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THE MECHANISM OF HORNIFICATION OF WOOD PULPS

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ABSTRACT

Hornification is the loss of swelling of the fibre wall resulting from a drying-and-rewetting cycle: it is associated with a stiffening of the fibres which reduces their ability to form inter-fibre bonds. In this paper, factors affecting the extent of hornification are examined using the solute exclusion technique to measure swelling. Two major observations are that hornification is a feature of low-yield pulps and that it is primarily brought about by the removal of water from fibre-walls rather than any associated heat treatments. The mechanism is proposed to be an increase in the degree of cross-linking between microfibrils due to additional hydrogen bonds formed during drying and not broken during rewetting. In high-yield pulps, the presence of lignin and hemicellulose between the microfibrils prevents this bonding. In low-yield pulps, the absence of these materials permits hornification to occur. However, hornification can be prevented by interfering with hydrogen bond formation either by i), partially substituting the cellulose hydroxyls by groups that do not hydrogen bond, or ii), drying pulps in the presence of additives that "bulk" the fibre wall and so effectively replace the ligno-hemicellulose gel.

INTRODUCTION

In 1944, Jayme (1) introduced an empirical procedure involving the determination of the amount of water retained by a pad of wet pulp after centrifugation for ten minutes at 2300 rpm. This quantity of water was termed the water retention value (WRV) and was claimed to be a measure of the level of swelling of a pulp. In the same paper, Jayme examined some of the factors that affect the WRV and found that "upon drying celluloses, ... the ability to bind water decreases and this property cannot be restored even after prolonged contact with water". He suggested that the loss of swelling was due to what he termed the "irreversible hornification" of the fibres.

Drying-and-rewetting and hence hornification are associated with other significant changes in a pulp. The sheets made from the pulp are less dense and have lower tensile strength than sheets prepared from the never-dried pulp (2,3). The collective effects are in the opposite direction to those induced by beating.

Emerton (4) summarized the concepts of several contemporary workers on the relationship between the level of swelling of a pulp and the properties of the paper made from it. In his textbook on beating, he wrote that swelling "is accompanied by the rupture of internal lateral bonds (internal fibrillation) which increases the extent to which the coaxial lamellae of the wall glide over one another and the capacity of the fibre wall to flow into extensive contact with neighbouring fibres during formation of the sheet." Acting in an opposite way to beating, drying and rewetting should therefore be associated with a tightening up of the structure of the fibre wall, an overall stiffening of the fibre and hence the formation of a weaker sheet through reduced inter-fibre bonding.

A precise method of measuring swelling and examining the internal structure of water-swollen fibre walls came with the work of Stone and Scallan (5,6). Using a solute exclusion technique with a macromolecule so large as to be totally excluded from entering even the largest pores in the wall, they were able to determine the total amount of water in the porous structure of the fibre walls. This total amount of water in the pores is termed the fibre saturation point (FSP). In addition, by progressively changing the size of the probe polymer to smaller sizes they were able to examine the distribution of pore sizes in wet fibre walls. Amongst other applications, the technique was used to examine the effect of drying-and-rewetting (7). As shown in Figure 1, the rewet pulp has a much lower FSP (the plateau value of inaccessible water) than the pulp in the never-dried condition and the distribution of pores falls in a lower range of sizes. Thus the porous structure of the wall is much more compact after drying-and-rewetting.

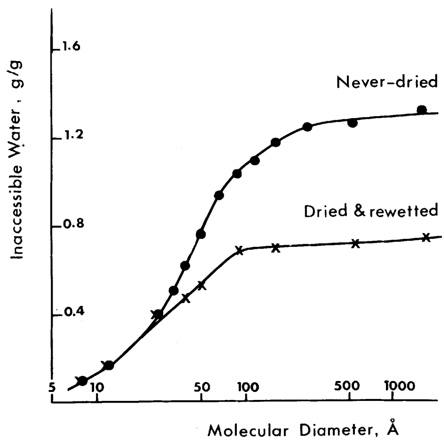

Figure 1 Solute exclusion curves for the long fibre fraction of a bleached kraft pulp. Drying-and-rewetting results in a more compact wall structure (7).

Following on from this brief description of hornification, our objective in this paper is to develop a picture of the mechanism causing the phenomenon. This will be based on both published and new work. Since hornification alters the internal structure of fibres, our approach will be to study hornification via changes in the FSP rather than by changes in the less fundamentally sound measurements of swelling used in the earliest work or by paper properties. Guided by the knowledge of the mechanism, we then examine treatments which prevent hornification.

FACTORS AFFECTING HORNIFICATION

Effect of Number of Cycles

Several authors have noted that the effects of drying-and-rewetting are most pronounced when first carried out on a never-dried pulp and that changes in properties are less with each successive cycle (8,9). For the most part these observations have been based on strength properties of sheets made from the pulps but more recently fibre saturation points have been found to follow the same trend (10). Typical data for a kraft pulp is shown in Figure 2. The discussion of drying-and-rewetting throughout the rest of this paper will be concerned with the large change shown in the first cycle.

