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ESTERIFICATION AS A MEANS OF IMPROVING THE PROPERTIES OF ONCE-DRIED FIBRES

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Synopsis Esterification of pulp fibres have been performed in pyridine and toluene. The influence on swelling and the mechanical properties of sheets are shown to be different at the same level of esterification obtained by the two methods. This is interpreted to be due to the topological position of the acetyl group in the cellwall. Thus, esterification in toluene tends to allocate the esterification to the surface while in pyridine the interior of the cellwall is made accessible. At low degree of esterification in pyridine an increase in swelling is obtained. Thus, the hydrophobic groups may be seen as structure-breakers primarily by keeping the carbohydrate chains apart which otherwise would tend to form water-inaccessible regions, due to extensive hydrogen bonding. This maximum in swelling is maintained even in the dry state. Thus, the equilibrium moisture content is higher in a fibre moderately esterified in pyridine than a nontreated fibre. The introduction of acetyl groups is also shown to have an influence on the reswelling of the fibre after drying. The loss in swelling after drying is considerably less after drying for a moderately esterified fibre than for a nontreated fibre. Consequently the retention of the strength of the sheet has been improved. Essentially moderately esterified fibres which have been once dried yield a sheet with a strength equal to never dried virgin fibres.

The experiments with the fibres esterified in toluene did not yield the same effect indicating that the presence of hydrophoric groups inside the cellwall is necessary in order to maintain the swelling properties of the fibres. The results indicate new ways of permanenting the strength potential of recycled fibres and have illustrated the fundamental mechanism leading to the decrease of strength potential due to the drying of virgin fibres.

Summary

THE scope of this work is to study the effect of acetylation on the recovery of fibre properties after drying.

Under the chairmanship of M. I. MacLaurin

The acetylation of the fibres was performed in pyridine and in toluene to demonstrate whether the reswelling of the pulp after drying was affected by the state of swelling of the fibres during esterification.

The results of the measurements of fibre swelling and mechanical properties show that sheets made from once-dried acetylated fibres have almost the same mechanical properties as sheets made from never-dried fibres. The swellability of once-dried acetylated fibres is not significantly lower than that of never-dried fibres. It is suggested that the healing of large pores during drying is mainly responsible for the irreversible swelling hindrances. It is further suggested that the effect of acetylation is to prevent the healing of these pores by blocking with hydrophobic groups.

Introduction

THIS investigation shows how esterification of the hydroxyl groups influences the reswelling of cellulose fibres after they have been dried. The esterification is shown to restore part of the swellability of the pulp which is lost on drying. Moreover, sheets made from pulp that has been esterified have mechanical properties better than or as good as sheets from a never-dried pulp, provided a specific degree of substitution has been reached.

The effect of acetylation of never-dried fibres has been measured on sheets made from both never-dried and once-dried fibres and various sheet properties have been determined as a function of the degree of substitution. Furthermore, swelling, drying stresses and density have been measured for sheets made from acetylated fibres.

Esterification has been carried out in a swelling agent (pyridine) and in a nonswelling agent (toluene) for cellulose in order to demonstrate whether the reswelling of the pulp after drying is affected by the state of swelling during esterification.

Background

Recycled fibres

IN general, the properties of sheets made from recycled fibres are poorer than those of sheets made from virgin fibres.(1–4) One of the major drawbacks is the low swellability of recycled fibres.

In Fig. 1 the situation is illustrated by plots of tensile strength *versus* water retention value (fibre swelling) and drainage resistance for virgin and recycled fibres. As is seen, the swelling level (WRV) and the strength level are considerably higher for virgin fibres. However, there is a correlation between strength and fibre swelling and it is possible to increase the strength by further beating the recycled fibres. This leads inevitably to an increase in the

