SOME ASPECTS OF THE THEORY OF THE BEATING PROCESS

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Summary

Three factors involved in the strength of paper are discussed — (1) the strength of the fibre, (2) resistance to failure by slippage of fibres and (3) interfibre bonding. The objectives of beating are considered to be the production of (1) the best conditions for maximum interweaving of fibres in the web and (2) the best conditions for bonding between fibres. Both of these desirable attributes must be produced with maximum possible avoidance of gross damage to the fibre.

The matters are discussed in some detail. Particular attention is drawn to other closely related topics — for example, fibre swelling and plasticisation, interfibre adhesion in suspensions and flocculation and the relationship of tearing strength to beating.

THIS discussion is not intended to be a critical or interpretative review of the very voluminous literature on beating. Many hundreds of contributions to the literature have been made on the subject. Of these, the majority deal with highly practical aspects of beating such as the relative merits of various forms of beaters, results obtained on alteration of variables in the use of any one form of beating machine, etc. Very little account can be taken of these presentations, since at best this type of information touches only on the fringes of a basic picture of the beating process. In those contributions dealing directly with the mechanism of the beating process, a considerable

difference of opinion is noted on several important points and an additional discussion of the subject has purpose and merit in the possibility of focusing attention on such topics of further research which might eliminate one possible mechanism and strengthen another, leading eventually to an acceptable concept of the fundamental mechanism of the process.

The beating of pulp fibres is carried out primarily for the purpose of strength development in the paper web to be manufactured from such fibres. Certain other desirable physical and aesthetic properties are enhanced at the same time, but, for our present purpose, we may focus on increased strength as the principal goal to be attained.

Factors in strength of paper

The strength of the eventual web will depend on a combination of three factors —

1. The strength of the fibre.
2. The degree of frictional resistance in the web to pulling out of fibres.
3. The strength and number of bonds between fibres.

There appears no doubt that all three of these factors play an important role in the strength of the paper web. To a limited extent, these factors can be separated. Thus, the web can be formed under conditions where possibilities of bonding are very largely, if not completely, obviated. Under such conditions, for example, the effect of frictional resistance to pull-out is shown to be large. If unbeaten fibres are formed into a sheet after the well-known technique of the displacement of water by non-polar organic media and subsequent evaporation of the latter, the strength of the web is extremely low. Interfibre bonding has been essentially eliminated and very little frictional resistance to failure is shown in such webs. If, however, the fibres are beaten in water and then the water/organic medium exchange is effected, the resultant webs possess a surprisingly great proportion of the strength of the normal web. These observations are illustrated by the following experimental data.

Bleached spruce in wet lap form was made into standard handsheets on the British sheetmachine, couched off and either pressed at 50 lb./sq. in. for 2 min., air dried on their blotters or removed from their couch blotters and immersed for 10 min. in alcohol, drained, then immersed for 10 min. in ethyl ether and finally dried in a vacuum desiccator over calcium chloride for not less than 30 min. These dried sheets were then pressed under 50 lb./sq. in. for 2 min. Similar sheets were prepared by the two methods described above from the same pulp beaten for 0, 20 and 35 min.

It was found that the densities of the normal sheets bore a constant ratio to the densities of the extracted sheets throughout the beating curve. This is taken as an indication that the effectiveness of water removal in the extracted unbeaten and beaten sheets remained constant. Despite this, however, the ratio of strength of the extracted sheets to that of the normal sheets continued to rise during beating. After 35 min. beating, this ratio was 30 per cent., compared with 6 per cent. for the unbeaten sheets.

Here again, interfibre bonding has been essentially eliminated, but the effect of increased interweaving of fibres following beating and consequent greatly increased frictional resistance to failure is a large one and in itself can bring about important strength increases. This aspect of strength development deserves more emphasis than it has received.

