the alkaline earth carbonates into chlorides or when experimenting with calcium chloride solutions in distilled water, no noticeable diminution in rate of beating is observed compared with tests in distilled water.

In Table 1, some of the more significant experiments in this connection are given.

TABLE 1
Bleached kraft pulp — Beating after distilled water washing

<i>Beating liquor</i>	<i>Jokro mill, no. rev.</i>	<i>Beating degree, °S.R.</i>	<i>Breaking length, m.</i>	<i>Bursting strength, kg./cm.²</i>	<i>Air permeability, ml./min.</i>
Tap water + HCl (0.1093 g./litre) — pH 6	4 000	23	7 630	4.2	100
	7 000	33	7 600	4.1	25
	10 000	44	8 200	4.6	19
Distilled water + CaCl ₂ (0.1663 g./litre) — pH 6	4 000	24	8 300	4.6	47
	7 000	35	8 300	4.4	25
	10 000	47	8 570	4.4	15
Distilled water + Ca(HCO ₃) ₂ (0.2428 g./litre) — pH 6	4 000	21	7 100	3.9	160
	7 000	29	7 800	3.9	90
	10 000	41	8 000	3.9	20
Distilled water — pH 5.8	4 000	24	8 340	4.6	45
	10 000	48	8 600	4.5	16

The aim of our tests was to clarify that the action of cations present in the cellulose water system had affected the cellulose solubility and therefore the stability of the cellulose gel, resulting from beating, following an ionic exchange on the carboxyl groups present in the macromolecules of a cellulose not submitted to refining processes, it being known that papermaking pulps have to some extent ion exchange properties. In our tests, we started from the consideration that soluble cellulose products (like carboxymethyl-cellulose and cellulose oxidised with nitrogen dioxide), owing to the great number of carboxyl groups present, have the property of being water soluble as sodium salts, considerably swollen but insoluble as calcium and magnesium salts and practically insoluble as aluminium salts. The phenomenon, although to a minor extent, because of a negligible number of carboxyls present in the entire mass and these also partially combined, is therefore reproduced through beating in the presence of sodium salts, because of ionic exchange.

During their first research investigation, the Australian authors ⁽⁸⁾ did not have sufficient grounds to support the theory that the carboxyl groups of cellulose were the cause of the different cation effect and therefore they stated that the phenomenon could be explained from the electrokinetic point of view.

In order to make the effects observed clearer, these authors ⁽⁹⁾ carried out work on the effect of anions, taking into consideration mono-, bi-, tri- and tetravalent anions as sodium salts.

Contrary to expectations, no valency effect was found as in the case of cations, only an improvement due to the presence of sodium ions was observed. The best results were obtained by using sodium hexametaphosphate and at very low concentrations (0.001 — 0.002 N). It was therefore necessary to reconsider the possibility that cellulose carboxyl groups played an important role, since cellulose has ion exchange properties through them and tends by chemical bonding to absorb the cations — that is, calcium and magnesium — with which it usually comes into contact.

The hexametaphosphate has water softening properties, sequestering calcium and magnesium ions in soluble form and releasing sodium ions. It is logical to assume that it releases from the cellulose calcium and magnesium ions (in fact, cellulose firmly holds them even when washed in distilled water) and it replaces them with its sodium ions, favouring a swelling greater than that obtained with other sodium anions, which do not have this property.

This may also explain the result of our experiments, which is that bivalent cations do not have any effect as chlorides, but a considerably negative action as bicarbonates. From the experiments quoted in this foreword, it may be concluded that, if we start from the beating rate in distilled water, the anion and cation action under consideration is generally speaking negative, with the exception of a very slight advantage obtained in the presence of the sodium salts of weak acids, chiefly due to an increase in pH. ⁽¹⁰⁾ In other words, the action of different salts that favourably affect pulp beating, is brought about only when annulling or neutralising that of bi- or trivalent cations.

