

EFFECT OF PULPING PROCESSES ON FIBRE PROPERTIES AND PAPER STRUCTURE

HANS WILHELM GIERTZ

DEPARTMENT OF CELLULOSE CHEMISTRY,
TECHNICAL UNIVERSITY OF NORWAY, TRONDHEIM

Synopsis

Based on the assumption that the most basic property of a paper is its apparent density, pulping effects such as yield, number of fibres per unit weight, lignin and hemicellulose contents and fibre strength are discussed with reference to the formation of bonds and paper structure. Special attention is devoted to the influence of different kinds of sulphite cooking such as conventional acid sulphite, bisulphite and two-stage cooking, also kraft cooking and bleaching. Finally, non-chemical operations in pulping such as chipping, fibre fractionation and drying are briefly surveyed.

L'effet des opérations de cuisson sur les propriétés des fibres et la structure du papier

En partant de la supposition que l'attribut fondamental du papier est sa densité apparente, l'auteur traite des effets de cuisson, tels que rendement, nombre de fibres par unité de poids, contenu en lignine et hémicellulose et la résistance des fibres individuelles. On étudie l'influence de ces effets sur la structure du papier et, en particulier, sur l'établissement de liaisons entre fibres. On traite particulièrement des effets des différentes méthodes de cuisson, tels que la cuisson au sulfite acide et au bisulfite, la cuisson en deux étapes et la cuisson au sulfate. On parle aussi des effets du blanchiment. Finalement, on étudie brièvement les opérations auxiliaires et non chimiques tels que le découpage du bois, le fractionnement des fibres et le séchage.

Der Einfluss von Aufschluss Verfahren auf die Eigenschaften der Fasern und die Struktur des Papiers

Auf der Basis der Annahme, dass die fundamentalste Eigenschaft von Papier sein Raumgewicht ist, werden Aufschluss Wirkungen, zum Beispiel Ausbeute, Zahl der Fasern pro Gewichtseinheit, Lignin und Hemicellulose Gehalt und Faser Festigkeit diskutiert mit Bezug auf das Entstehen von den Bindungen zwischen den Fasern und Papierstruktur. Besondere Aufmerksamkeit wird der Wirkung von verschiedenen Typen von Sulfitkochungen, zum Beispiel der konventionellen sauren Bisulfitkochung, der reinen Bisulfitkochung und der Zweistufenkochung, auch der Sulfatkochung und dem Bleichen geschenkt. Zuletzt werden 'nicht chemische' Verfahren, zum Beispiel Hackschnitzel Produktion, Sortieren der Fasern und Trocknen einem kurzen Überblick unterworfen.

General considerations

VERY little is known about the influence of the pulping process on the structure of paper, the simple explanation being that the present knowledge of fibre properties and the structure of paper is limited. Naturally, much practical experience has been collected about and systematic scientific investigations devoted to the problem of how the properties of the paper—and primarily the strength properties as measured with conventional laboratory instruments—are influenced by the pulping process. When in the following an attempt is made to describe such interrelationships, the effect of pulping has therefore to be described more in terms of conventional paper test values than in terms of paper structure.

It seems justifiable to state that when once the structure of a piece of paper has been defined in suitable terms its strength and other properties can be deduced. It is unfortunate, however, that the opposite situation does not hold.

The papermaking properties of a fibre depend both on its size and dimensions and on the pulping process. The former aspect is treated in another paper at this symposium. In describing the influence of pulping in the present paper, only one kind of fibre is dealt with and, as the author's experience is based on Scandinavian conditions, Norwegian spruce has been chosen. In the field of pulping, it is only rarely that conclusions drawn from one kind of wood do not hold for another. When this is the case and if it is considered to be of importance, it will be specially pointed out.

The fibre influences the structure of paper in many ways —

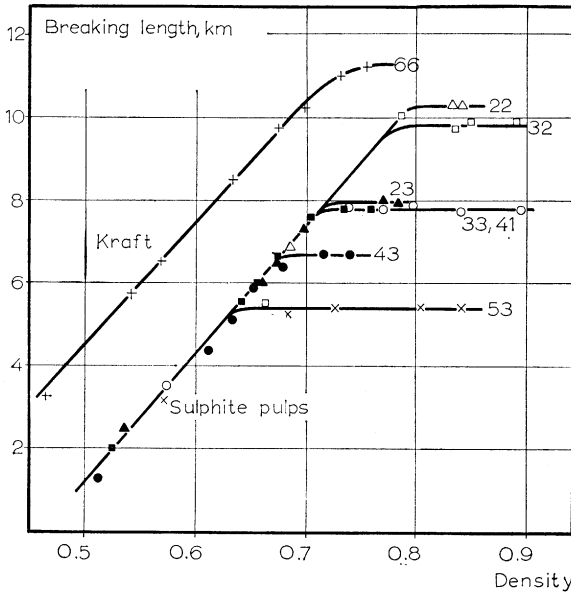
1. Even before the sheet is formed, the fibres tend to *flocculate*, thus disturbing the uniform formation of the paper. This property is primarily affected by fibre length, but also by shape and surface properties (*see* Andersson's symposium paper).
2. *The number of fibres* per unit weight is perhaps the most fundamental factor influencing the structure.
3. *The form of the fibre*—that is, if they are straight or curled.
4. When the fibres are drawn together by surface tension forces during drying, the *wet flexibility* of the fibre will control to what extent the fibres are brought into contact with each other.
5. In areas of fibre-to-fibre contact thus created, the *ability* of the surface material *to form bonds* will be of importance.
6. The degree of *fibre swelling* will influence the degree of shrinkage on drying, thus the stretching of the bonding material and the dried-in stresses in the paper.

All of these properties are greatly influenced by beating and thus the behaviour of the fibre in the beating process has also to be considered. Other properties of importance for the strength of the paper, but not directly influencing its structure, are —

7. *The strength of the fibre.*
8. *The strength of the bonding material.*

Perhaps, the most basic property of a paper is its apparent density. When fibres of a particular type are arranged and bonded to give a certain density, many mechanical and optical properties of the paper are also fixed as shown in Fig. 1–3. In the Fig. 1 relationship between breaking length and density for handsheets made from a great variety of sulphite pulps, the density has been varied by the kind of fibre and by the degree of beating. It is of interest to note that the tensile strength is the same for a given density, irrespective of whether, for instance, an unbeaten hemicellulose-rich pulp or a highly beaten, hot alkali refined pulp with low hemicellulose content is used. The close relationship holds, of course, only as long as further strength is developed with beating. When a certain amount of fibre-to-fibre bonding has been achieved, breakage takes place no longer mainly between the fibres, but across the fibre itself as well; optimum strength has been obtained and increasing the density does not result in a stronger paper.