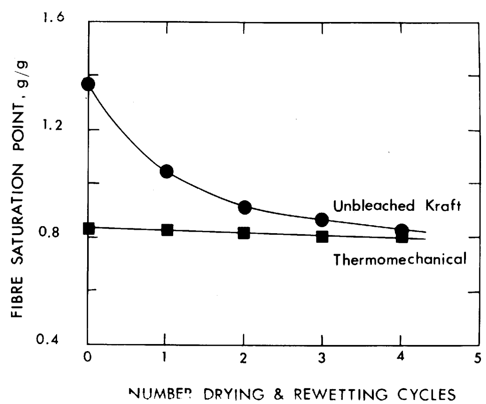

Figure 2 The effect of multiple cycles of drying-and-rewetting upon the swelling of pulps. Hornification, when it occurs, is greatest in the first cycle (10).

Effect of Pulp Yield

As shown in Figure 2, in contrast to a low yield kraft pulp, a thermomechanical pulp showed no changes on drying-and-rewetting and other workers have noted that mechanical pulps "recycle" much more reversibly than low-yield ones (8,9). However, what about pulps of intermediate yield? For kraft pulping, the change in swelling with a first drying-and-rewetting cycle as a function of yield is shown in Figure 3. The swelling of high-yield pulp, like mechanical pulp, is totally recovered upon rewetting but swelling becomes progressively less reversible as the yield is decreased (11). A similar diagram has been published for pulps prepared by the acid sulphite process and it shows essentially the same trends (12). Thus hornification is a feature of low-yield pulps and is not specific to a particular pulping process.

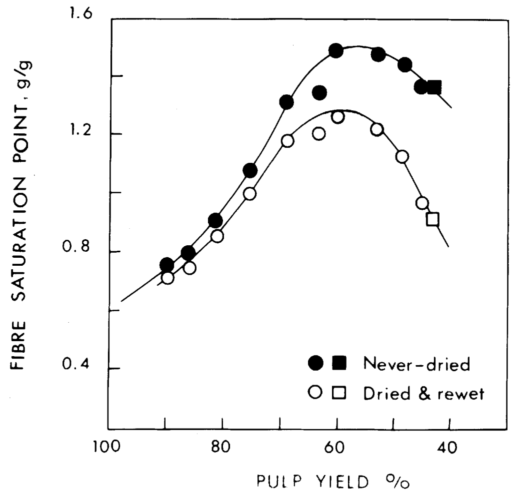

Figure 3 The levels of swelling of kraft pulps in the never-dried and dried-and-rewetted states are shown as a function of pulp yield. The square symbols refer to a bleached pulp. Hornification is a feature of low-yield pulps (11).

Chemical pulping removes lignin and hemicelluloses from wood and removal is almost complete in a bleached kraft pulp. Such a pulp is the lowest yield pulp and the least reversible pulp in Figure 3. It follows that cellulose must be the cell-wall component most involved in the hornification process. In support of this, it is notable that cotton which is essentially pure cellulose exhibits hornification. Never-dried cotton (obtained from unopened green cotton bolls) has double the water retention value of the dried-and-rewetted material (13).

Effect of Water Removal

Jayme examined the swelling level of rewet chemical pulps as a function of drying conditions and concluded that the degree of hornification (fractional loss of WRV) of a pulp increased with the extent to which the moisture content was reduced by drying (1). However in his experiments the lower moisture contents were obtained by raising the temperature of drying and thus did not separate the effect of moisture content from that of temperature. Robertson dried a pulp to progressively higher solids content at room temperature and then measured the swelling of the pulp after reslushing (14). He observed that the reslushed pulp was less swollen the lower the moisture content attained in the prior drying. However, his technique of measuring the moisture content of a pad of the pulp after exposure to a certain hydrostatic tension is now known to be only an approximate measure of swelling. Nevertheless, Robertson's observation as to the effect of the final moisture content was confirmed by de Ruvo and Htun who repeated the experiment using the WRV as a measure of swelling (15). In addition, these workers emphasized that hornification only occurred when the fibres were dried below a certain "critical" moisture content. This critical moisture content was found to be higher for higher initial levels of swelling of the virgin material.

We have also performed experiments to test the concept that merely removing water from fibre walls is sufficient treatment to cause the hornification of pulps. Portions of a low-yield pulp were dried at room temperature to progressively lower moisture contents. The partially-dried pulps were then redispersed in water and the fibre saturation points determined. Figure 4 gives the FSP of the reslushed pulp as a function of the water content of the partially-dried pad. The data show that the fibre saturation point is maintained when the water content in the partially-dried pad is greater than the FSP of the pulp in the never-dried state. However the swelling of the reslushed pulp drops upon drying to moisture contents below the FSP. An interpretation of these results is that evaporative drying first removes water from spaces between the fibres and that, during this period, there is no effect on cell wall swelling. However pore volume is irreversibly lost as soon as the moisture content drops below the FSP and water is removed from the fibre wall. The fibre saturation point is thus the "critical" moisture content of de Ruvo and Htun - a fact missed by them perhaps due to less precise nature of the WRV determination.