Action of direct dyes of the benzidine class

A comparison was made of the action of some dyestuffs used in the paper industry on the beating behaviour of a bleached kraft softwood pulp. Beating tests were carried out with the Jokro mill, keeping constant the molar concentration of the dyestuff added to the mass (2 millimole/litre). The breaking length, bursting strength and air permeability properties (expressed in ml./min.) were measured on the sheets.

Only the results of tests on 10,000 rev. Jokro mill treatment are given in Table 2 for comparison. More comprehensive information is given in one of the papers mentioned earlier.⁽⁵⁾

TABLE 2

Dye	Class of dye	Beating degree, °S.R.	Breaking length, m.	Bursting strength, kg./cm. ²	Air permeability, ml./min.
Tap water	—	39	8 800	6.0	30
Distilled water	—	42	9 100	6.0	30
Congo Red	Direct	64	11 000	6.6	20
Benzopurpurine 10 B	Direct	54	10 640	6.2	20
Benzopurpurine 4 B	Direct	54	10 700	6.3	23
Congo Corinth G	Direct	48	9 560	6.1	22
Chicago Blue 6 B	Direct	59	10 000	6.4	25
Benzoazurin G	Direct	47	9 630	5.8	27
Direct Blue 2 B	Direct	51	10 000	6.2	27
Direct Black, conc. extra	Direct	47	9 640	5.8	30
Erika BN	Direct	39	8 900	5.9	30
Brilliant Paper Yellow	Direct	51	9 700	6.2	22
Fuchsin S	Acid	40	9 000	5.5	36
Brilliant Croceine 3 B	Acid	43	8 940	5.8	35
Bordeaux, conc. extra	Acid	38	9 300	5.8	47
Tartrazin J	Acid	40	9 520	5.9	40
Safranin, conc. extra	Basic	33	7 930	4.8	70
Vesuvium 4 BG	Basic	36	7 870	4.3	50
Victoria Blue B, conc.	Basic	35	7 450	4.2	72

From the comparison, it appeared that Congo Red has the strongest action both on the beating rate and on the increase in strength properties of sheets, as well as on the decrease in air permeability.

We have therefore continued our research work on the behaviour of various qualities of pulp in the presence of this dye, using three grades —

- (a) commercial bleached kraft softwood (for paper).
- (b) commercial bleached sulphite softwood (for paper).
- (c) highly refined linter (for acetylation).

We chose these qualities in order to test three types of raw materials having widely different behaviour on beating and giving different paper properties.

Beating was carried out in a Jokro mill, using a standard 6 per cent. stock consistency. After treatment at the strictly constant speed of 150 r.p.m., the pulp was brought to 0.8 per cent. consistency and, after thorough mixing, made into sheets weighing 60 g./sq. m. on the Rapid-Köthen sheet-machine according to German standard specifications.

With the exception of processing in tap water — for which no initial washing was carried out in distilled water, only slushing in tap water — the procedure was as follows —

1. Slushing of pulp in distilled water.
2. Washing in distilled water.
3. Soaking in beating solution.
4. Beating at 6 per cent. consistency in beating solution.
5. Dilution to 0.8 per cent. consistency in softened water.
6. Reading of the freeness (°s.R.) following dilution in softened water.
7. Sheet preparation following dilution in softened water.

The solutions used were—

1. Tap water	pH 7.3
2. Softened water	pH 8.0
3. Water + hexametaphosphate (0.004 N)	pH 6.8
4. Water + Congo Red (0.002 N)	pH 6.8

Sheets were submitted to mechanical tests after conditioning for 48 hr. at 20°C and 65 per cent. R.H. The properties measured were as follows —

1. Breaking length (expressed in m.).
2. Bursting strength (expressed in kg./cm.²).
3. Air permeability (expressed in ml./min.).

The results of experiments are shown in Tables 3 — 5 and in the graphs marked *L*, *B*, *K* for linters, sulphite pulp and kraft pulp, respectively, in Fig. 1, 2 and 3.