As a close relationship exists between bursting and tensile strengths, the influence of paper density on bursting strength will be more or less the same. As shown by Van den Akker⁽¹⁾ and further dealt with by Giertz and Helle,⁽²⁾ tearing strength will, for purely physical reasons, depend largely on



Symbol	No.	Type of pulp	Yield, % of wood	Gamma-cellulose, % of pulp	Cuoxam viscosity, 1% solution
△	22	Neutral sulphite	52.8	17.5	250
▲	23	Neutral sulphite-sulphate	40.7	3.9	140
□	32	Strong sulphite	51.0	14.1	200
■	33	Pulp 32 hot alkali refined	40.9	5.5	200
○	41	Soft sulphite	44.6	7.5	40
●	43	Pulp 41 hot alkali refined	33.1	1.5	38
×	53	Overcooked sulphite ..	38.8	4.0	14
+	66	Ordinary sulphate ..	44.8	(5.6)	—

Fig. 1—The relationship between breaking length and apparent paper density for some different sulphite pulps and one sulphate pulp—all pulps are bleached and were prepared from the same lot of spruce wood, the slush pulps were beaten in the Valley beater

the density of the paper as is shown in Fig. 2. Finally, as higher density means fewer voids in the structure, thus fewer light-scattering surfaces, opacity also must be closely related to density as is shown in Fig. 3.

From these general facts, it can be predicted that, if the pulping or other treatments influence those properties of the fibre that affect the density of the

sheet, then they will most likely affect many other important properties of the paper. In the following, much attention will therefore be paid to the way and extent to which the treatment in question influences the properties of the fibre from the point of view of paper density.

The main object of pulping is to separate the individual fibres of the wood. This can be done by mechanical or chemical means or by a combination of both. Today, the range of pulps produced extends from ground-

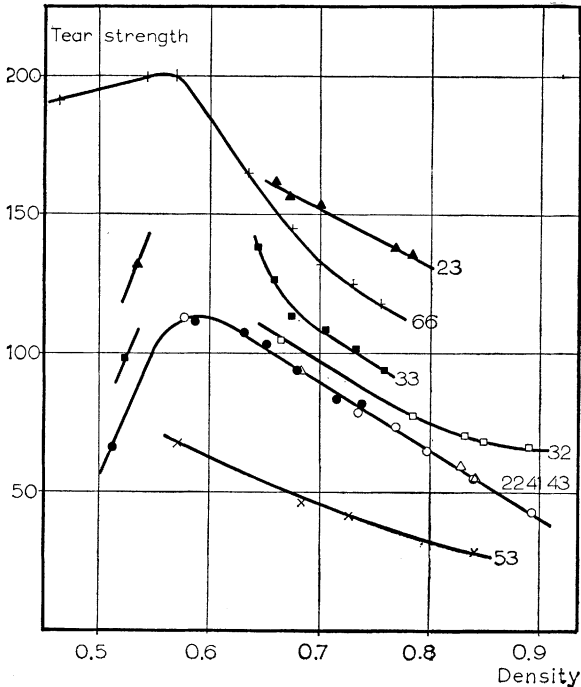


Fig. 2—Tearing strength against apparent paper density (same pulps as in Fig. 1)

wood with the same chemical composition as the wood to highly purified chemical pulps consisting of practically pure cellulose. In the following, most attention will be paid to the semichemical and chemical processes, including bleaching.

Chemical pulping involves dissolving the lignin and, at the same time, the hemicelluloses are degraded and partly dissolved. Depending upon how far these reactions are allowed to proceed, pulps are obtained in different

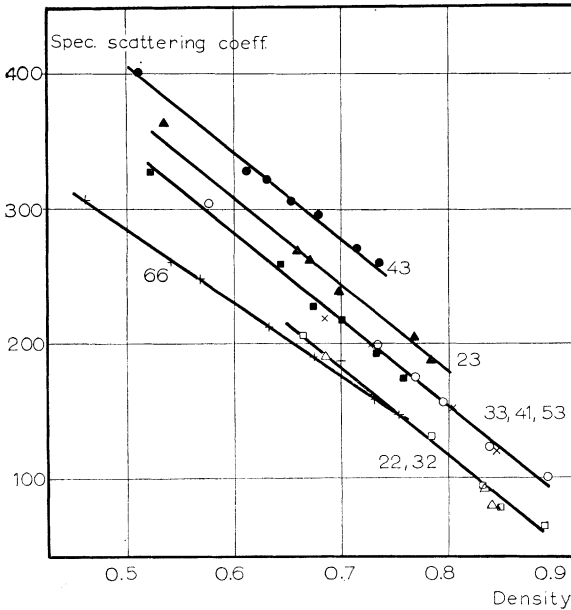


Fig. 3—Specific scattering coefficient plotted against apparent paper density (same pulps as in Fig. 1)

yields and with different lignin and hemicellulose contents. A simultaneous attack on the cellulosic microfibrils, which involves a weakening of the fibre, seems to be unavoidable.

Pulp yield

FROM an economic point of view, the yield of pulp is of the greatest importance. It must be kept in mind, however, that the number of fibres in a certain amount of raw material is fixed and cannot be increased in the pulping process. Yield therefore has a somewhat different meaning in pulping than in ordinary chemical processes. Today, strong papermaking pulps are produced in the yield range 40–70 per cent of the wood. When prepared from the same kind of wood and compared on a weight basis, the pulp obtained at 40 per cent yield contains 75 per cent more fibres than that of 70 per cent yields. The difference in yield therefore only means that the fibres of the higher yield pulps contain more lignin and hemicellulose, the value of which, from a papermaking point of view, is debatable. This point seems generally to have been overlooked. It is quite obvious, however, that

the structure of paper must be influenced greatly by the number of fibres in a certain area of a given basis weight.

Among actual paper properties, tearing strength and opacity are especially dependent on pulp yield. In the case of tear, the work of rupture will partly depend on the number of fibres involved in rupture⁽²⁾ and, in the case of opacity, light scattering will obviously increase with the area of fibre surfaces within the sheet.

There is one other point to be mentioned in this connection. Generally, the middle lamella is completely dissolved in chemical pulping, thus the fibre surface consists of the primary wall S1. At high yields, however, the middle lamella is incompletely dissolved and therefore partly covers the fibre surface of semichemical pulps after defibration. This is the case also with chemical, workable pulps obtained in high yield—for instance, bisulphite pulps. It seems likely that such surface materials might influence the bonding properties of the fibre. Because of the chemical reactions taking place in the pulping process, however, the lignin is mostly changed and its swelling and bonding properties altered, making it difficult to predict its influence on the paper structure.

It is known, too, that rupture takes place in different ways when defibring wood or chemically softened wood chips. In the grinding process, for instance, rupture takes place both between the fibres in the middle lamella and within the cellulosic secondary wall, whereas in the Asplund high temperature process it is predominant in the middle lamella, which fact may partly explain the higher tensile strength of mechanical pulps compared with wallboard pulps. It has been shown that, in the cold soda process, which gives comparatively strong pulps without appreciable delignification, the cleavage during defibration takes place within the secondary wall.

Lignin content

IN wood, the lignin is located mainly in the compound middle lamella and to a lesser extent in the interfibrillar spaces between the cellulose microfibrils of the fibre wall. In both cases, it is deposited along with the hemicelluloses, forming a homogeneous substance that is apparently held together by a three-dimensional network of lignin molecules and chemical bonds between lignin and hemicellulose. Native lignin is hydrophobic and the way in which it is mixed with the hemicelluloses in the wood makes the whole lignin-hemicellulose compound hydrophobic and prevents it from swelling. This is of greatest importance from a papermaking point of view.