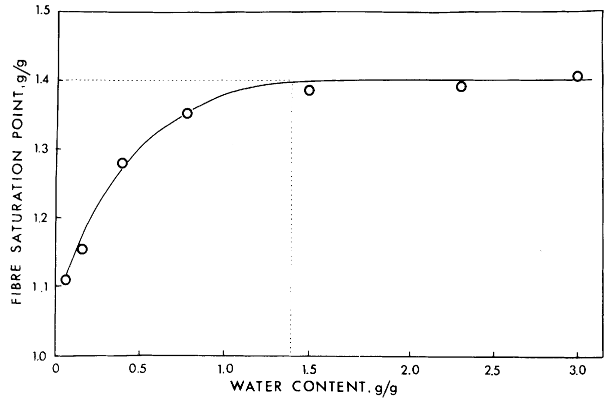

Figure 4 The effect of the moisture content to which a pad of pulp was allowed to dry at room temperature upon its swelling when reslushed. Hornification is associated with removal of water from the fibre walls.

From the above experiments, it is clear that hornification is caused by water removal and there is no necessity for any associated heat treatment. The water need not even be removed by evaporative drying: Carlsson and Lindström have shown by WRV measurements that hornification can result when water is removed from pulp pads by wet pressing (16). Again, it is necessary to remove water to below the fibre saturation point. Since it is difficult to press far below the FSP (17,18), the extent of hornification readily attainable by this method is less than by drying.

Effect of Temperature

Only a few investigations have been carried out, designed to separate the effects of temperature and water removal during drying. Lyne and Gallay avoided this problem by heating without drying; in their experiments wet handsheets were heated to 95 °C for three minutes in an atmosphere saturated with water vapour before air drying (19). The tensile strength of the sheet was lowered by 14% when compared to that of an unheated control. The result shows that the heat treatment led to a reduction in the extent of interfibre bonding; which they attributed to a loss of swelling of the pulp upon heating.

Stone and Scallan went to the opposite extreme of drying a low-yield pulp to zero moisture content at several temperatures prior to reslushing and forming handsheets (20). Drying-and-reslushing at 25 °C dropped the breaking length from 7.3 km for the virgin sheet down to 2.7 km. Raising the drying temperature to 105 ° and to 150 °C further lowered the breaking length to 1.6 and 0.6 km. From this study it is apparent that the major reduction in sheet strength is due to water removal and that heat causes an additional reduction which is much smaller in magnitude.

MECHANISM OF HORNIFICATION

Cell Wall Model

Discussion of the mechanism of hornification is best considered with reference to a model of cell-wall structure and one readily adaptable to this purpose is that in Figure 5 (21). The diagram shows the wall after complete removal of hemicellulose and lignin and therefore composed entirely of fibrils of cellulose. It is proposed that, in the dry cell wall the fibrils are all tightly packed and totally hydrogen bonded as depicted in Figure 5A. With the progressive swelling of the structure, bonds between fibrils are broken leading to the patterns of internal fibrillation illustrated by 5B to 5D. If, as in the initial presentation of this model, it is considered that Figure 5C represents approximately the arrangement of the microfibrils in wood and throughout pulping, then several of the factors of hornification can be explained.

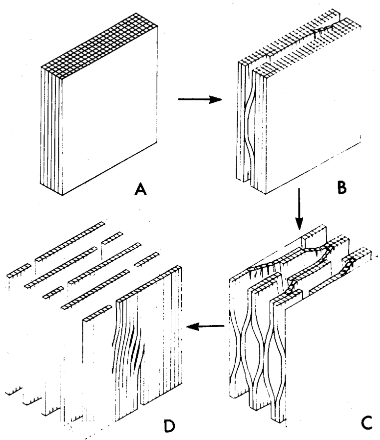

Figure 5 A section of a fibre wall showing the decrease in hydrogen bonding between microfibrils as a result of swelling, A to D (21). Hornification is a movement in the reverse direction and involves increased bonding.

With complete drying of a low-yield pulp for the first time, the structure of the wall may be visualized as moving from 5C to 5A and then upon rewetting returning only to 5B. The incomplete return is considered due to hydrogen bonds formed on drying and not broken upon rewetting (22,23). The final structure (5B) is less swollen and the pores smaller than that of the never-dried fibre, a structural change in agreement with experiment (Figure 1). Of course, it is not necessary to go to complete dryness before observing hornification upon rewetting (Figure 4). Partial drying causes movement from 5C towards 5A and results in some "zipping up" of the lenticular-shaped pores and that rewetting causes only incomplete "unzipping".