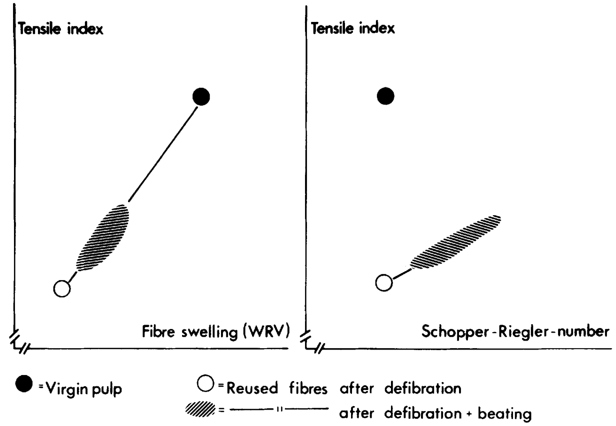

Fig. 1—The curves show that the strength of the recycled fibres can be increased by beating to increase the fibre swelling. As a result of beating the drainage resistance has also increased

drainage resistance. Thus the problem with recycling is to achieve a balance between the strength desired and the drainage resistance acceptable on the paper machine.

Acetylation of fibres

Esterification of cellulosic materials has been thoroughly described in the literature.(5–12) The most widely recommended procedure is to use acetic anhydride together with a suitable catalyst. Pyridine, sulphuric acid or perchloric acid have been recommended as catalysts. In order to obtain a high degree of substitution a polar solvent must be used. With a nonpolar solvent such as toluene, the degree of acetylation that can be reached is limited. This is due to the inability of the solvent to swell the cellulose structure sufficiently to allow bulk acetylation.

The effect of acetylation on the properties of sheets has been thoroughly described. The most obvious effect is the decrease in strength achieved at higher degrees of acetylation and the decrease in moisture regain. However, many authors have noted that both strength and moisture regain pass through a maximum at an intermediate degree of acetylation, mostly around 5 per cent acetyl content by weight. It is suggested in the literature that this is due to the fact that the hydrophobic acetate groups hinder the recombination of hydroxyl groups in their environment. Thus the net effect will be a somewhat higher accessibility to water at these low acetyl contents. However, with increasing esterification, this effect will be overshadowed by the general increase in hydrophobicity of the whole cellulose matrix.

Experimental

Acetylation

ACETYLATION of the fibrous material was performed both in pyridine and in toluene. Before subjecting the pulp fibres to the final reaction mixture, water was removed by solvent exchange in different solvents. The washing procedures followed the scheme given in Table 1. After acetylation, the pulp fibres were finally washed in water.

TABLE 1—SOLVENT EXCHANGE STEPS FOR THE FIBRES BEFORE AND AFTER ACETYLATION

	Solvent		*Amount* *ml*	*Time* *h*
Before acetylation	Ethanol	Ethanol	1 × 1 500	15
	Ethanol	Ethanol	1 × 1 500	1
	Acetone	Acetone	2 × 1 500	1
	Pyridine	Toluene	1 × 1 500	15
	Pyridine	Toluene	1 × 1 500	1
After acetylation	Pyridine	Toluene	2 × 1 500	0·17
	Acetone	Acetone	2 × 1 500	0·17
	Ethanol	Ethanol	1 × 1 500	0·17
	Ethanol	Ethanol	1 × 1 500	0·5

There was only one major difference between the two routes chosen for the solvent exchange. In the one case toluene and in the other case pyridine was used in the step where the pulp was prepared for esterification.

The pulp was washed in a fine mesh wire cage and the filtrate was passed through the pulp three times in order to restore fines lost during the washing. This is important as the fines have a considerable influence on the mechanical properties of the sheet.

The degree of acetylation was determined by a technique described by Bethge and Lindström.(13) The degree of substitution was expressed as the percentage by weight of acetyl groups calculated on the total amount of cellulose.

Table 2 summarises the reaction conditions in pyridine and in toluene. As seen, the amount of acetic anhydride and the reaction time were increased in order to achieve higher degrees of substitution. In the case of toluene, however, the degree of substitution was low in spite of a long reaction time. On the other hand, it was difficult to achieve a low degree of substitution in pyridine due to the high reaction rate. In these experiments, the degree of substitution was therefore limited to a minimum of 4 per cent in the case of pyridine and a maximum of 3·5 per cent in the case of toluene.