The strength of the fibres themselves must be regarded as a limiting factor, at least in a negative way. It does not appear likely that this strength can be enhanced by beating, but it is rather a matter of the maximum preservation of the very high strength inherent in the unbeaten fibre. There can be no doubt of the vast amount of damage done to the fibre as a result of extensive beating, so strikingly observed in the appearance of such beaten fibres even under low magnification. One aspect of this fibre strength, discussed several years ago by the writer,[1] would seem to deserve emphasis again for our present purpose. The strength of a fibre is generally considered the tensile strength in the direction of the fibre axis. The fibre strength in a paper web can, theoretically at least, be obtained by the use of closely spaced jaws in a tensile test of the web, such as in the so-called zero span test. It is desired to emphasise here that such a measurement is of very limited value as an indicator of damage to fibres to be related to web strength. Such a test measures at best the tensile strength of the fibres in the direction of the fibre axis. This tensile strength is relatively very high and is of a different order than the strength of the web. The vast majority of the molecules in the fibre are aligned essentially in the direction of the fibre axis and it is apparent that much of the damaging effect of mechanical work on the fibre will be the creation of fracture lines, which will also be in the direction of the fibre axis. Aside from the transverse faults brought about by partial chopping and pinching and bending the fibre well beyond the elastic limit, the highly oriented structure will develop fracture lines, which must run mainly longitudinally. Such lines and zones of weakness would have to be evaluated in terms of tensile strength normal to the fibre axis and no techniques have as yet been developed for such measurements. This consideration will be further developed below in conjunction with a discussion of bonding among fibres.

No work has ever been published on any attempt to examine the bonding between fibres isolated from the effect of frictional pull-out. Such research would in the author's view be of very great fundamental value in the whole field of fibre properties and the structure of paper. This is not to say that we should obtain quantitative values for the strength of a bond between two fibres in an isolated system. Such an evaluation would probably have little meaning in terms of bonding strength in the web. Such an investigation is strongly advocated rather from the point of view of determining the validity or fallacy of the assumption that failure on stressing occurs at the bond between fibres. During the pulping and bleaching processes, later in beating, the fibres are exposed to strong damaging influences, both mechanical and chemical. As pointed out above, much of this damage will result in fracture lines in the direction of the fibre axis, that is, essentially parallel to the line of bonding. Stress between two bonded fibres in the web will be intermediate between a shearing force and a tensile component normal to the fibre axis. It appears quite conceivable that failure may occur within a fibre at an appreciable distance from the molecules involved in the bond, rather than within the zone involved in the bond. Certainly this is quite common experience in systems of highly crystalline synthetic resins and, indeed, generally this location of failure is looked upon as a criterion for a well-formed bond.

In this connection, another closely related type of possible failure through stress must be emphasised. A great deal has been written concerning fibrillation arising through beating and, indeed, many workers in this field have stressed an assumed value of fibrillation in playing a major role in strength development. The assumption has been to the effect that the production of so-called fibres must lead to greater strength through the creation of new opportunities for bonding. Methods have been laboriously worked out to measure the extent of such fibrillation in the hope that the values obtained might be related to strength of the web. Unfortunately, all too little consideration has been given to the obvious fact that any relatively high crystalline system must be relatively brittle and that the breaking out of 'branches' from the fibre must be accompanied by a serious fracture line or zone at the base of such a 'branch'. Accompanying the splitting producing such 'fibrils', there must be brought about serious damage in other areas of the fibre also. It seems logical to assume therefore that this so-called 'fibrillation', far from being a key factor in promoting strength development, is rather an obvious visual indication of gross damage done to the fibre. This is not to say that bursting and tensile strengths do not increase while fibrillation is made evident; comparative examination of strength develop-

ment and photomicrographs obviously show that these strengths are enhanced during this period. Fibrillation may in fact be an evil inherent in the action of our presently available beating machines, leading eventually to the decrease in strength noted with very extensive beating. It should be emphasised in this connection that the rapid rise in strength in the early stages of beating is accomplished with no evidence of appreciable fibrillation.