TABLE 3
Linter cellulose

Beating liquid	Jokro mill, no. rev.	Beating degree, °S.R.	Breaking length, m.	Bursting strength, kg./cm. ²	Air permeability, ml./min.
Tap water	6 000	17	1 420	0.60	—
	12 000	37	1 920	0.68	500
	18 000	60	2 140	0.76	110
Softened water	6 000	19	1 300	0.70	—
	12 000	44	1 960	0.76	270
	18 000	62	2 340	0.84	90
Distilled water + hexametaphosphate	6 000	20	1 600	0.70	—
	12 000	47	1 970	0.80	180
	18 000	64	2 300	0.84	63
Distilled water + Congo Red	6 000	26	1 870	0.70	—
	12 000	60	2 630	0.88	170
	18 000	77	3 440	1.08	30

Fig.1

Linter Cellulose

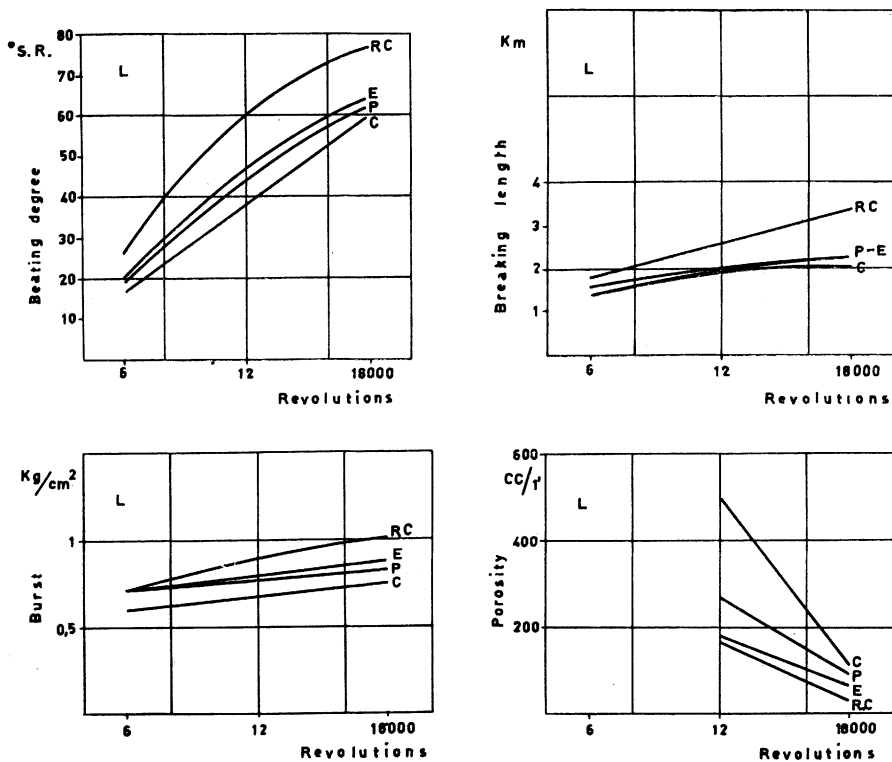


TABLE 4
Bleached sulphite pulp

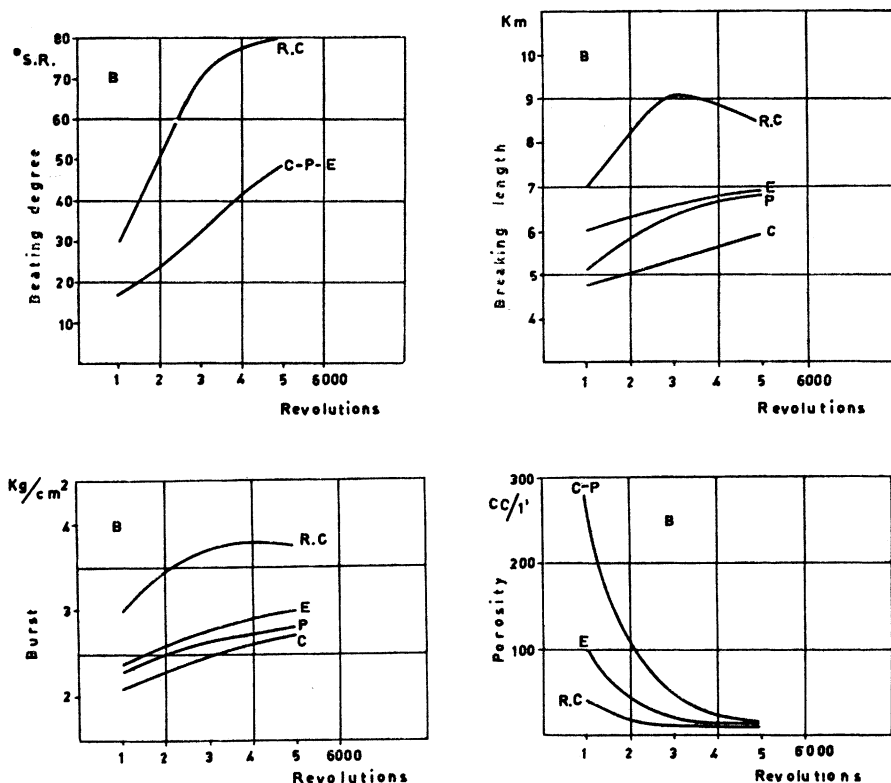
<i>Beating liquid</i>	<i>Jokro mill, no. rev.</i>	<i>Beating degree, °S.R.</i>	<i>Breaking length, m.</i>	<i>Bursting strength, kg./cm.²</i>	<i>Air permeability, ml./min.</i>
Tap water	1 000	17	4 750	2.1	270
	2 000	22	4 660	2	110
	3 000	31	4 940	2.46	35
	4 000	42	6 150	2.8	25
	5 000	48	6 170	2.7	15
Softened water	1 000	17	5 030	2.3	260
	2 000	23	6 350	2.6	100
	3 000	31	6 460	2.6	35
	4 000	42	6 720	2.8	25
	5 000	49	6 700	2.7	15
Distilled water + hexametaphosphate	1 000	18	6 050	2.4	100
	2 000	25	6 300	2.6	40
	3 000	33	6 600	2.76	30
	4 000	43	6 860	2.76	20
	5 000	49	6 750	3.04	15
Distilled water + Congo Red	1 000	31	6 990	2.96	40
	2 000	50	7 700	3.5	15
	3 000	72	9 170	3.7	13
	4 000	78	8 690	3.78	12