TABLE 2—THE REACTION CONDITIONS FOR THE ACETYLATED FIBRES

Solvent	*Acetic anhydride (%)*	*Reaction time (h)*	*Acetyl content (%)*	*Reacted hydroxyl groups (%)*	*Degree of substitution (DS)*
Pyridine	6·7	0·25	3·9	5·0	0·15
	20	0·25	5·7	7·4	0·23
	40	0·50	8·3	11·0	0·33
	40	2	12·1	16·3	0·49
Toluene	4·7	0·5	1·4	1·8	0·05
	4·7	22	2·6	3·4	0·10
	18·7	22·5	3·5	4·5	0·13

Materials and testing procedure

THE pulp used in these experiments was a never-dried commercial bleached kraft pulp. It was beaten to 22 °SR in a PFI-mill. The mechanical tests were performed according to SCAN-standard testing methods. The swelling of the fibres was measured as the water retention value (WRV) according to methods described in reference 14. Drying stress was measured according to the method described in the contribution to these proceedings prepared by Htun and de Ruvo.

Results and discussion

THE mechanical properties of sheets made from never-dried pulp acetylated in pyridine or toluene and from the once-dried pulp are shown in Tables 3 and 4. The emphasis of this paper is, however, focused on the effect of acetylation on the recovery of the properties after drying. The data are therefore presented in Figs. 3–9 as relative changes with reference to the virgin pulp after it had been solvent exchanged, but neither esterified nor dried. In this context it may be pointed out that the relative strength with respect to virgin fibres of sheets made from once-dried fibres is 0·6–0·7.

TABLE 3(a)—THE MECHANICAL PROPERTIES, DRYING STRESSES AND THE DENSITIES OF SHEETS MADE FROM *NEVER-DRIED* PULPS ACETYLATED IN PYRIDINE

Acetyl content (%)	*Density (kg/m^3)*	*Elastic modulus (MN/m^2)*	*Tensile index (Nm/g)*	*Strain to failure (%)*	*Drying stress (MN/m^2)*
—	591	3 682	63·4	3·64	4·31
3·9	577	3 779	72·2	3·73	4·93
5·7	548	3 353	63·2	3·34	3·92
8·3	518	2 756	47·8	3·22	3·32
12·1	462	1 644	22·6	2·14	1·61

TABLE 3(b)—THE MECHANICAL PROPERTIES, DRYING STRESSES AND THE DENSITIES OF SHEETS MADE FROM *ONCE-DRIED* PULPS PREVIOUSLY ACETYLATED IN PYRIDINE

Acetyl content (%)	*Density* (kg/m^3)	*Elastic modulus* (MN/m^2)	*Tensile index* (Nm/g)	*Strain to failure* (%)	*Drying stress* (MN/m^2)
—	536	2 576	38·9	2·90	3·70
3·9	571	3 284	58·3	3·74	4·43
5·7	542	3 369	56·0	3·20	3·96
8·3	519	2 849	43·5	2·67	3·36
12·1	470	1 520	19·4	1·81	1·57

TABLE 4(a)—THE MECHANICAL PROPERTIES, DRYING STRESSES AND THE DENSITIES OF SHEETS MADE FROM *NEVER-DRIED* PULPS ACETYLATED IN TOLUENE

Acetyl content (%)	*Density* (kg/m^3)	*Elastic modulus* (MN/m^2)	*Tensile index* (Nm/g)	*Strain to failure* (%)	*Drying stress* (MN/m^2)
—	588	3 630	52·7	2·90	5·43
1·4	583	3 600	52·1	2·85	5·55
2·6	562	3 310	58·5	3·50	5·05
3·5	537	3 020	52·9	3·40	4·35

TABLE 4(b)—THE MECHANICAL PROPERTIES, DRYING STRESSES AND THE DENSITIES OF SHEETS MADE FROM *ONCE-DRIED* PULPS PREVIOUSLY ACETYLATED IN TOLUENE