The model may also be used to explain why mechanical and high-yield pulps do not exhibit hornification. In wood and high-yield pulps, the wall is represented by 5C but with the interfibrillar spaces filled, not just with water, but with ligno-hemicellulose gel (6,24). Assuming that this gel behaves reversibly upon drying-and-rewetting and also, by preventing any direct contact between cellulosic surfaces during drying, the gel forces the wall as a whole to behave reversibly (11).

Evidence for the Hydrogen Bonding Mechanism

The cell wall model described above was proposed primarily in order to explain microscopic evidence of the structure of the wall (21). However, the applicability of such "multi-lamella" models to providing a pictorial description of the structural change occurring during drying-and-rewetting had been noted some years earlier (20). Perhaps the most debatable point about the model in the present context is the role of hydrogen bonding particularly in holding the structure in a more compact form after drying and rewetting.

As shown earlier, hornification is a property of low-yield pulps and is clearly associated with the cellulose component of the wall. Some workers have considered that drying (particularly using heat) could lead to degradation of carbohydrate chains and that this would lead to the formation of crosslinks in the wall (25). However, the formation of these has not been proven. Certainly, such reactions do not occur at room temperature while hornification does. The possibility of ester crosslinks formed between the carboxylic acid groups and hydroxyl groups in pulps has been suggested (26,27) but it has recently been shown that the acidic group contents of kraft pulps are unchanged by drying-and-rewetting (11). By a process of elimination we are left with hydrogen bonding between hydroxyl groups as the only possible source of chemical bonding occurring during drying-and-rewetting of cellulose particularly at room temperature.

Evidence of the role of hydrogen bonding in cellulose structure has been gathered by infrared analysis of cellulose coupled with deuterium exchange between heavy water and cellulose (Figure 6). Firstly, it has long been known from the position of the hydroxyl peak in the infrared spectra of cellulose that all the hydroxyl groups in dry solid cellulose are engaged in hydrogen bonding between one another (28). Secondly, when dry cellulose is wetted some of these bonds are broken by water and new hydrogen bonds are formed between the hydroxyl groups and the water molecules. This has been established by Mann and Marrinan (29) from observation of the changes in the infrared spectrum of dry cellulose following treatment with heavy water and redrying. The appearance of a deuterated hydroxyl peak (OD) shows that some of the hydroxyls are exchanged and these are considered to be in the amorphous regions and on the accessible surfaces of the microfibrils. The absorption band of the hydroxyl groups (OH) is much reduced by the treatment and is transformed into a number of well defined peaks considered to correspond to OH groups inaccessible to exchange due to being within the crystal lattice or on the bonded surfaces of the microfibrils (30,31).

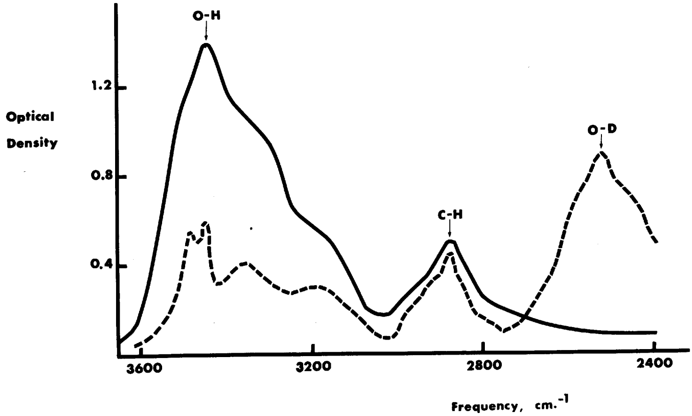

Figure 6 The infra-red spectra of viscose film before (solid plot) and after (dotted plot) exchange with heavy water (31). Accessible OH groups are exchanged to OD, inaccessible ones remain unchanged.

Sumi and coworkers have carried out deuteration experiments which have indicated very directly that additional hydrogen bonds are formed during drying-and-rewetting (32). They prepared membranes of bacterial cellulose and determined the accessibility of hydroxyl groups to deuteration following various drying-and-rewetting treatments. Table 1 summarizes their results. The data show that 39.9% of the hydroxyl groups in never-dry membranes were accessible to deuteration and that this percentage dropped to 31.4% when the accessibility was measured following a cycle of drying and rewetting. This reduction indicated that some of the previously accessible hydroxyls had been incorporated into the water-inaccessible regions as a result of drying-and-rewetting. An interesting corollary was an experiment in which a sample was deuterated in the never-dry state, was dried and was then washed with water (H_2O) in order to rehydrogenate the deuterated groups. The sample still contained 6.9 % deuterated hydroxyl groups - a further demonstration of the formation of additional inaccessible regions by drying-and-rewetting. Others have carried out similar experiments with other types of cellulose (29).

Treatment	% Deuteration
Deuteration of never-dried	39.9
Deuteration of dried-and-reswollen	31.4
Deuteration in never-dried state, dried and then washed in H_2O	6.9

Table 1. Accessibility of Hydroxyls of Bacterial Cellulose (32).