	5 000	81	8 400	3.68	12

TABLE 5
Bleached kraft pulp

<i>Beating liquid</i>	<i>Jokro mill, no. rev.</i>	<i>Beating degree, °S.R.</i>	<i>Breaking length, m.</i>	<i>Bursting strength, kg./cm.²</i>	<i>Air permeability, ml./min.</i>
Tap water	4 000	21	6 380	3.2	150
	7 000	29	7 780	3.56	45
	10 000	41	7 700	3.52	25
Softened water	4 000	22	7 430	3.9	150
	7 000	32	7 700	3.8	45
	10 000	44	8 300	3.8	20
Distilled water + hexametaphosphate	4 000	24	7 750	4	120
	7 000	32	7 900	4.28	22
	10 000	47	8 300	4.3	20
Distilled water + Congo Red	4 000	35	8 520	4.48	20
	7 000	57	9 440	4.56	15
	10 000	63	10 340	5.20	15

Fig. 2

Bleached Sulphite Pulp



In the figures, beating degree expressed in $^{\circ}$ S.R., breaking length expressed in km., bursting strength in kg/cm^2 and air permeability in ml./min. are plotted against Jokro mill revolutions.

The curves corresponding to the four treatments are shown with *C* for tap water, *P* for softened water, *E* for hexametaphosphate and with *RC* for Congo Red.

In order to find additional factors to explain basically the phenomena that determine the highly accelerating action of Congo Red during beating, we have carried out research aiming at determining how the addition of dyestuff affects the already beaten pulp and the changes resulting from the extraction of the dyestuff from the pulp beaten in the presence of the dyestuff.