Acetyl content (%)	*Density* (kg/m^3)	*Elastic modulus* (MN/m^2)	*Tensile index* (Nm/g)	*Strain to failure* (%)	*Drying stress* (MN/m^2)
—	502	2 740	38·9	2·1	3·73
1·4	528	2 860	43·7	2·6	3·91
2·6	537	3 560	60·8	3·0	4·43
3·5	528	3 220	59·7	3·2	4·01

In Fig. 2 it can be seen that the swelling of the pulp measured as WRV is maintained up to 4·5 per cent acetyl content on esterification in pyridine. Thereafter a gradual decrease takes place. After drying, a characteristic decrease in WRV is observed for the nonacetylated pulp. However, acetylation of the never-dried pulp leads to a gradual increase in the WRV which is followed by a decrease as the acetyl content is increased above 5 per cent. In the case of the esterification in toluene a high degree of substitution could not be attained. However, at a low degree of esterification it is clear that the influence on the WRV is of a similar character to that in pyridine. Thus the WRV is slightly decreased for the never-dried pulp, while for once-dried pulp the WRV increases with degree of acetylation.

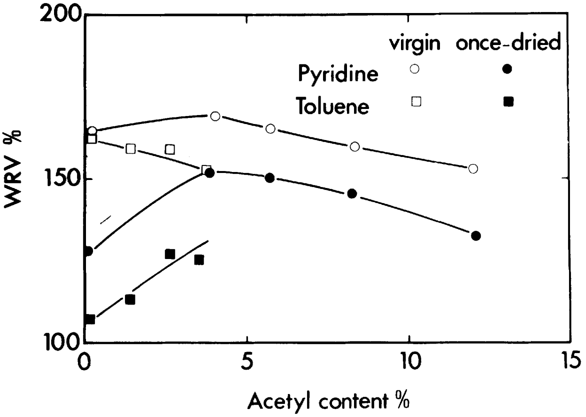

Fig. 2—The water retention values of never-dried and once-dried pulp fibres plotted against the acetyl content. Effect of acetylation in pyridine and toluene is shown

As can be seen in Fig. 3, the ratio of the WRV value of the once-dried fibres to that of the reference displays a maximum at 4–5 per cent acetyl content for pulps esterified in pyridine. Fibres esterified in toluene also show an increase in the WRV and the relative effects are of the same magnitude as in pyridine. However, the drying of fibres solvent-exchanged in toluene-leads to a much more drastic reduction in WRV than the drying of fibres

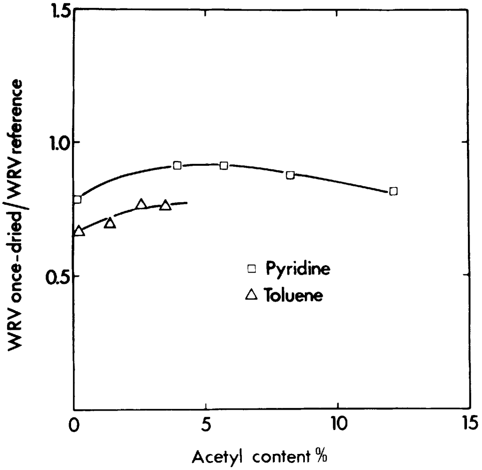

Fig. 3—Relative swelling on once-dried and reference pulp fibres plotted against acetyl content

solvent-exchanged in pyridine. Thus the gain in WRV due to initial esterification from a lower WRV value. The explanation of the fact that the reduction in WRV after drying the pyridine-treated pulp is smaller than for the toluene-treated pulp may be that a small amount of pyridine is still left in the cellulose matrix. It is well documented in the literature that polar solvents display a strong interaction with cellulose which makes it difficult to wash them out.(15, 16) Thus, residual pyridine in the cellulose may act in the same way as a covalent blocking of the hydroxyl groups.