High lignin content affects the papermaking properties of the pulp

mainly in three ways—the fibre is stiff, the bonding activity of the surface is decreased and swelling is inhibited.

Keeping in mind that lignin in the plant gives the woody tissue its stiffness and strength, there is nothing remarkable in the fact that partially delignified fibres are still stiff and that lignin-rich fibres remain stiff even during beating. They are thus difficult to beat to high strength, as the lignin prevents the hemicellulosic material from swelling and being plasticised. For the same reason, the fibres are mainly cut when beaten in knife-type beaters.

One important concept of the theory of the formation of paper bonds is that the hemicellulose molecules on the surface of the fibres and fibrils are at the same time both fixed to the fibre material and partly dissolved in the water. Surface tension draws this gel into contact with neighbouring units as the water evaporates and, finally, a solid 'cellulose film' bond is formed when drying is complete. The presence of lignin will obviously prevent the mobility of the hemicellulose molecules and consequently will also reduce the bonding capacity.

Both fibre stiffness and poor bonding activity will result in a bulky sheet, this being also the most typical feature of papers prepared from pulps with high lignin content, ranging from mechanical pulps through different types of semichemical pulp to high-yield kraft pulps. Beating is slow and the papers are characterised by low tensile and bursting strengths, low double folds, but high opacity. Tear is not directly influenced by the lignin content of the fibre, but is more, in a complex way, a result of the paper formation.

The influence of lignin is clearly demonstrated when bleaching NSSC pulps. The breaking length of unbeaten pulp is increased from 5 000 m to 8 000 m and, after beating the bleached pulp, strength values are obtained that are in the optimum range for this type of fibre. Tearing strength, when compared at the same tensile strength, is scarcely affected.

For the same reason as given above, lignin restricts the internal swelling, thus the normal lateral expansion of the fibre in water. Consequently, lignin-rich fibres do not shrink much when dried and do not give rise to internal stresses in the paper, which means that the dimensional stability is good. On the same basis, it can be argued that the bonding material is not stretched when a paper made from a lignin-rich pulp is dried and that the bond is therefore weaker than in a delignified paper.

When speaking about lignin above, the term *lignin* refers to the native, hydrophobic type. Should the lignin be made hydrophilic and able to swell as by the introduction of sulphonic acid groups in the sulphite process, the influence of lignin is not so marked any longer. This has to be kept in mind when dealing with, for instance, NSSC and high-yield bisulphite pulps. The

latter, obtained in the yield range 60–65 per cent, has a high lignin content (Klason lignin 10–15 per cent), the fibres are stiff, but their surface is slippery and the breaking length of the unbeaten pulp is more than 8 000 m. After desulphonation, however (which, for instance, takes place in the soda stage of the Sivola process), the hydrophilic nature of the lignin is drastically changed; the chips are again difficult to defibrate, the pulp becomes free and the strength of the unbeaten pulp is low (5 000 m).

Hemicellulose content

TODAY, there is no doubt that the hemicelluloses play an important role in papermaking. Recently, our knowledge of the chemical structure of wood hemicelluloses has been greatly enlarged. The hemicelluloses have been found to consist of heteroglycans, most of which have branched molecules and this fact explains the disordered molecular organisation of the native hemicellulosic material. As a consequence, the hemicellulosic material of the fibre is penetrated by water and, after delignification, swells considerably, forming a gel inside the fibre, in the interfibrillar spaces and on the surface of fibres and fibrils. The adhesive effect of such a swollen surface gel seems generally to be accepted.

The important question, however, is to what extent the amount of hemicellulose is responsible for the properties of the paper. The problem has been studied repeatedly and, in the case of sulphite pulps, good correlations have been shown to exist between paper strength and certain hemicellulose indicators such as pentosans, accessible material and gamma-cellulose (*see* Cambridge symposium). On the theory that the hemicellulosic material is the adhesive between the fibres of the paper, it is tempting to postulate that the greater the amount, the stronger the paper. Against this, however, it can be argued that only a certain amount of surface adhesive is needed to form the bonds and that further amounts of hemicellulose, particularly if located inside the fibre, is of less or of no importance. It should be remembered, too, that, in all experiments in which the amount of hemicellulose was varied, other properties of the fibre were affected at the same time, making it very difficult or impossible to draw definite conclusions. This will be dealt with further under the section on sulphite pulping.

On the other hand, it seems likely that the amount of hemicellulose inside the fibre will greatly influence the lateral swelling of the fibre. It must be remembered that isolated hemicellulose is water soluble. Therefore, the native, lignin-free hemicellulose has not only a strong tendency to swell, but also to dissolve in water, causing an appreciable swelling pressure inside

the fibre, which is restricted by bonds inside the gel and by the fibre structure. It is to be regretted that no data are available concerning the degree of this lateral swelling as affected by the amount of hemicellulose or by the nature of the pulping process. Obviously, the degree of lateral fibre swelling must be of the utmost importance to the structure of paper owing to the shrinkage and consequent formation of dried-in stresses and to micro-cracking that will take place when the paper is dried.

The interfibrillar hemicellulosic material is supposed to play an important role in beating, it imbibes water and acts as an internal lubricant making the fibre flexible; furthermore, the swelling pressure contributes to the loosening of the structure and to fibrillation. Here again, the amount of hemicellulose must be of importance and, generally, if delignified sufficiently, hemicellulose-rich or high-yield pulps are easily beaten. A special group is formed by the greaseproof pulps and similar pulps intended for dense papers, in the preparation of which the hemicellulose content is kept as high as possible. In this special case, the hemicelluloses not only facilitate 'hydration' and fibrillation, but by their gel-like nature increase the density of the paper.

It is generally believed that high hemicellulose content means low opacity. This is certainly true if the comparison is made on unbeaten pulp or after the same amount of beating, or at the same freeness. When compared at the same paper strength (tensile, burst), however, hemicellulose-rich pulps are as opaque as soft pulps.⁽³⁾

It is well known from the textile and plastic industries that the tensile strength of high polymer materials is closely related to the degree of polymerisation (D.P.) of the compound in question. A minimum value of D.P. is necessary for the development of any mechanical strength. Beyond this critical value, strength increases with D.P., but levels out at a certain molecule size, which is characteristic for each high polymer. For cellulose, this levelling-out D.P. has been shown to be about 250. For a long time, paper scientists have been interested in determining the degree of polymerisation of the bonding material in paper, but not until quite recently has it been possible to determine the D.P. of the hemicellulose fraction of pulps. According to investigations by Öhrn and co-workers, the D.P. of the gamma-cellulose from birch pulps, dissolved in 5 per cent sodium hydroxide solution, is about 140 for kraft, 115 for NSSC and 70 for acid sulphite pulp.⁽⁴⁻⁶⁾ The quality of the bonding material depends not only on the D.P., but also on the chemical composition, type of branching and mobility of the actual hemicelluloses and on the presence of cellulose microfibrils. Much important knowledge is still lacking on this point.

As lignin is an undesirable and hemicellulose a desirable component of

papermaking pulps and as hemicellulose is dissolved simultaneously with the lignin in industrial pulping processes, pulpmill chemists have always endeavoured to separate the two reactions in favour of the delignification reaction. The difficulties involved in such an attempt will be discussed later.