Beating was carried out in the Jokro mill in the manner mentioned earlier, using two commercial softwood pulps — a bleached kraft pulp and an unbleached sulphite pulp. Tables 6 and 7 show the beating degree ($^{\circ}$ S.R.), breaking length, folding endurance and air permeability figures, grouping under each heading (from left to right) the figures corresponding to pulp beaten with water alone (A), in presence of dyestuff (A'), after extraction of dyestuff from pulp A' (A'') and after addition to the pulp A of dyestuff after beating (A''').

Dyestuff extraction was carried out with a 50 per cent. pyridine solution.

Fig. 3

Bleached Kraft Pulp

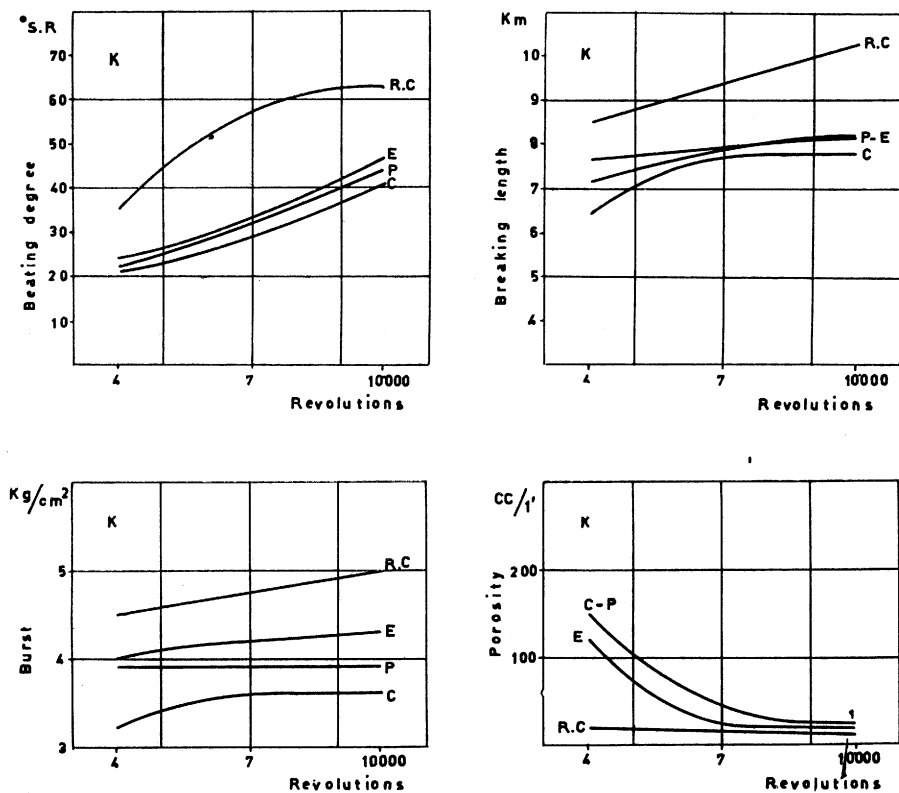


TABLE 6
Unbleached sulphite pulp

Jokro mill, no. rev.	Beating degree, °s.r.			Breaking length, m.			Air permeability, ml./min.			Double folds						
	A	A'	A''	A	A'	A''	A	A'	A''	A	A'	A''				
1000	16	24	21	18	6 750	8 900	7 450	7 285	353	100	120	375	2 865	3 100	3 750	2 840
1500	19	42	26	21	7 640	10 050	9 300	7 900	200	17	33	250	3 300	3 650	4 850	2 540
2500	23	58	33	28	9 060	9 900	9 200	8 250	91	5.8	11	110	4 030	3 800	5 200	3 200

TABLE 7
Bleached kraft pulp

Jokro mill, no. rev.	Beating degree, °s.r.			Breaking length, m.			Air permeability, ml./min.			Double folds						
	A	A'	A''	A	A'	A''	A	A'	A''	A	A'	A''				
3000	18	28	21	22	6 840	9 550	8 000	7 150	400	140	150	375	8 100	8 650	10 100	7 300
4500	21	37	26	29	8 520	10 400	9 150	7 650	250	58	70	300	7 220	8 520	11 000	7 300
7000	27	52	33	36	8 130	10 000	8 850	7 650	170	22	26	250	6 330	7 450	8 850	6 400