The following conclusion may be drawn from these experiments. The blocking of hydroxyl groups is effective in hindering the formation of irreversible swelling hindrances during drying and reduces the difference between the properties of sheets made from once-dried and from never-dried pulp. Furthermore, pyridine does allow penetration of the reactant into the cell wall matrix since high degrees of substitution may be reached. However, it is virtually impossible to reach acetylation levels above 5 per cent in toluene. This indicates a low accessibility for hydroxyl groups in the cellulose matrix. Despite this difference, a similar improvement in WRV is obtained whether the esterification is carried out in pyridine or in toluene. Apparently the hydroxyl groups responsible for part of the swelling hindrance, which

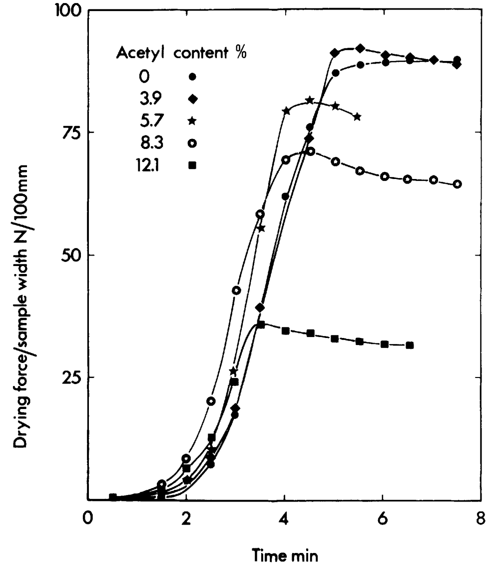

Fig. 4—Drying force per sample width plotted against time of drying for sheets made from nonacetylated and acetylated fibres

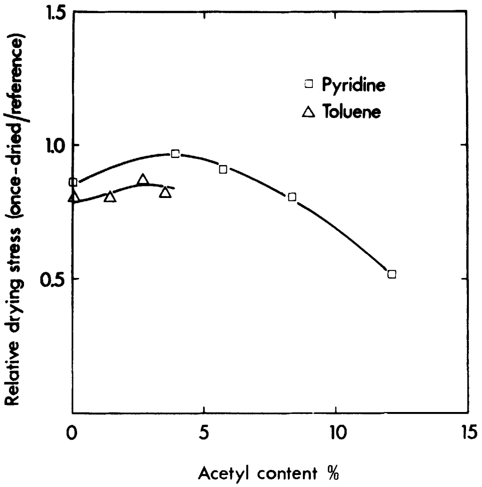

Fig. 5—Relative drying stress of once-dried and reference sheets plotted against acetyl content

develops during drying, are accessible to esterification independent of the state of swelling of the cellulose matrix.

To characterise further the effect of acetylation, drying stresses during restrained drying were measured for never-dried fibres. The results are shown in Fig. 4. As seen, the reference sample exhibits a maximum value which remains constant at the end of drying. However, sheets made from acetylated fibres show a stress relaxation. In general, this may be explained as being due to a more thermoplastic character of the acetylated carbohydrate chain. Apparently, acetylation has enhanced the stress dissipation that takes place in the cell wall at the end of drying. It may be noted that it has been suggested in the literature that the formation of hydrogen bonds, during the straining of the amorphous carbohydrate chain, may work as a molecular lock hindering the plastic flow of the microfibrils.(17, 18) A blocking of hydroxyl groups would effectively prevent this mechanism. Furthermore, the increased stress relaxation may be beneficial; relieving stress concentrations, and therefore improving the strength properties of the sheet.

From Tables 3 and 4 it may be noted that the drying stress is improved significantly for once-dried pulp at intermediate degrees of substitution in both pyridine and toluene. This is summarised in Fig. 5 where the drying stress relative to that of the reference pulp is given *versus* the degree of acetylation for once-dried pulp.