Mechanism of beating

Reverting now to an hypothesis of beating, it would appear therefore that we must attempt to produce two positive results, while avoiding at the same time a third result that tends to accompany the two desirable developments. These may be listed as follows —

1. Production of the best conditions for maximum interweaving and entanglement of fibres in the web.
2. Production of the best conditions for interfibre bonding.
3. Avoidance to the maximum extent possible of gross damage to the fibre.

It is to be noted that these three aims are indeed very closely interrelated, but, for the purpose of this discussion, some separation of exposition might be excused.

Interweaving of fibres

The pulp fibre is relatively highly crystalline and, as such, is stiff and springy. Such fibres on deposition from dilute suspension on a wire mesh, will tend toward a brush-heap type of mat, with a high sedimentation volume and a minimum number of contacts among fibres. On passage through the press section, the intimacy of association among the fibres will not increase greatly in view of the elasticity of the structure in the thickness dimension. Because of the high sedimentation volume and accompanying high void space on water removal, shrinkage of the fibres will play only a minor role in assisting toward a drawing together of the fibres for bonding purposes. The degree of entanglement will be low and the frictional resistance to pulling out of fibres on stressing will be correspondingly low.

It would appear that one of the important aims of beating must be towards effecting an improved positioning of the fibres in the web for entanglement with consequent improved opportunities for bonding and increased frictional resistance to fibre displacement and consequent failure on stressing. In order to accomplish this, a further degree of plasticity must be afforded to the fibres. This can be carried out only through the introduction of more plasticiser — that is, water — into the fibre structure. Our

present general picture is that of a matrix of a highly organised crystalline cellulose structure interspersed with areas of faults occasioned by the presence of either non-crystallisable molecules (such as branched-chain structures) or molecules of comparatively low weight that are readily hydrated by water to an appreciable degree of swelling. These areas of lesser degree of orientation permeate the structure and lend to the unbeaten fibre the degree of toughness it possesses. In order to provide more plasticity, the entrance of more water must be facilitated and it would appear that this can be accomplished only by effecting localised fractures in the crystalline areas. The adsorption of water allowed in this way brings about a considerable increase in freedom of motion of neighbouring areas relative to one another, so that the modulus in flexure of the whole fibre is reduced and plasticity over short lengths in the direction of the fibre axis is greatly enhanced. The fibre thus undergoes a limited swelling. The primary stage in the swelling of linear polymers is adsorption of the liquid concerned, followed by imbibition of further quantities of the liquid. The total swelling may be very large when the mobility of the molecular chains permits of the immobilisation of large quantities of liquid. Some polymers show restricted swelling where residual points of bonding maintain a structure; in other cases, unrestricted swelling leads to complete dissolution. The cellulose fibre shows restricted swelling in view of the tightly bound crystalline areas. It is of particular interest to note that the effect of beating increases markedly with decrease of temperature. Adsorption is thermodynamically negative and it would be expected that further adsorption of water within the fibre would be enhanced at a lower temperature. It is altogether likely that further immobilisation of water in swelling is thermodynamically neutral. The additional degree of swelling through beating is of particular importance from the point of view of the increase of plasticity and decrease in elasticity of the beaten fibre.

The positioning of fibres of greater plasticity in the web may be expected to be markedly different from that of highly elastic, more rigid fibres. On deposition on the wire, following the bending effects of collisions with other fibres and of convection shearing forces, the beaten fibres will have a lesser volume of sedimentation and will show a much greater involvement and entanglement with one another. The effect of the presses will be retained to a much greater extent in view of the plasticity. The effect of surface tension of the water envelopes around groups of fibres, discussed by the author in publications on wet web strength,[2, 3] will be greater in effecting a reduction in thickness of the web. Eventually, the shrinkage of the fibres in the dryer section will bring about a greater mutual effect among the fibres

in densification of the web in all dimensions. The final drawing together of polar groupings of adjacent fibre surfaces for ultimate interfibre bonding will be assisted by the greater entanglement.