Support for the proposed mechanism also exists in the nature of treatments which are successful in preventing hornification. A description of these follows.

PREVENTION OF HORNIFICATION

Carboxymethylation

Lindström and Carlsson (27) have observed that hornification can be prevented if sufficient of the hydroxyl groups in a never-dried bleached kraft pulp are replaced by carboxylic acid groups using the carboxymethylation reaction:

$$\text{Cell - OH} \longrightarrow \text{Cell - OCH}_2\text{COOH}$$

We have repeated their experiments using solute exclusion rather than the WRV to evaluate swelling and have obtained similar results which we now present.

Figure 7A shows that the swelling of the never-dried fibre increases only slightly with the acidic group content when the acidic groups are in hydrogen form. The lower line shows the level of swelling of the pulps following a drying-and-rewetting cycle while maintaining the hydrogen form: all the samples undergo hornification.

In contrast, Figure 7B shows the effects of carboxymethylation when the acidic groups are maintained in their sodium salt form throughout experimentation. In this case, the introduction of acidic groups increases the swelling level of the never-dried fibres in a pronounced manner. The swelling level of the rewet fibres also increases with the acidic group content but at an even greater rate than the never-dried fibres. Hornification is progressively reduced and is totally prevented when the acidic group content exceeds 250 meq/kg.

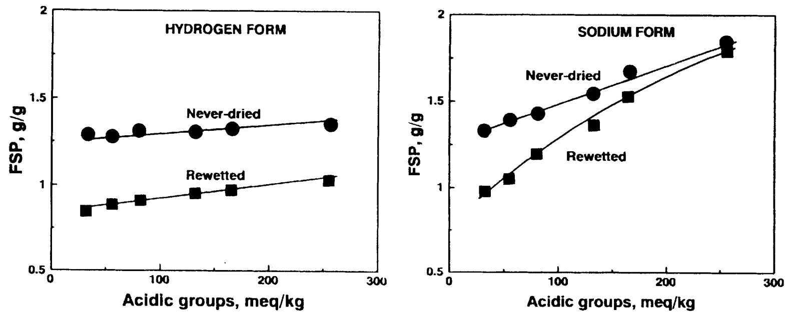

Figure 7 The effect of carboxymethylation upon the swelling of a bleached kraft pulp. Hornification still occurs if a modified pulp is dried with the acidic groups in the hydrogen form but is reduced if drying is carried out with the groups in the sodium form.

The effect of the acidic groups on the swelling of the pulps in the never-dried form is due to the entry of additional water into the fibre wall to reduce the osmotic pressure created by the ionized counterions of the acidic groups (11). The sodium salts are highly ionized and have a large effect, the hydrogen forms of the acidic groups are only slightly ionized and have very little effect.

Of most interest in the present context is, as recognized by Lindström and Carlsson (27), the importance of the ionic form of the acidic groups in the prevention of hornification. As to why pulps in hydrogen form undergo hornification, the simplest explanation is that the carboxymethyl groups in hydrogen form are as equally capable of forming hydrogen bonds as the original hydroxyl groups. With the acidic groups in sodium form, sufficient interference with hydrogen bonding could be possible. An alternative mechanism for the behaviour of the pulp in sodium form could be that the ions generated during rewetting create an osmotic pressure which ruptures any additional cross-links formed during drying.

Methylation

In order to investigate which of the latter mechanisms was dominant in the prevention of hornification we used methylation to substitute the hydroxyl groups in a bleached kraft pulp with methoxy groups:

$$\text{Cell - OH} \longrightarrow \text{Cell - OCH}_3$$

Methoxy groups are incapable of forming hydrogen bonds and do not induce osmotic swelling. As shown in Figure 8, the methylation procedure does increase swelling slightly in the never-dried state. More importantly, the figure also shows that low levels of hydroxyl group substitution are effective in preventing hornification. A 1% methoxy content corresponds to replacing 2.2 % of the hydroxyl groups. Thus, all hydroxyls need not be substituted. Apparently disrupting long sequences of hydrogen bonds is sufficient to prevent hornification. The new group introduced should, of course, not be capable of hydrogen bonding as appears to be the case with the protonized carboxymethyl group. However, the new group need not be an ionizing one.

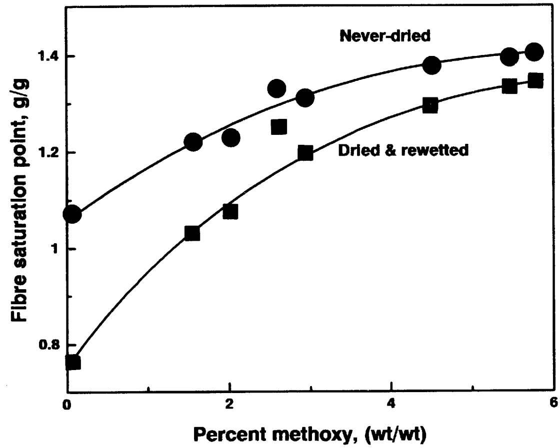

Figure 8 The effect of methylation upon the swelling of a bleached kraft pulp. The methoxy groups interrupt hydrogen bonding and prevent hornification.