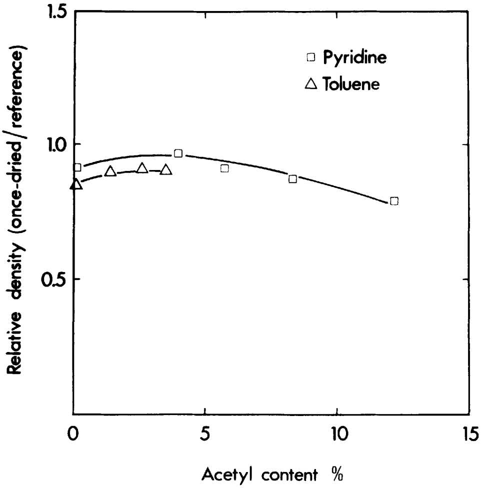

Fig. 6—Relative density of once-dried and reference sheets plotted against acetyl content

The same tendency is observed with regard to the relative density of the once-dried pulp. Thus, the density of sheets made from pulp once-dried and acetylated to around 4–5 per cent is the same as that of the reference pulp. This is shown in Fig. 6.

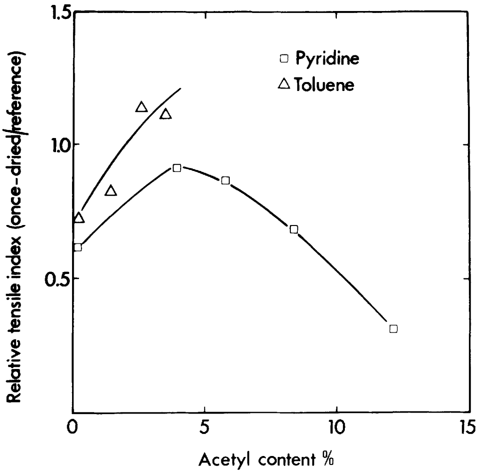

Fig. 7—Relative tensile index of once-dried and reference sheets plotted against acetyl content

As expected, the strength properties follow the same general pattern. This is shown in Fig. 7. Compared with sheets made from the reference pulp, a strength improvement is noted even for once-dried sheets made from fibre acetylated to the levels which gave the maximum WRV and drying stresses.

Sheets made from once-dried fibres without acetylation exhibit a strength decrease of 25–30 per cent. Thus acetylation is an effective way of conserving the strength of sheets made from once-dried fibres. Other mechanical properties follow the same pattern. In Figs. 8 and 9 it is seen that elastic modulus and strain to failure show values, for sheets made from acetylated pulp, greater than those for the reference sample. Previously it has been suggested that the blocking of hydroxyl groups would enhance the flow of the microfibrils. This serves as an explanation for the stress relaxation at the end of the drying. It may also explain the measured higher strain to failure in tension for sheets made from acetylated fibres.

Final remark

It is generally accepted that the swelling of the cell wall comprises the following two phenomena:

(*1*) Swelling of the cellulosic matrix controlled by the thermodynamic equilibrium between the solvent inside and outside the cell wall.

(*2*) Cracks or physical voids in the wall introduced by the mechanical treatment of chemical processes.

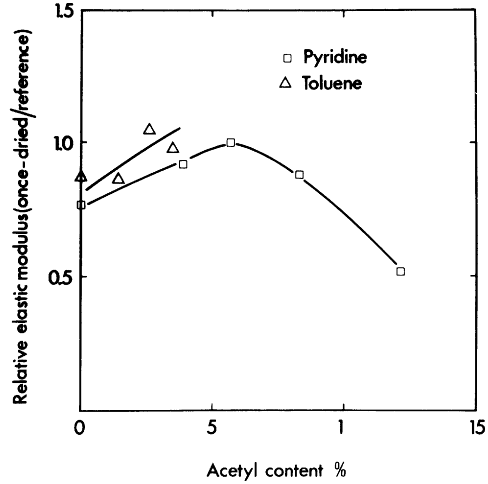

Fig. 8—Relative elastic modulus of once-dried and reference sheets plotted against acetyl content

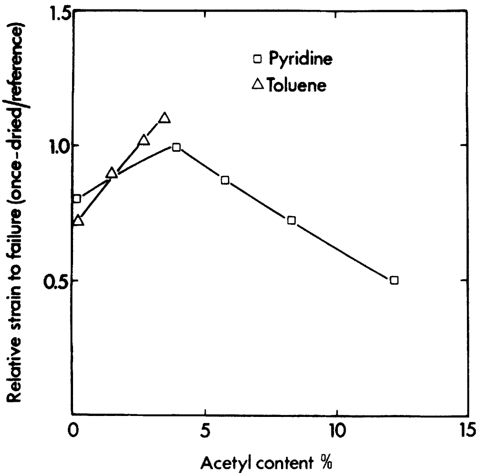

Fig. 9—Relative strain to failure of once-dried and reference sheets plotted against acetyl content