It need hardly be added that there is here no intimation of any suggestion that beating alters the fibre from something resembling a steel spring to something akin to a soft plastic. It is considered rather that a modest increase in swelling and consequent modest increase in plasticity is attained and that such an increase is adequate to bring about a very important increase in degree of interweaving of the fibre with consequent reflection in increase in strength of the web.

Bonding of fibres

A great deal has been written on the subject of the mechanism of bonding between pulp fibres with rather insufficient reference to well-established general principles of adhesive action.

Excluding purely mechanical types of adhesion, such as that obtained in the hardening of an adhesive in surface spaces having re-entrant angles, adhesion is obtained through physico-chemical linkages. Both substrate and adhesive must possess chemical groupings of a reasonable degree of polarity in order to provide for sufficient attractive force at each point of adhesion. In addition, there must obviously be a multiplicity of such groupings for reinforcement in number, therefore the molecular weight must be relatively high. Alignment of the molecules is important in order to bring the multiplicity of individually weak linkages into play. If the adhesive is not used in the molten form, a medium must be provided in which the molecules of the adhesive are highly dispersed. An adhesive will therefore be a material of high molecular weight, with available polar groupings (such as, OH, NH_2, etc.) largely amorphous in character and dispersible in a suitable solvent. Starch and a variety of carbohydrate gums in water are typical examples of adhesives.

The mere presence of a large number of suitable polar groupings on adjacent fixed surfaces is insufficient, since no mechanism is available for bringing such groupings sufficiently close for interaction. Freedom of motion through a suitable swelling medium is necessary and the physico-chemical bond is subsequently obtained on removal of the liquid. The variety of carbohydrates, at present rather ill-defined, that we generally denote under the inclusive term hemicelluloses are typical adhesives. They are soluble in alkali, but are capable of swelling in water. Swelling is a phenomenon peculiar to high molecular weight materials in a lyophilic solvent and

denotes, as pointed out above, a partial solution of the molecules with adsorption and imbibition of the swelling liquid.

Pulp fibres may be regarded therefore as possessing 'built-in' adhesives of a type suitable for the production of the desired bonding. Since bonding is obviously a surface phenomenon, however, it is necessary to obtain sufficient of this adhesive material at the surface in the swollen condition. A major function of beating would therefore appear to lie in the preparation of the surface of the fibre for bonding.

From analogies with other relatively highly crystalline systems, it is unlikely that conditions as laid down above for the status of an adhesive would obtain to any marked degree with any fibre that had undergone no damage in extraction and processing. In ordinary unbeaten pulp, however, it appears likely that sufficient disruption of the crystalline organisation at the surface has already occurred to allow some measure of bonding to take place. This hypothesis is strengthened by results obtained by the author in a study of the development of wet web strength.[3] In this work, considerable evidence was produced tending strongly to the conclusion that an appreciable inter-fibre adhesion exists at a very early stage in papermaking, that is, with a water content of 75 per cent. or more in the system. This is not to be confused with the final bonding that occurs at a late stage of drying, but the underlying mechanism is considered to be the same.

No change in surface properties or structure occurs during partial removal of water, therefore a surface condition that obtains for the final bonding will also be present at any dilution as a property of the fibre. If we accept the theory of bonding through hydrogen linkages arising through combination of groupings that possess a degree of mobility — and this theory has now met with general agreement — then it is apparent that the surface of the pulp fibre must possess a degree of tackiness. Normally, we speak of tackiness only with reference to a surface that has been moistened with a suitable liquid, but there appears no good reason why the phenomenon of tackiness should not be operative on surfaces immersed in such a liquid, so long as the mobile groupings involved remain at the fibre surface and are not dissolved away into the body of the liquid. The property of tack is general to adhesives and is a forerunner of the eventual firm bond that is developed on evaporation or polymerisation or other mechanism of hardening of the adhesive.