Fibre strength

IN all industrial pulping methods, the cellulose molecules of the microfibrils are to some extent degraded, and this is generally considered to weaken the fibre structure and to reduce fibre strength. Our knowledge of the strength properties of the individual fibres is still meagre, because of the difficulties involved in the technique of measurement. As a result, no exact data are available on the effect of fibre strength on paper properties and all theories are based on assumptions.

The concept of *fibre strength* is not clearly defined. Generally, high strength means, as in the case of cotton and rayon filaments, high tensile strength in the fibre direction. It is unknown whether strong, delignified fibres are also strong in the lateral direction and if they are, for instance, stiff and straight. Such properties may be due equally to the amount, quality and internal bonding of the hemicellulosic interfibrillar material. It seems likely that the fibre strength will not markedly influence the structure of paper, but in this connection it should be pointed out that it has been known for overcooked or overbleached pulps to form denser paper than would be expected from their opacity.⁽⁴⁾

The effect of fibre strength on paper structure first becomes obvious when the paper is loaded and ruptured. Tensile strength, for instance, is supposed to depend both on the amount and quality of bonding between the fibres and on the strength of the individual fibres. When beating is slight (Fig. 1), interfibre bonding is the determining factor for breaking load, thus breaking length will increase regularly with beating and with the consequent increase in the density of the paper. When fibre-to-fibre bonding has been brought to a certain level, however, rupture will no longer occur between the fibres, but across the fibres. From this point on, further beating does not result in higher tensile strength, despite the fact that it still makes the paper denser. According to this theory, the optimum tensile or bursting strength depends on the average fibre strength.

Fibre strength becomes important both in the beating process and in the final paper. There seems to be a close relationship between fibre strength and beatability (in the sense of increasing slowness). Strong pulps develop tensile strength without being 'cut' and they remain free during beating.

There is no type of pulp known that can be considered to be a strong pulp and that can easily be beaten to low freeness and good formation. All means of increasing beatability involve a weakening attack on the fibre structure, whether it is by overbleaching, by acid hydrolysis in sulphite cooking or by serious overcooking in the kraft process; in all cases, it results in a significant lowering of D.P.

Tearing strength also is greatly influenced by fibre strength. The likely explanation will not be given here, as it is an obvious consequence of the theory of tear rupture given by Van den Akker.^(1,2) In the same way, double folds can be closely related to fibre strength and this seems to be quite natural.

The degrading effect of the pulping process on the fibre is heterogeneous because of variations in accessibility and there are indications that, for one reason or another, it can be directed to certain parts of the fibre and to certain fibres. Forgacs has shown that the weak points for softwood tracheids are located at the sites that were in contact with the ray cells in the wood.⁽⁷⁾ This might be the explanation of the well-known fact that ordinary viscosity determinations or D.P. values, which give the average degree of polymerisation for the total cellulose material, do not correlate generically with such paper strength properties as optimum tensile or tearing strength.

From the way the problem has been presented here, the conclusions might be drawn that lignin content, hemicellulose content and fibre strength are the only factors influencing the structure of paper. This was not the intention. Our knowledge is still very limited and discussion therefore has to be concentrated on certain points where facts are available and seem to be of importance. It should, at the same time, be pointed out that it is extremely difficult, if not impossible, to separate the influence of one factor from that of another, because of the complexity of the pulping process. In all commercial pulping processes, delignification, hemicellulose dissolution, cellulose depolymerisation and fibre attack take place simultaneously. It is impossible to eliminate any one of these effects completely; it is only possible to some extent to vary their respective intensity. Many striking relationships between pulping, pulp composition and paper properties have been described in the literature and such correlations have been used to draw conclusions on cause and effect. It is clear, however, that, because of the complexity of the problem, one must be extremely careful when drawing such conclusions. This will be further exemplified when the influence of the main pulping processes on the structure and properties of paper are dealt with in more detail.

Sulphite cooking

SULPHONATION is one of the few known methods—and the best industrial way—of making lignin water soluble. The lignin-sulphonic acid formed is a strong acid and therefore ionised in both its acid and salt forms. The molecule is therefore also highly hydrated in water under acid conditions and is easily soluble even in the form of large molecules.

Acid hydrolysis plays an important role in sulphite cooking. According to present theories, the sulphonation reaction is catalysed by hydrogen ions. The lignin molecule is protonised in the alpha-carbon position and becomes reactive towards substitution reactions such as sulphonation and alkoxylation; also to condensation with phenols (pinosylvin in pine heartwood, tannins) or with other lignin molecules. Furthermore, acid hydrolysis is necessary to liberate the solid sulphonic acid by splitting bonds between lignin molecules or between lignin and hemicellulose molecules, this reaction being considered as rate controlling in sulphite cooking. At the same time, the hemicelluloses are hydrolysed, degraded and partly dissolved and the cellulose partly degraded. To obtain various pulp qualities, it is necessary to be able to control these different hydrogen ion catalysed reactions.

Before dealing with this problem in greater detail, a new type of hemicellulose reaction will be mentioned, which seems to be of greatest importance in the understanding of the behaviour of certain hemicelluloses during sulphite cooking. Recently, Rydholm and co-workers⁽⁸⁾ have shown that acetylated glucomannan, which in spruce wood amounts to 18–20 per cent, is rapidly deacetylated at above pH 6 and that the dissolved and deacetylated molecule can be reabsorbed on to the fibre. This reaction takes place in two-stage cooking with the first stage neutral or alkaline (Stora, Kramfors), resulting in a higher yield than with acid sulphite cooking. The same type of glucomannan adsorption seems also to take place to some extent in bisulphite cooking (pH 4) and in slow acid cooks performed at low temperature. Because of low glucomannan content (birch wood about 3 per cent), however, this kind of reaction is of no technical importance in the sulphite cooking of hardwoods.

The amount of acid hydrolysis during the sulphite cook depends on the pH value of the cooking liquor, the temperature and the time of reaction.

In conventional acid calcium sulphite liquors, the acidity is given by the amount of base used or the amount of combined sulphur dioxide, which is the same thing. The bisulphite ions form a fairly well-buffered system. During cooking, the base is used up by the strong liginosulphonic acid formed and, if the amount of base is insufficient (less than 30 kg combined sulphur

dioxide per metric ton oven-dry spruce wood) the liquor becomes highly acidic. The combined sulphur dioxide is therefore the most important variable in sulphite cooking. By varying it between 35 and 50 kg per ton of wood and at the same time adapting the temperature within the range 120–145°C, it is possible to obtain the whole series of sulphite pulps ranging from a typical hemicellulose-rich greaseproof pulp (52 per cent yield, 4 per cent lignin, 14 per cent gamma-cellulose) through different types of ordinary papermaking pulp to a high alpha-type dissolving pulp (42 per cent yield, 1 per cent lignin, 6 per cent gamma-cellulose).