These two basic features have been mentioned previously, most prominently by Stone and Scallan.(19) In their work, a solute exclusion method was applied to measure the change in void distribution that occurred during drying. They concluded that preferentially large voids were irreversibly closed during drying. It seems reasonable to assume that esterification of the surfaces of the voids yields a hydrophobic lining that must effectively hinder any permanent healing of the cracks which may occur during drying. Moreover, only large pores or micro-cracks would be accessible to esterification in both a swelling and a nonswelling medium.

This may explain the analogous effects with regard to the recovery of mechanical properties and swelling observed for sheets and fibres acetylated in pyridine and toluene.

Acknowledgement

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Transcription of Discussion

Discussion

Prof. H. Giertz The effect of acetylation was much discussed in our first symposium. Everything seems to go back to Bialkowsky's doctoral thesis in the mid-thirties. He acetylated pulp and showed the increase in swelling and the improvement of papermaking properties. The earlier explanation has been that in acetylation the hornified hemicellulose areas are broken up and acetyl groups are introduced which keep the molecules apart with the effect that the non-acetylated hydroxyl groups are ready to be hydrated. The whole structure is opened up as long as the degree of acetylation is low. At higher degrees, 10 per cent or more, the cellulose becomes hydrophobic.

de Ruvo That is what I thought at first, but it works for toluene and for pyridine also, and therefore, the penetration into the hemicellulose gel system does not seem necessary. There are certain differences, however. You will see from the paper that the pyridine has the tendency to act in a slightly different way from toluene. It could mean that both effects are combined. Also, the hydrophobic lining, as we call it, is an important aspect of the closing up of the larger pores.

Mr A. T. Luey I have a comment on the water retention values and the importance we are associating with it for the strength properties of recovered fibres. There is another important property involved here, and that is in dewatering the papers and paper boards made from recycled fibres. The low water retention value is associated, I believe, with the fact that you can dewater these webs at much higher levels of consistency than you can webs from virgin fibres. This is a very important factor. So, if you could balance the properties associated with strength and high water retention values, against those associated with dewatering in the presses and low water retention values, it would be a wonderful development.

Prof. P. Luner A question to Dr de Ruvo. I wonder if you have considered the incorporation into cellulose of small molecules, either organic or inorganic,

Under the chairmanship of M. I. MacLaurin to 'heal' the fibres. There has been some work on the incorporation of urea and various other salts, concerning their effect on drying.

de Ruvo The original ideas which we based this work on came from Peterlin. He used never-dried cotton fibres, that is, the natural cotton balls. He noticed to his surprise that the fibres, which have about 80 per cent crystallinity, stand a strain of 12–20 per cent. These fibres had never been exposed to relative humidities below that in their natural growing condition. As soon as they are dried down they become brittle. Peterlin showed by X-ray work that in the natural fibre the microfibril are not yet joined and can slide in shear. Upon drying they are bonded to each other irreversibly. Peterlin incorporated epoxy groups in the never-dried fibres, and now they retain their straining properties after drying. The epoxy groups had prevented the bonding of the crystallites. This was the kind of mechanism we thought about, but whereas we can do all manner of things in the laboratory, it is very difficult to think of a suitable technique if you want to take it further. One could think of a solvent molecule that has a high affinity to cellulose. We know from gel chromatography work that DMF is a very good coupler to cellulose and maybe it exposed hydrophobic groups to the surrounding space that will prevent the bonding up of the structure.

Dr A. H. Nissan I wonder whether glucose would form a 'zippable' bond and, being a small molecule, could be removed later, having prevented the small voids from closing up by acting as a temporary barrier.

de Ruvo That could be possible but it is difficult to say. A suitable small molecule could do the trick because they put their polar end to the cellulose and their non-polar end to the outside, but this is just speculation.