Tackiness is inconceivable on a surface composed of molecules locked into a strongly crystalline system. If the exterior surface of a pulp fibre were composed of molecules in a fully crystalline state, bonding between fibres

would be impossible. Unfortunately, it would be extraordinarily difficult to make available pulp fibres with any semblance of guarantee that the fibre surfaces remained undamaged during manufacture. Ordinary unbeaten fibres do show an ability to bond and it would appear that there is in such fibres a certain amount of hydroxyl groupings in the mobile, non-organised or tacky condition to produce bonding.

The role played by beating in furthering this ability must still remain speculative, pending further work. The effect of beating in flexibilising of the fibre has already been dealt with and it is conceivable that this might be the sole effect of beating, in that bonding ability is already available and that it is a case merely of further areas of contact being required for greater total bonding. It seems logical, nevertheless, to assume that further mechanical disruption of the crystalline system at the surface through beating should make available a greater amount of the built-in adhesive for firmer or more extensive bonding.

On this basis, we would conclude that a preparation of the surface is another aim of the beating process in addition to a flexibilising action. This preparation might take the form of an actual removal of an exterior non-tacky layer or merely a disorganisation to bring into play an extra amount of swellable adhesive material.

Structure of the fibre

A great deal of investigation has been devoted in recent years to a study of the intimate structure of the pulp fibre, particularly with regard to evidence concerning the alignment of molecules in various zones of the cross-section of the fibre. Mention has been made also of a series of structures and sub-structures as pre-existing entities in the natural fibre. In view of the fact that important stresses, both chemical and physical, had already been applied to these fibres during their production and preparation for examination, some degree of caution must be exercised in the interpretation of what is seen. It is apparent that the danger of artefacts is very great. Whether fibrils, sub-fibrils, etc. actually exist in the natural fibre or whether we should consider the fibre as homogeneous — that is, from the point of view of individual cellulose molecules — is probably of no great importance in so far as a beating mechanism is concerned. The direction of alignment of the molecules and the distribution of hemicelluloses, however, are very important considerations. A great deal of evidence exists showing a relatively transverse orientation in the outer portion of the fibre compared with a longitudinal orientation in the majority of the fibre structure. Exaggerated

swelling of the fibre, as in phosphoric acid, has been shown to produce a very striking imbibition of fluid by the main body of the fibre, constrained by portions of the exterior transversely aligned layers. The latter undergo rupture and shifting as a result of the swelling.

There has been some speculation that we need to remove a large portion of the 'primary wall' in order to assist in bonding. If indeed the outer layers of molecules on the fibre are virtually completely crystalline, say, through the lack of swellable hemicelluloses, this would appear to be reasonable. The assumption would have to be made also that a partial removal has already occurred in pulping, etc. in order to explain the bonding ability of unbeaten fibres. If, on the other hand, the so-called primary wall is distinguished only by different molecular alignment, then the production of more surface tackiness, without wholesale removal of this zone, would be sufficient as discussed above. It has been shown that unduly large swelling of the main portion of the fibre is undesirable, since the strength of the web eventually produced is drastically decreased by a loss of integrity of the main body of the fibre.

Flocculation

It is well known that beating brings about an increase in flocculation of pulp fibres. Flocculation of fibres on the wire results primarily in a disturbance of evenness of distribution (formation), but has attendant results also on a wide variety of physical properties and fitness for use in many applications.

Considerable investigation has been devoted to studies of flocculation, largely from the point of view of bracketing the effects of common variables and chemicals such as consistency, temperature, effect of beating, pH, alum, etc. Some notable effects in reducing flocculation can be obtained with certain carbohydrate gums.