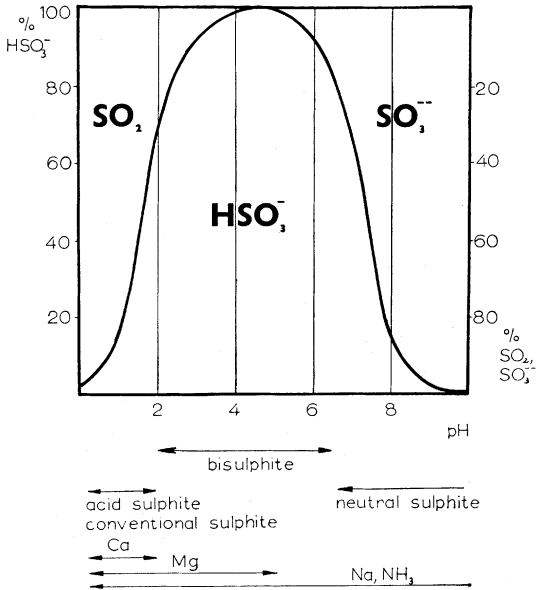


Fig. 4—The distribution of sulphur dioxide as SO_2 , HSO_3^- and SO_3^{--} at various pH values, 20°C

Owing to the poor solubility of calcium bisulphite, calcium liquors have to be acid (below pH 2.5), therefore the acidity can be varied only within a rather limited range. When using sodium as base, however, no such limitations exist and liquors of any pH value can be used. The same largely holds for ammonia also, but, as magnesium monosulphite is insoluble, the pH value of magnesium sulphite liquors is restricted to the range 1–5 (Fig. 4). The introduction of these soluble bases into the sulphite industry has opened up quite new possibilities. Neutral sulphite cooking (pH 7–9) has been

practised technically for more than 20 years, two-stage cooking for some years and bisulphite cooking (about pH 4) is just about to be introduced.

The temperature influences the sulphite cook in two ways. The speeding-up of the reaction with higher temperature is self-evident. Of interest for the pulp quality, however, is the possibility of favouring the delignification reaction rather than the hemicellulose hydrolysis, because of differences in the energy of activation of the two reactions. The energy of activation of the delignification reaction has been estimated to be about 22 kcal/mol,^(9,18) indicating that diffusion reactions might play some role, whereas that of the hydrolysis of different kinds of hemicelluloses is about 28 kcal/mol.⁽¹⁰⁾ This means that cooking at low temperature favours the delignification reaction to some extent—in other words, that a certain degree of delignification can be obtained with higher hemicellulose yield, if the digestion is carried out at low temperature.

Rusten⁽¹¹⁾ has recently studied the possibility that the same kind of differences might exist between the cellulose degradation reaction and the dissolution of hemicelluloses. He estimated the energy of activation of the cellulose degrading reaction of the sulphite cook to be 28–30 kcal/mol, thus of the same order as for the hemicellulose reaction. This is in agreement with the observation made by Ogait that bleached yield and viscosity of ordinary sulphite pulps follow each other closely.⁽¹²⁾

When speaking about the effect of temperature, the glucomannan readsorption reaction of Rydholm should also be kept in mind. As pointed out earlier, this takes place if the hydrolysis activity is low. In the case of conventional acid sulphite cooking, the only way of delaying the hydrolysis is by increasing the temperature slowly or by performing the cook at a low maximum temperature. With a soluble base, however, the same effect is obtained by working at a higher pH value as in two-stage and in bisulphite cooking. Obviously, it is the combination of acidity and temperature that is the cause.

From the general conditions given here, it is possible to indicate under what conditions a sulphite pulp should be cooked to give the desired papermaking properties.

Delignification is facilitated by conditions that favour the sulphonation reaction in competition with the lignin condensation reaction—such as good impregnation at high pressure, high base content, high sulphur dioxide concentration. When delignification is performed under non-condensing conditions, the dissolution of hemicelluloses follows the delignification reaction closely, the reason being that both reactions are controlled by the hydrogen ion activity (pH value, temperature) of the liquor. Two ways are

known to obtain a somewhat higher hemicellulose content at a certain degree of delignification —

1. Cooking at low temperature.
2. Readsorption of glucomannans by slow hydrolysis (low temperature, high pH value).

The degradation of cellulose finally follows the hemicellulose dissolution closely and the only exceptions are pulps with readsorbed glucomannans.

From this review, it is clear that the properties of the pulp are a direct result of the amount of hydrolysis that has been allowed to take place. The three factors—delignification, hemicellulose dissolution and cellulose degradation—are very closely intercorrelated and there are only slight possibilities of changing one without changing the other two correspondingly. As a consequence, it is impossible to obtain certain desirable combinations for the papermaker with sulphite cooking, for instance —

1. High degree of delignification with a high hemicellulose content and strong fibre.
2. Low hemicellulose content and strong fibre.

Of interest in sulphite cooking is the wide spectrum of pulps obtainable, from mildly treated groundwood-type pulps at 90 per cent yield through high-yield strong bisulphite pulps at 60–70 per cent yield to the conventional acid sulphite pulps, which comprises the whole range from ordinary strong sulphites to very soft rayon-type pulps. This is exemplified in the table of Fig. 1.

Kraft pulping

IN alkaline pulping, bonds within the lignin molecule are broken and new phenolic hydroxyl groups are formed at the same time. The phenolic alkali lignin is a very weak acid and has to be in its salt form to be ionised and soluble in water. Consequently, the black liquor has to contain some active alkali (above pH 10) at the end of the cook. High temperature and high alkali concentration throughout the cook are therefore important conditions for alkaline cooking.

As in sulphite pulping, the lignin has a tendency to condense in alkaline processes. The chance of condensation is greatly reduced in the case of sulphate cooking, the explanation being that the reactive groups of the lignin are sulphidised, thus made unreactive for condensation. This explains the more rapid and complete delignification taking place in sulphate cooks compared with soda cooks.

Some reaction possibilities between alkali and cellulose and hemicellulose are today well-known facts. The reaction can start on any available carbonyl group and, by mechanisms different from case to case, the glucose (or other) unit in question is attacked and the glycosidic bond to the next unit is split. If the carbonyl group is located within the chain, this means depolymerisation; should the reaction point be the end group, the alkali attacks this unit and forms a new aldehyde group at the end of the chain, which again can react and so on, until the reaction stops for one reason or another. Such a 'peeling off' process is supposed to be the principal reaction between alkali and carbohydrates in the kraft cook. Because of their accessibility, mainly the hemicelluloses are attacked, but cellulose also is broken down and dissolved to some extent (2-3 per cent of the wood).

These reactions between alkali and cellulose and hemicellulose start at a temperature of about 100°C and are largely completed when the cook has reached 150°, when delignification becomes of importance. The corresponding consumption of alkali is about 12 per cent (sodium hydroxide on oven-dry wood), which explains the high consumption of alkali in the kraft cook. In order to maintain a high enough alkali concentration (4 per cent on wood) to render the lignin soluble, the initial concentration must be very high, which means that there will always be plenty of alkali for hemicellulose reactions and that no such reactions will be suppressed because of the lack of alkali. Consequently, all possible hemicellulose and cellulose reactions will take place freely during the heating-up stage of the cook. As a matter of fact, the important end phase of the cook (that is, in the yield range of 55-48 per cent) seems to be one of pure delignification. With some exaggeration, it can be said that hemicellulose dissolution has been terminated in alkaline cooking, thus the quality of the pulp settled before delignification starts. Kraft pulps are therefore all of more or less the same type and quality and existing differences are due far more to the composition of the raw material and type of fibre than to the way of cooking.