Chemical Additives

While the substitution of the hydroxyl groups in a never-dried pulp can lead to the prevention of hornification, any such treatment is probably impractical on a commercial scale from chemical costs alone. An alternative approach could be to add to a suspension of pulp a soluble material capable of becoming attached to the hydroxyl groups via hydrogen bonding. Held in the walls by these bonds during drying, the material could block the close approach of microfibrils and hinder the formation of long sequences of hydrogen bonds between the microfibrils. Such was the approach of Higgins and McKenzie who studied the effect of drying pulps in the presence of different reagents upon subsequent handsheet properties (22). Sucrose and glycerol were found to be successful when added in sufficient concentration. On the other hand, sodium chloride had little effect although electrolytes are generally considered as effective in interfering with hydrogen bonding.

Experiments were carried out to verify these concepts using solute exclusion. Samples of a never-dried pulp were soaked in solutions of different concentrations of the additive. Pads were prepared from these suspensions and were air-dried. The pads were then rewetted and the pulps thoroughly washed prior to FSP measurements. As shown in Figure 9, the positive roles of sucrose and glycerol as observed by Higgins and McKenzie were closely reproduced in these experiments. Sodium chloride had a slightly positive effect in our experiments rather than the slightly negative effect previously observed.

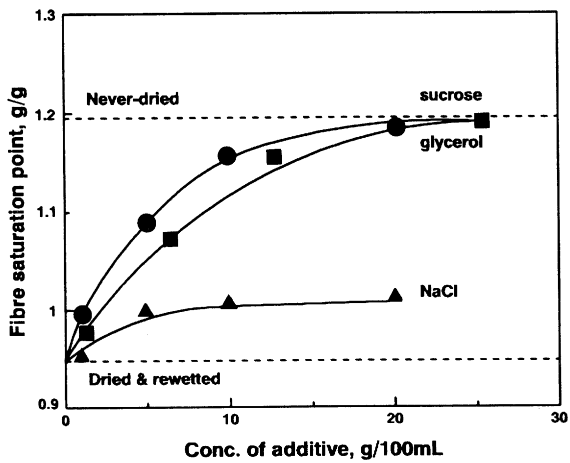

Figure 9 The effect of drying a bleached kraft pulp in the presence of additives upon the swelling of the rewet pulp. Sucrose and glycerol prevent hornification by acting as bulking agents within the fibre wall.

While drying a pulp in the presence of such soluble chemicals prevents hornification, it does so only for a single cycle of drying-and-rewetting: the additive is released into the water surrounding the fibres upon the rewetting and is not available during the second drying. This we have confirmed by experiment. A second problem from a practical viewpoint, is the very high level of addition of these chemicals required for complete prevention of hornification.

In order to achieve high efficiency at low concentration, various polymeric additives such as starches were considered by Higgins and McKenzie (22). They acknowledged that the penetration of these into the wall would be limited by their molecular size and indeed dramatic effects were not observed. Handsheets dried in the presence of many of the polymers were somewhat stronger than those dried without additives but they concluded that this was due to the improvement of the "adhesiveness" of the outer surfaces of the fibres (33).

High-yield Pulping

Clearly, the simplest method of preventing hornification is to leave the naturally occurring polymers, the matrix of lignin and hemicelluloses, within the wall. As seen in Figure 3, the loss in the level of swelling following a drying-and-rewetting treatment is negligible for high-yield kraft pulps. This reversibility of swelling has also been demonstrated for high-yield sulphite pulps which are of much more interest commercially (12), thermomechanical pulp (Figure 2), and stone groundwood (34).

REVERSAL OF HORNIFICATION

Beating

One of the principal actions of beating is to increase the swelling of fibres (4,35). That it does indeed cause swelling has been demonstrated by solute exclusion (7,11). That beating can specifically cause the swelling of a rewetted chemical pulp to rise to the level of the never-dried pulp and even beyond was confirmed by us in a recent experiment (Figure 10). This action of beating is represented in Figure 5 by movement of the wall from 5B through 5C and towards 5D. What then is the problem with using beating to reverse the effects of hornification? It is claimed that, while beating a rewet pulp regenerates the papermaking capacity of fibres, extra fines are produced which seriously reduce the ease of drainage of the pulp (9,15). It has also been proposed that the original fines in a chemical pulp lose their contribution to bond strength through hornification and that this cannot be reversed by beating (36).