From an examination of these two tables, the following conclusions may be reached —

1. The extent of the beating of the pulp expressed in °s.R. considerably increases if beating is carried out in the presence of dyestuff, but, after extraction, the degree of beating is reduced to much lower figures, though these are always higher than those of fibre beaten in water alone. The difference between the °s.R. of pulp beaten in water alone and of pulp beaten in the presence of dyestuff and later extracted with pyridine is greater the higher the beating degree. The addition of dyestuff to the pulp already beaten in water alone involves a °s.R. increase within narrow limits.
2. As repeatedly mentioned earlier, breaking strength increases as a result of the presence of Congo Red during beating. In general, the presence of Congo Red accelerates all beating effects, beating action included and also the strength reversion effect that occurs above certain beating levels.
The extraction of Congo Red from pulp beaten in the presence of Congo Red causes a decrease in the breaking length; however, the latter is always higher than the breaking length of sheets made from pulps beaten in water alone. The addition of Congo Red to the pulp beaten in water alone does not particularly affect the breaking length. From a comparison of relative figures (A and A''), at times an increase and at times a decrease in the breaking length is observed, but differences are always confined within narrow limits.
3. So far as air permeability is concerned, the phenomena observed are similar to those encountered with the breaking length.
4. From the figures of the folding endurance, although essentially the effects are of the same magnitude, a peculiar increase in this property is observed following pyridine extraction of pulp beaten with dyestuff.

In order to explain these phenomena and the latter in particular, we have extracted with 50 per cent. pyridine woodpulp beaten in water alone, the aim being to examine solely the action of pyridine on their properties, irrespective of the dyestuff's effect.

Results so far obtained lead us to conclude that the action of pyridine on the fibre submitted to rather gentle beating is brought about in that it increases the folding endurance, leaving practically unchanged both the °s.R. of the pulp and the breaking length of the paper.

Discussions of results based on certain considerations of beating mechanism

A few years ago, we carried out a comparative study on the structure of paper sheets and regenerated cellulose films, arriving at the conclusion that between the structures of the two types of products, processed by two entirely different methods, extremely interesting similarities exist. ^(6, 7)

In the regenerated cellulose films, a definite selective orientation of the splitting lamellar planes of the cellulose structure is observed.

In paper, too, the orientation of these planes, which are those more easily hydrated, takes place in a direction parallel to the surface of the sheets.

This selective orientation depends on the nature of the fibres, on the rate and method of beating and on the compression stress on the sheet during formation.

The lamellar structure of paper revealed on a sub-microscopic scale through X-ray studies ⁽⁶⁾ is quite detectable even on a microscopic scale from an examination of sheet cross-sections. ⁽¹²⁾

It may therefore be stated that beating action is revealed by the splitting of the cellulose fibres into layers or, more precisely, into ribbon-like elements in which the higher hydrated cellulose planes of the lattice structure, which correspond to the cleavage planes, are arranged parallel to the ribbon surface.

This hypothesis is an explanation of cellulose fibrillation, assuming that the cellulose fibre consists of a bundle of ribbon-like elements in a spiral inclined to the axis of the fibre.

It has been demonstrated that cellulose cleavage planes have a selective orientation on the surfaces of the ribbon-like fibrils; ⁽¹³⁾ we have demonstrated also from the present research carried out by our institute that these planes are arranged parallel to the fibre lumen, that is, they have a selective orientation on the surface of the various co-axial layers.

It is therefore quite likely that the beating effect consists of tearing these layers and in splitting them into lamellar elements. This splitting could be more or less deep, according to the duration and strength of the mechanical action on the water swollen fibres.

The increase in the water retaining capacity of fibres would thus be explained by the fact that the more easily hydrated surfaces of the cellulose structure would be exposed.