A kraft cook reaction of great interest was discovered by Yllner.⁽¹³⁾ He showed that some of the dissolved xylan molecules during cooking were able to reprecipitate on the fibrous material.

According to the proposed mechanism, the branched methyl-glucuronoxylan molecules dissolve and when in solution the side chains are split off, whereupon the unbranched molecule can be adsorbed by or crystallise on cellulosic surfaces. The re-adsorbed xylan is not of the same kind as the native one; most probably it is laid down in a better ordered system and crosslinking between microfibrils may also take place. The precipitated xylan will not dissolve again in the alkaline liquor and it can be expected not to swell to

the same extent as the branched native xylan. This reaction may partly or entirely explain such well-known characteristics of kraft pulps as the high xylan content and its insolubility in alkali at concentrations that produce swelling in cellulose, the strength of the fibre and its poor swelling properties, as well as the difficulty with which the pulp is beaten. The methyl-glucuronoxylan content is high both in softwoods (spruce 8–10 per cent) and hardwoods (birch 30–32 per cent).

With the exception of overcooking, no technical means are known by which the quality of the kraft pulp can be markedly influenced. The important variable in kraft cooking is the amount of charged alkali, which primarily

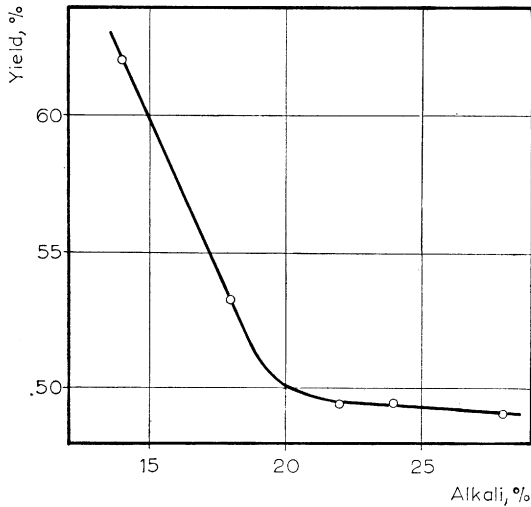


Fig. 5—The influence of effective alkali ($\text{NaOH} + \frac{1}{2} \text{Na}_2\text{S}$) on pulps yield in kraft cooking of pine wood

determines the degree of delignification and, as a consequence, also the yield. This relationship is shown in Fig. 5. The amount of hemicellulose dissolution seems to be astonishingly constant within the actual range of kraft cooking as is also the attack on the fibre as measured by the tearing strength.

It is impossible to delignify kraft pulps to the same extent as sulphite pulps, which is explained by the extensive lignin condensation in kraft pulping. If an attempt is made to force the delignification process further by adding more alkali and extending the cooking time, the cellulose is markedly attacked and the fibre weakened. This is what happens in soda cooking.

The lignin content influences the properties of the kraft fibre in the same general way described earlier. With higher lignin content, the fibre becomes stiffer, it is more difficult to beat and forms a bulkier, thus a weaker sheet, though tearing strength and opacity after bleaching are, when compared at the same tensile strength, unaffected by the degree of delignification. How beatability is influenced by yield and lignin content is shown in Fig. 6.

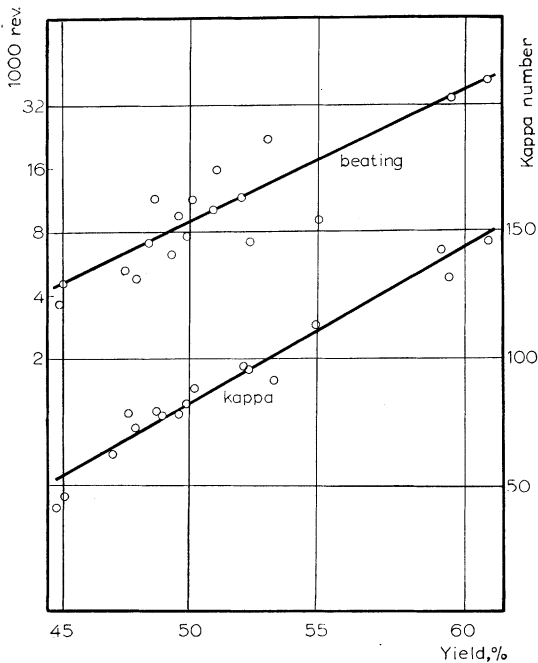


Fig. 6—Kappa number (ICCA) and beating time plotted against total yield of unbleached sulphate pulps: the pulps were obtained by varying the amount of charged alkali, the method of impregnation, the cooking time schedule and the maximum temperature; beating time is given as number of revolutions in the PFI mill to obtain a breaking length of 10 000 m (log scale)

Obviously, the kraft process does not offer the same possibilities of controlling the cook and varying the pulp properties as does the sulphite process. This is particularly true in the case of high-yield pulping.

The commercial way of increasing yield is by decreasing the charge of

active alkali. The first apparent effect is the formation of uncooked chip cores as a result of heterogeneous penetration and used-up alkali. This occurs at a yield of about 50 per cent for spruce and 48 per cent for pine wood. At higher yields (55–60 per cent), the percentage of uncooked chips is so high that the cook should be classified as semichemical and the chips have to be defibred before refining. Such high-yield pulps are being produced commercially, but, as the increase in yield is mainly a consequence of higher lignin content, these pulps are very coarse and can be used only for such products as board and kraft liner. Still higher yields mean extremely coarse pulps of no commercial interest.

In the structure of paper, there is a very important difference between sulphite and sulphate pulps. Sulphate pulps form bulkier papers than do sulphite pulps, which is specially evident when the comparison is made at the same tensile strength (Fig. 1). As a consequence, bleached sulphate papers are more opaque than sulphite papers and the higher tear of kraft papers might partly be explained on the same basis. The full explanation of the fundamental differences between sulphite and sulphate pulps has not yet been given.

Bleaching

IN pulping, bleaching involves the final delignification of the fibre, along with some hemicellulose dissolution.

As most pulps to be bleached are cooked to a low lignin content for economic reasons, the direct effect of delignification on fibre properties is insignificant. For lignin-rich pulps, in which the drop in yield with bleaching will be about 10 per cent, improved strength properties have been reported as a result of bleaching. This might partly be an effect of delignification, but at the same time the influence of the increment of the number of fibres must be kept in mind. When bleaching high-yield and semichemical pulps, however, the typical change in fibre stiffness, bonding ability and beatability must be attributed primarily to the effect of delignification.

The most important effects of bleaching are caused by oxidising side reactions. The cellulose is partly depolymerised, which is evident from the reduction in the viscosity of the pulp; at the same time, the hemicelluloses must be degraded correspondingly, even if this has not yet been shown experimentally. As a result, the strength of the fibre itself and of the bonding material can be expected to be reduced by bleaching and, as a matter of fact, most bleaching operations decrease all paper strength properties to some extent. It is still not known whether this is primarily the result of fibre damage or of hemicellulose degradation.

Partial overbleaching first of all shows up in the reduction of double bonds. Tearing strength is also markedly influenced, which might be taken as an indication of fibre damage, whereas tensile and bursting strengths are less affected.