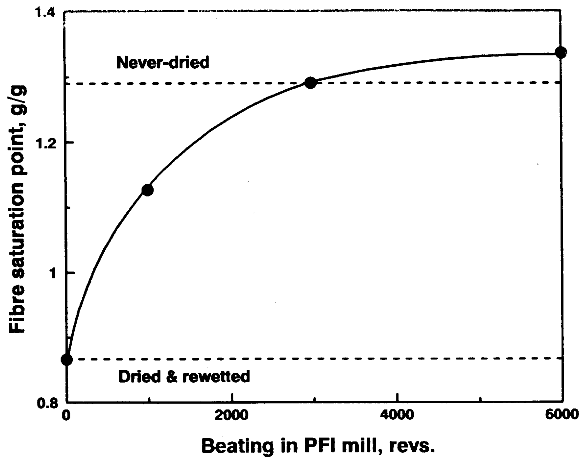

Figure 10 A commercial dry lap of bleached kraft pulp was beaten in a PFI mill and the swelling of the long fibre fraction measured. The swelling level of the never-dried fibres was attained at 3000 revs.

Derivative Formation

To produce swelling without fines generation, a possibility is to avoid the severe mechanical action of beating and employ a chemical method to promote swelling. Carboxymethylation can also be used for this purpose. The similarity of its effect to beating has been observed by, for example, Nelson and Kalkipsakis (37,38) using WRV measurements. Low degree acetylation is another method of swelling that Ehrnrooth et al. (39) have specifically applied to improving the properties of once-dried fibres. From their various experiments, they conclude that the hydrophobic groups must be introduced inside the fibre wall (as opposed to a surface reaction) and that they act by interfering with hydrogen bonding. Thus these techniques support the mechanism of hornification forwarded in this text but, as with the use of derivative formation for the prevention of hornification, the approach is too elaborate and expensive for practical papermaking.

FINAL REMARKS

Information from the literature has been supplemented by new experiments to support a picture of the mechanism of hornification. Procedures for preventing hornification have been presented but while these indicate what is required in a treatment they are not commercially viable themselves. High-yield pulps do not hornify and the use of these is a very practical way of avoiding the problem where other specifications permit. Beating reverses hornification in fibres but the quantity and quality of the fines are reportedly changed in a detrimental way.

EXPERIMENTAL

Pulps

A number of never-dried bleached kraft pulps commercially prepared from black spruce wood were used in this work. The fines passing through a 100 mesh screen were removed using a Bauer-McNett classifier prior to methylation reactions and additive treatments.

Drying

Unless otherwise stated, drying was carried out by allowing thin pads of pulp to air-dry at room temperature overnight. Re-dispersion was carried out in deionized water with gentle mechanical action from a laboratory stirrer.

Measurement of Swelling

Fibre saturation points were determined by solute exclusion using dextran with a molecular weight of $2x10^6$ and are reported in terms of the weight ratio of water to dry solid (5).

Carboxymethylation

The never-dried pulp (25g oven-dry weight) was first solvent-exchanged from water to methanol. A pad was then prepared and was dispersed in a solution of 7.5 g sodium hydroxide in methanol under reflux at 65 °C. The reaction was initiated by the addition of 22 g sodium chloroacetate in methanol bringing the total volume of methanol to 750 mL. Different degrees of substitution were obtained by varying the reaction time from 30 min to 6 hrs. Following reaction, the pulp was washed extensively with deionized water thus retaining the acidic groups in sodium form. A portion of the pulp was ion-exchanged to hydrogen form (11) for experimentation with this ionic form and also for determination of the acidic group content (40).

Methylation

Portions of never-dried pulp (4 g oven-dry weight) were soaked for 10 min in 160 mL 2N sodium hydroxide and were filtered to remove excess liquid. The fibres were then dispersed in 140 mL toluene and reaction initiated by the addition of dimethyl sulphate. Different levels of methylation were obtained by varying the quantity of dimethyl sulphate from 0 to 24 mL. After 1 hr, the pulps were filtered and washed extensively first with methanol and then with deionized water. Methoxy contents were measured according to TAPPI Test Method T 209 and calculated as the weight fraction of OCH_3.

Chemical Additives

Samples of never-dried pulp (1.5 g oven-dry weight) were soaked for 30 min in 100 mL solutions containing from 0 to 20 g of the additive. The suspensions were drained to form pads of 7.5 g weight and these were allowed to air-dry. Fibre saturation points were determined after re-dispersion and extensive washing of the pulps in deionized water.

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Transcription of Discussion

THE MECHANISM OF HORNIFICATION OF WOOD PULPS

A M Scallan

Prof J Roberts, UMIST, UK

Tony, thanks for making a subject, which ought to be simpler, very clear. Your explanation is perfectly correct. My comment is that at the start of your talk you said that hornification was unique to this industry - I certainly don't agree with that. The word hornification isn't even unique to this industry - it might not be in the Oxford English dictionary but it is littered in the polysaccharide literature and I guess that the closest example would be the retrodegradation of amylose which is the linear fraction of starch and which shows irreversible drying effects very similar to cellulose. The causes are the same as you propose for cellulose. In fact the reason we are able to buy fresh bread which remains fresh for a week or so is because the starch is substituted to inhibit retrodegradation and inhibit irreversible hydrogen bonding.

A Scallan

I did not mean that the phenomenon was unique to this industry but that the word was unique. What word do they use for it in the starch industry?