Dr G. Hunger A comment on the last point made by Dr Nissan. There was a patent in 1954 by Dr Schlosser from Crown Zellerback or Weyerhauser, which described the addition of many soluble substances to pulps in order to suppress hornification after drying. The best were wetting agents but they work for one cycle only.

Dr H. G. Higgins I would like to make a statement which may sound a little esoteric but I believe it is basic to the whole question of recycling. Solubility and swelling are, of course, related—here is the connection with recycling. One can look at the question of solubility in water either in thermodynamic terms or in structural terms. It is the latter approach I want to comment on, particularly with respect to the remarks from Dr Goring and Dr Nissan on the insolubility of cellulose. We have to consider a few important facts. A clue is perhaps that iso-octane wets ice, which can probably be explained in terms of complete internal satisfaction by strong hydrogen bonds of the hydrogen bonding capacity of the OH donors and the oxygen receptors. It is important to distinguish between strong and weak hydrogen bonds. They are realities which show in spectral frequencies of the bonded hydroxyl groups and in other ways. Thus, in this situation a hydrophobic surface is presented and the iso-octane spread over the ice. Now, both amylose, which is a glucane with a 1,4,α-link, the hydroxyl being presented axially of the carbon atom 1, and laminarin, which is a 1,3,β-link, although with an equatorial link, are more soluble than cellulose. In a glucane such as cellulose the 1,4,β-linkage combined with the C1-conformation of the pyranose ring permit linear molecules with complete internal satisfaction of hydrogen bonding by strong hydrogen bonds within the crystallite. The strong H-bonds are between equatorially disposed hydroxyl groups. When these conditions are not met, either through axial glycosidic links as in the case of amylose, which distorts the straight chain and produces a spiral structure, or because the non-linear or rather, non-straight, chains as in laminarin, then the hydroxyls engaged in weak strain bonds are presented to the surface and a more vulnerable structure results. Of course, cellulose can be rendered soluble by limited methylation, which is related to the acetylation effects described by Dr de Ruvo. But this methylation disturbs the internal satisfaction of the strong hydrogen bonds between the equatorial groups within the crystallites and possibly the C1 conformation. Cellohexose, mentioned by Dr Goring has a similar structure to cellulose as we know, for example, from infrared spectroscopy and X-ray diffraction, but when you go down in DP to cellotriose and cellobiose the structure is rather different, and solubility begins. Most of the things I have said are not just speculations. They do find quite considerable support from spectroscopy and other physical observations.

Dr E. L. Back I would like to point out another important fundamental aspect. We all know that there are radicals around, even on cellulose. They are initiated by different types of radiation, heat or light, and they have a positive charge. This follows, among others, from the work by Stannett and co-workers on radiation grafting. The important thing is that lignin, too, forms radicals. From the indications we have these radicals have a negative charge and function as radical scavengers for cellulose. This is shown in work by Stannett and Philips, and we have found indications of it in our work on fire retardants and their effect on cellulose. This may produce a difference in the appearance of various types of pulp. It is the positive cellulose radicals which quickly react and are the first to start the crosslinking reactions I talked about this morning. Lignin can function as a scavenger but we do not know much about the mechanism.

Dr D. A. I. Goring I would like just to record a few references. The reason why people do not dissolve in water when they have baths or swim is because hydrophobic bonding in people is important, and the reference to that would be Némethy, G. and Scheraga, H. A., *J. Chem. Phys.* 1962, **36**, (11), 3382–3400. Rees, D. A. and Skerrett, R. J., *Carbohyd. Res.* 1967, **7** (3), 334–348, suggested that insolubility of cellulose water was due to hydrophobic bonding between the ribbon-like cellulose chains, ringed in stacks, according to the effect shown by Warwicker and Wright. My suggestion is that in cellulose there is a hydrophylic and a hydrophobic bonding system and that perhaps changes in the hydrophobic bonding system are important in irreversible hornification.