This degradation during bleaching seems to proceed in very much the same way, but not to the same extent, irrespective of bleaching agent or bleaching conditions. There exists therefore a close relationship between, for instance, the drop in viscosity during bleaching and paper strength (Fig. 7).

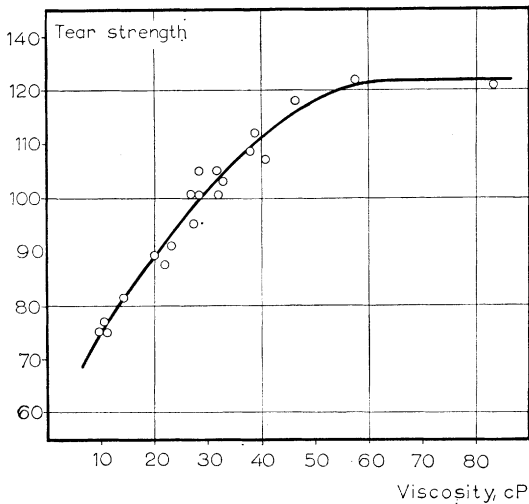


Fig. 7—Tearing strength plotted against cuoxam viscosity (1 per cent solution) of bleached sulphate pulps—the same lot of an ordinary kraft pulp was bleached by combining chlorination, alkali extraction and hypochlorite and chlorine dioxide bleaching in different ways

It is a well-known fact that the viscosity can be allowed to decrease to a certain level, typical for each kind of pulp, without involving a substantial loss in strength, though further attack means lower paper strength.

Besides its degradation effect, oxidation also involves the introduction of carboxyl or carbonyl groups, which, because of accessibility, most likely involves the hemicellulosic material of the fibre. Very little is known about such groups' influence on the papermaking properties of the fibre. It has been reported that the formation of the reducing type of oxycellulose increases both primary and secondary wet strength⁽¹⁴⁾ and the effect has been made

use of commercially, for instance, when making filter paper. The effect might be referred to the strong type of hydrogen bond formed by carbonyl groups. The similar effect of oxycelluloses on colour stability is outside the scope of this paper.

In a multi-stage bleaching sequence, one or more alkali extraction stages are usually included. If one of these stages is performed under drastic conditions (that is, a reaction temperature above 95°C and 5 per cent alkali or more), the hemicelluloses and to some extent also the cellulose are attacked and dissolved in the same way as in the case of alkaline pulping. For obvious reasons, the treatment is effective only with sulphite pulps. It is used in the ordinary production of high alpha dissolving pulps, but has also been utilised in the making of rag-type speciality papermaking pulps.⁽¹⁵⁾ It is the only known way of obtaining the combination of a strong sulphite fibre and a low hemicellulose content.

Because of the low hemicellulose content, such pulps beat slowly and form a bulky and opaque sheet with low tensile strength and high tear. The tensile strength, however, can be greatly increased by beating (pulp 33 in Fig. 1-3).

Non-chemical operations

IN the chipper, the wood is exposed to very high compression forces both across the log and along it. The main damage caused is in that part of the chip where the knife enters, but it also seems likely that the whole chip is compressed.⁽¹⁶⁾ The amount of chip damage is greatly dependent on chipper type and knife condition. It influences the quality of the pulp in that the fibre-weakening attack proceeds more rapidly in the damaged regions than in the undamaged ones. Delignification and hemicellulose dissolution are, however, not affected. The weakening effect causes a serious problem in sulphite pulping, but is of less importance in kraft cooking.⁽¹⁷⁾ Quite new chipper constructions, in which the knives cut the wood parallel to the fibre axis, are said to produce less damaged chips.

In modern sulphite mills, the pulp is fractionated on special screens in order to remove resin and resinous ray cells. As the material removed, which amounts only to 2-3 per cent, consists of small fibres and fibre fragments, its removal will certainly affect the structure of the paper to some extent. To what degree, however, is unknown.

The number of operations in pulpmills has been continually increased and, particularly if a multi-stage bleaching plant is included, the fibres will be exposed to mechanical action in pumps, pipelines and agitators that should not be overlooked. The total effect is similar to that taking place in

the very first phase of beating and the corresponding effect on the paper has been noticed. The fibre is said to be kinked and to become more flexible, but here again no actual data are available.

The fibre undergoes important physico-chemical changes when being dried. The phenomenon is generally called hornification and involves shrinkage and the formation of hydrogen bonds, some of these effects being irreversible. Owing to the high degree of swelling and to the movability of the molecules, hornification takes place for the main part within the hemicellulosic material of the fibre. The phenomenon is of the greatest importance in the case of hemicellulose-rich pulps. When rewetted, the fibre does not swell to the original slush dimension. The limited swelling can, however, be overcome by beating the pulp, which results in the restricting bonds being mechanically broken. Hornification greatly influences the papermaking properties of the fibre and the effect is probably due both to restricted fibre swelling and reduced flexibility and to inactivation of the surface bonding gel. The degree of hornification depends, among other things, on the speed and the temperature of the drying process. If drying is not uniform, as when drying pulp commercially, the effect is noticeable even at an average dry solids content of 60–65 per cent. With uniform drying, however, no change in papermaking properties is observed before a dry solids content of 70–75 per cent has been reached, depending on the hemicellulose content of the pulp; from there on, hornification increases markedly with further drying.

After drying, the pulp forms a bulkier sheet with lower tensile and bursting strengths, higher tear and higher opacity than does the slush pulp. This is certainly true when the comparison is made on unbeaten pulps or on pulps having been equally beaten. It is possible, however, to beat the dried pulp to almost the optimum tensile strength of the slush pulp and, if compared at the same breaking length, there is no noticeable difference in tear and opacity between slush and dried pulps. The essential effect of drying is therefore on the beatability of the pulp and, after enough and suitable beating, which is needed to break the restricting bonds of the hornified gel, almost the same pulp characteristics can be obtained as for the slush pulp.

It can be said that drying is a way of inactivating the fibre, making it possible to get a less bonded, bulkier and softer sheet. In the same way, it is easier to obtain a certain amount of cutting and formation without forming too many bonds (bulk, opacity) when beating a dried than when beating a slush pulp.

The same phenomenon occurs when drying the wood. After pulping, however, the effect is less marked and the only result of commercial interest

is that pulps prepared from green wood have a tendency to form somewhat more highly bonded sheets than do pulps from dried wood.