J Roberts

The word hornification is used widely in the polysaccharide literature is what I mean. Xylans are another example. I think Bob Marchessault some years ago showed that if xylans are mildly acetylated, as they are in their natural form, they show considerably greater water absorbency. They even exhibit monohydrate crystalline forms. Whereas if you remove the acetyl groups, they become very irreversibly hydrogen bonded and hornified.

A Scallan

There is no reason why hornification should not happen with other carbohydrates. It certainly happens in cotton.

P de Clerck, Avebe (Far East) Pte Limited, Singapore

Thanks John. I was going to bring up the same point about amylose retrodegradation. One other thing I was going to question was your figure looking at sucrose and glycerol and the effects on hornification. Did you actually measure the retention of these materials in the sheet - you said you had very high addition levels. How were these actually retained on the fibres?

A Scallan

It is not possible to say exactly how the additives are retained. We dry the pulps in the presence of a known amount of solution and end up with all the additive visibly coating the fibres. We don't know how much of the additive is inside the wall and how much is on the outside. Before we measure the fibre saturation point again, we wash well and we do know that none of these additives survives a good washing treatment.

Dr J L Brander, Arjo Wiggins R&D Limited, UK

All this talk of xylan and simple sugars makes we wonder whether you see a difference in hornification between hardwoods and softwoods.

A Scallan

We have done some work on hardwoods. They seem to behave in a similar manner to the softwoods. That is, we have observed hornification and we have checked out that some of the preventative treatments work on hardwoods.

Dr K Ebeling, Kymmene Corp, Finland

Tony could you please comment a little bit more on your comment about the role of temperature in hornification. As I understood the temperature is not important. If I recall correctly Prof Giertz published long ago similar results as the ones your last slide showed that paper made from pulp dried in air required a certain amount of PFI treatment to reach the tensile strength of the paper made from never dried fibres. If you dried the pulp against 100°C laboratory surface you needed to double the refining time and if you had kept the dry pulp sheet for half an hour at 150°C, which really cured the hornification, you needed to refine it for ever and you did not reach the tensile strength of handsheet anymore. There certainly is an effect of temperature in estimating the hornification. Everyone working with heatset offset knows that after such a treatment the surface of the paper is really hornified.

A Scallan

Yes, heat does make hornification occur to a greater extent and also makes it more irreversible but my main point is that you don't need heat to obtain the basic effect. In discussing the basic mechanism therefore, one should not suggest that reactions are taking place that require heat ie covalent reactions. These might occur at elevated temperature and accentuate the effects.

Dr J Phipps, ECC International Limited, UK

In figure 7 you show the difference between the effect of carboxymethylation in the hydrogen form and in the sodium form. In order to convert to the sodium form you must have performed the experiment at a reasonably high pH. Since alkaline conditions are believed to promote swelling, would you not expect some increase in the Fibre Saturation Point and some reversal of hornification at the higher pH, even in the absence of carboxymethylation?

A Scallan

Carboxymethylation is carried out at high pH and so the acid groups are in sodium form when first introduced – to obtain the sodium form of the pulp one simply washes to pH 8 to remove excess reagent. Some of this pulp can then be converted to hydrogen form by washing to pH 4 or thereabouts. A high acid group content produced by carboxymethylation is necessary to see the effects of ionic form. There are not enough acid groups in low-yield pulps to see the effects.

When the effect of the nature of the counterion was first observed by Lindström and Carlsson about 10 years ago, they were not sure of the mechanism. They did however feel that the experiments showed that introduction of acid groups in ionised form was a route to preventing hornification. In my presentation I have tried to show that the acid groups are not important per se and that carboxymethylation acts through a blocking action. Methylation works equally well and involves no acid groups.

Dr W Raverty, Amcor Research & Technology Centre, Australia

A question regarding the relatively massive amounts of sucrose and glycerol. Is it possible in that case that these materials are simply exerting the normal effects as humectants in the food and pharmaceuticals industry in preventing the removal of water rather than acting by steric inhibition?

A Scallan

We have thought about that. When we dried pulps in the presence of additives, we did so from a certain consistency and weighed the resultant pad. A mass balance was then made and it was calculated that the moisture content of the fibres did indeed go down to the usual 8%. The sugars and glycerols etc weren't just preventing evaporation or attracting water.

J Waterhouse, IPST, USA

Are you familiar with the work of Gunnar Gavelin and co workers* using critical point drying to look at so called hornification effects in mechanical pulps. The critical point drying prevents surface tension effects when the surfaces come together, but if they don't do that, they have a very tight gelatinous mass. Do you have any comments on the role of surface tension or that work?

* Gavelin, G., Kolmodin H & Treiber, E; Critical point drying of fines from mechanical pulp; Svensk Papperstidning 17 603-608 (1975)

A Scallan

I don't know that particular work but we've tried reducing the surface tension by adding surfactants prior to drying-and-rewetting and we did not find very much effect.