Under equal conditions for all other factors, the beating rate of pulp will be inversely proportional to the cohesion of intermediate layers existing between the various coaxial layers into which a cellulose fibre may be ideally divided.

Certain research workers have already tried for some time to find a connection between the non-cellulose content and the fibre behaviour on beating; tests have always been carried out by progressively eliminating lignin during cooking and hemicellulose by extraction with sodium hydroxide solutions in increasing concentrations.

Results tend to show that the beating rate (consequently, the strength of paper) at first increases by eliminating a small quantity of the hemi-

cellulose substances, it reaches a peak value and then decreases as the cellulose refining process continues. The hypothesis that hemicellulose substances are chiefly located between the co-axial layers of the cellulose wall (that is, the splitting area of the structure) may prove to be quite helpful in the interpretation of these phenomena. Moreover, preliminary removal of binding materials may favour their swelling tendency in water and, by lessening cohesion between the layers, facilitate the lamellar splitting of fibres, whereas their complete removal tends to cause decrease in fibre plasticity and the possibility of their splitting into layers. This occurs chiefly when the purification of cellulose is carried out with rather concentrated solutions of sodium hydroxide.

In any case, removal of hemicellulose is accompanied by considerable swelling and great structural changes that may cause the bonding between cellulose co-axial layers so that the fibres become inert to beating action.

In order to increase the splitting rate of fibres during beating, it is necessary to perform this operation in the presence of a substance that can bond itself to lamellar surfaces and can increase hydration, so as to act as a plasticiser between them.

The substances used for our research work meet these requirements. Molecules of direct dyes obtained from benzidine have the following properties —

- (a) A linear structure.
- (b) On the one hand, they contain groups capable of forming hydrogen bonds with cellulose.
- (c) On the other hand, they carry $-\text{SO}_3\text{Na}$ groups, which may be dissociated and which are highly hydrated.

These molecules combine with those of cellulose as shown schematically in Fig. 4.

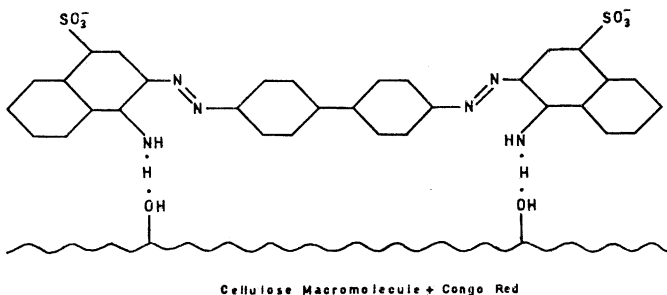


Fig. 4

Certain measurements of the extent of lamellar orientation, carried out on sheets obtained from beaten pulps in water alone, with water to which Congo Red was added and after mercerisation have given the figures shown in Table 8.

TABLE 8

<i>Pulp</i>	<i>Jokro beating time, min.</i>	<i>Beating degree, °S.R.</i>	<i>S.O.D.</i>
Linter (without Congo Red)	120	75	61
Linter (with Congo Red)	120	85	67
Linter (mercerised)	120	35	32
Spruce (sulphite, without Congo Red)	20	32	60
Spruce (sulphite, without Congo Red)	35	69	64
Spruce (sulphite, with Congo Red)	20	71	69
Spruce (sulphite, with Congo Red)	35	84	75
Spruce (sulphite, mercerised)	20	13	44
Spruce (sulphite, mercerised)	35	14	50

Under the microscope, it was noted that fibres beaten in the presence of Congo Red show a particularly noticeable lamellar splitting; sheets obtained from pulp beaten as above ⁽¹²⁾ show an even greater lamellar splitting.

It may therefore be assumed that direct dyes, by penetrating preferably in those loose areas between the co-axial layers of the fibre, increase hydration, so facilitating splitting by mechanical action.

Moreover, by removing the dyestuff by pyridine extraction, it is noted that the freeness increases noticeably, whereas the physical properties of sheets, which result from the greater lamellar splitting brought about by the presence of dyestuff during beating, decline to only a limited extent.