REFERENCES

1. Instrumentation Studies: XLVI, *Paper Trade J.*, 1944, **118** (5), 13-18
2. Giertz, H. W. and Helle, T., *Norsk Skogsind.*, 1960, **14** (11), 455-469 (French translation available)
3. Giertz, H. W., *Svensk Papperstidn.*, 1951, **54** (22), 769-775; 1952, **55** (3), 72-77; (23), 897-900 (English translations available)
4. Petterson, S. E. and Rydholm, S. A., *Svensk Papperstidn.*, 1961, **64** (1), 4-17
5. McPherson, J. and Öhrn, O. E., *Svensk Papperstidn.*, 1960, **63** (21), 762-768
6. Öhrn, O. E. and Enström, B. F., *Svensk Papperstidn.*, 1960, **63** (22), 817-822
7. Forgacs, O. L., *Tappi*, 1961, **44** (2), 112-119
8. Annergren, G. and Rydholm, S., *Svensk Papperstidn.*, 1959, **62** (20), 737-746
9. Yorston, F. H., *Dominion Forest Service Bulletin 97* (Ottawa 1942), 56
10. Konkin, A. A. and Shukalova, E. A., *Zhur. Priklad Khim.*, 1959, **32** (5), 1 076-1 080 (Ref. *A.B.I.P.C.*, 1960, **30** (2), *Abs.* No. 722 148)
11. Rusten, D., *Studies on the sulphite cook hydrolysis of wood carbohydrates* (Thesis, Trondheim, 1960): to be published in *Norsk Skogindustri*
12. Ogait, A., *Das Papier*, 1958, **12** (718), 126-136
13. Yllner, S. and Enström, B., *Svensk Papperstidn.*, 1956, **59** (6), 229-232
14. Meller, A., *Tappi*, 1958, **41** (11), 679-683
15. Rasch, R. H., *J. Res. Nat. Bur. Stand.*, 1926, **3**, 469; 1931, **7**, 465, 765
16. Rys, L., Aron, G. and Overbaeck, W., *Tropical woods and agricultural residues as sources of pulp* (FAO, Rome 1952), 83
17. Stone, J. E. and Nickerson, L. F., *Pulp & Paper Mag. Can.*, 1958, **59** (6), 165-173
18. Morud, B., *Studies on the chemistry of sulphite cooking* (Thesis, Trondheim, 1958)

Transcription of Discussion

DISCUSSION

MR. P. E. WRIST: One statement made during the presentation of this paper was of great interest to me—that beating has the effect of stiffening a fibre. I think this is an important statement and worthy of more discussion.

It is often stated in the literature that one of the effects of beating is to make the fibre more flexible. In our studies of fibre networks in suspensions, however, we have always had difficulty in explaining why the network strength of a beaten pulp was lower than that of the unbeaten pulp. The two effects of fibrillation and of increased fibre flexibility (which are usually attributed to beating) should both have made the flocs stronger and the only factor by which we could explain this weakening of the floc structure was the shortening of the fibres. Having measured fibre lengths, we found that in the cases we studied we had not shortened the fibres very much. An enormous dependence of strength on fibre length would therefore offset the other two effects. If we can accept, however, that beating stiffens the fibres in suspension, then our experimental data can be explained more reasonably.

The distinction you have made between increased stiffness in the wet swollen stage and increased flexibility during the drying phase is not adequately appreciated in the literature.

DR. O. J. KALLMES: With regard to discussions on the flexibility of fibres, we must keep in mind the axis of reference of the fibre's cross-section. Fibres that have undergone mechanical treatment tend increasingly to collapse, making them more flexible around their y axis, but less around their z axis. The former effect enhances the bonding ability of fibres, the latter makes them more rigid within the sheet when the sheet is strained.

PROF. G. JAYME: Giertz has pointed out the difficulties of removing lignin from plant materials without removing hemicelluloses. There are two approaches. Maass showed about 30 years ago that a sulphite cook of wood at 50°C will yield a pulp that may be regarded as a holocellulose containing practically all of the hemicelluloses originally present. Another way has recently been used by us—a cold soda pulp was prepared from poplar wood at about 93 per cent, which could be delignified easily with sodium chlorite practically without removal of hemicelluloses. These could be removed by treatment with caustic soda solutions of various concentrations. The strength data on the pulp prepared in this way indicated that strength increased very

Discussion

considerably with lignin removal, whereas the influence of the hemicelluloses was less pronounced. The highest strength data were obtained when all the lignin and part of the hemicelluloses were removed.

DR. G. N. RICHARDS: To what extent is fibrillation affected by hemicelluloses alone? For instance, what is the fibrillation behaviour of a holocellulose in which only the lignin has been removed and all the hemicelluloses remain?—are the fibrils held together by a hemicellulose glue?

PROF. H. W. GIERTZ: It is quite possible to fibrillate holocellulose fibres, but, because of the slippery consistency, it must be done in the right machine. The Lampén ball mill, for instance, is unsuitable.

DR. S. G. MASON: Giertz has stated that lignin is hydrophobic. In view of the fact that water is sorbed by lignin (as shown by our own work and that of Christensen in Australia) and that water acts as a plasticiser for lignin, I find this concept doubtful. What is the experimental evidence for this claim?

PROF. GIERTZ: For small molecules, the terms *hydrophilic* and *hydrophobic* are well-defined. A problem occurs when dealing with large molecules and macro-molecules. Propanol, glycerol and phenol are hydrophilic and anisole (methoxybenzene) is hydrophobic—but what about lignin? Many substances are neither typically hydrophilic nor typically hydrophobic, they are something in-between and may be graded in this respect over a very wide spectrum.

From a practical point of view, the words should in each case be used appropriate to the conditions concerned. Let me take an example. Secondary cellulose acetate with a D.S. of 2.0–2.5 is less hydrophilic than cotton and viscose rayon are, because it absorbs less moisture and is plasticised less in laundry operations. As a textile, secondary cellulose acetate belongs to the hydrophobic filaments. This is still truer for cellulose acetate with a D.S. of 2.8–2.9. On the other hand, a cellulose acetate film with a D.S. of 2.9 is considered to be hydrophilic when used as a loudspeaker membrane, because it becomes slightly plasticised by the moisture in the air. For this purpose, it has to be a true triacetate.

Hemicellulose is hydrophilic, but a sol of cellulose micelles, prepared by hydrolytic degradation of wood cellulose is classed by Rånby as hydrophobic, despite the fact that the precipitated sol material absorbs moisture. There is such an important difference in behaviour towards water between a ground-wood fibre and a holocellulose fibre or between precipitated gamma-cellulose and precipitated alkali lignin that to my mind this difference is expressed most simply and accurately by using the words hydrophilic and hydrophobic.

Fibre properties and papermaking

MR. J. W. SARGENT: I should like some comment on the fact that patterns of microfibrils similar to those Giertz has visualised for the S2 cell wall layer are to be found in such two completely different fibres as bleached sulphite and unbleached kraft.

PROF. B. G. RÅNBY: It is not a question of the strength of the individual hydrogen bonds and we know that the hydrogen bond energies are between 3 and 10 kcal/mol. Under certain conditions, you can form many ordered hydrogen bonds (as in crystalline regions), in ordered adsorption of hemicellulose chains on to cellulose microfibrils or in ordered aggregation (association) of a bundle of cellulose microfibrils. The resistance of such systems, say, to swelling with water is because the swelling reagent must give a simultaneous opening of a whole sequence of identical bonds and this is thermodynamically unfavourable, because it is unlikely. The insolubility of cellulose in water can be interpreted along these lines.

PROF. JAYME: The influence of hemicelluloses on light scattering in handsheets is very marked. Jayme and Pommer proved many years ago, using the Kubelka-Munk method and formula, that the scattering coefficient of handsheets closely followed the alpha-cellulose content changes obtained by the caustic soda treatment of pulps—with progressive removal of hemicelluloses, the handsheets became more opaque.