During tests, furthermore, it was noted that sheets obtained from fibres beaten in the absence and in the presence of Congo Red, after having been dried and extracted with pyridine and washed in water, have a very different appearance and behaviour when wet. While the former slush easily in water, the latter may be handled without excessive care, since they have a far greater resistance to water, because of the greater bonding of fibres to each other and, thus, because of the greater wet strength of the sheet.

We are not giving quantitative figures at this stage, these tests still being under way, but the qualitative results already mentioned in brief confirm the assumption that the action of the dyestuffs under examination is by decreasing the bond existing between the co-axial layers of the fibres as a result of greater hydration induced by their presence. The exposing of the more active surfaces of ribbon-like elements on which the planes (101) of the

lattice structure of cellulose are oriented is thus facilitated. During the drying process, these planes bond to each other and the strength properties so developed remain even after the removal of the dyestuff that caused them.

Although the greater ease of beating cellulose fibres by direct dyes might not be used for practical purposes, direct dyes represent molecular *models* to be borne in mind as a guide in the effort of finding or preparing for synthesis moderately cheap and non-dyeing substances having a similar effect.

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Transcription of Discussion

DISCUSSION

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

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

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

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

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

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

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

Influence of calendering on sheets formed in different media

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

O = original

C = calendered

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

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

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

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

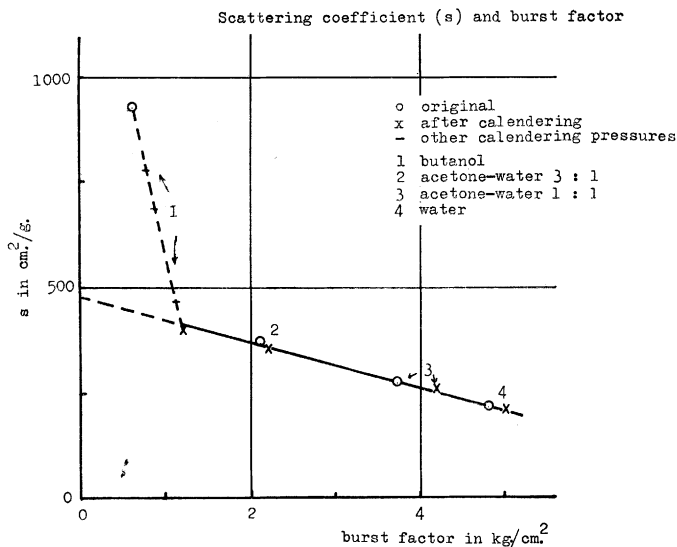


Fig. R

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

MR. NORDMAN: That is so.

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

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

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

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

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

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

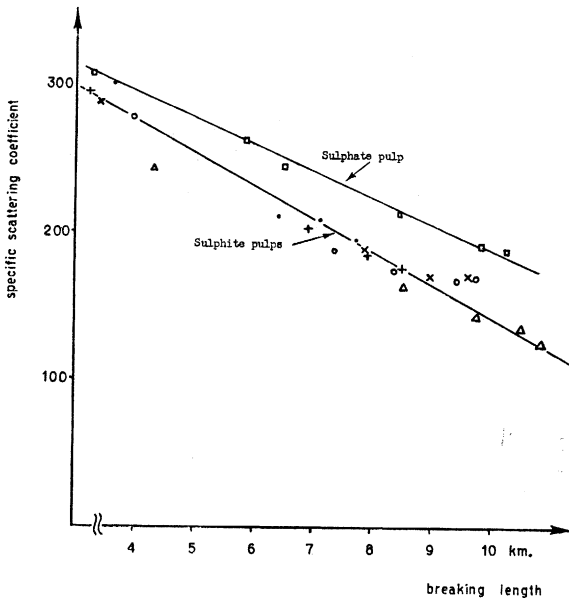


Fig. S — The relationship between specific scattering coefficient (opacity) and breaking length

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

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

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

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

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

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

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

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

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

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

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

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

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

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