With regard to mechanism, most of the studies have generally accepted a hypothesis of dispersion stability through an electrokinetic charge on the surface of the fibres. The effects of chemical additions have been explained on the basis of reduction or reinforcement or reversal of this charge. In addition, it has been generally accepted that flocculation has a mechanical aspect through entanglement of fibres in the suspension.

It is desired particularly for our present purpose to draw attention to the probability of interfibre adhesion as a logical basic mechanism for flocculation, superimposed on the purely mechanical effect of entanglement. It has been noted above that a surface tackiness must be present for bonding and

that evidence is available for interfibre adhesion at consistencies in the range of 25 per cent. or even less. It is considered that this tackiness, as a property of the fibre, will make itself evident in very dilute suspensions, when the interfibre adhesion will bring about flocculation. Such chemicals as alum will have a very distinct effect on free hydroxyl groups with consequent changes in interfibre adhesion. Highly hydrophilic dispersing agents very probably form a hydrated lubricating layer on the fibre surface, which would be expected to block interfibre adhesion. Highly purified dissolving pulps, with virtually no interfibre adhesion (and very low dry sheet strength), show comparatively much less tendency to flocculate. The effect of beating is to increase flocculation. Part of this may be due to increased mechanical entanglement with more flexible fibres, part to the increased interfibre adhesion brought about by beating.

Tearing strength

Beating produces a decrease in tearing strength, at least after a certain minimum of bonding has occurred. This lowering of tear is generally explained partly on the basis of a general shortening of fibres by cutting action and partly on the basis of a restriction or concentration of the tearing stress over a small area of the paper with increased bonding.

The latter concept undoubtedly has merit and analogies are available from the low tear of regenerated cellulose film and the greatly lowered tearing strength in a woven fabric after heavy sizing with starch. One additional possibility, however, is worthy of note in a discussion of the effect of beating on tear. Omitting from consideration the decrease in average fibre length, the flexibilising of the fibre frequently referred to above might be expected to produce some degree of non-linearity in positioning of the fibre. In other words, some of the fibre segments between points of bonding should be looped and kinked and generally be longer than the actual distance between the bonds. Such a positioning as a result of beating should aid materially in diffusing stresses and thus increase tearing strength.

If it were possible to attain the direct aims of flexibilising the fibre and preparing the fibre surface for bonding, without gross damage to the fibre in the form of cutting or transverse cracking, then it is possible to conceive of much less degradation of tearing strength with burst and tensile development during beating.

REFERENCES
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2. Lyne, L. M., and Gallay, W., *Pulp & Paper Mag. Can.*, 1954, **55** (11), 135
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Transcription of Discussion

DISCUSSION

MR. G. HUNGER: Dr. Gallay, you said you had displaced the water in the sheets by different solutions — how did you prepare the sheet?

DR. W. GALLAY: The sheets were prepared from the pulp stock in normal fashion up to the couching stage. They were then removed from the blotters and immersed in alcohol, drained, immersed in ether and dried in a vacuum desiccator over calcium chloride.

MR. HUNGER: A sheet formed in water will have thin layers of water at its contact regions, where one fibre touches the other. This water is kept there by hydrogen bond forces and I doubt whether it might be possible to extract this water by the different organic solvents applied. It may be very interesting to have a sheet prepared by putting a wet pulp into the different solvents — that is, to have the pulp standing for one night in the first solution, this being removed the next day, then suspending the pulp in the next solution and so on, lastly, forming a sheet from the fibre suspension in the last organic solvent. I wonder if you would still get the high strength that you found then. A pulp totally surrounded by the organic solvent would not have such a high strength, I think.

DR. GALLAY: We considered the method you have proposed, but felt that there were objections that would detract from the general principle. Notably, a radical change might be expected in the mode of deposition of the fibres from suspension in the organic liquid. We therefore consider it preferable to use water as the medium of deposition. It is considered from our data that little difference exists between beaten and unbeaten sheets in so far as thoroughness of water removal is concerned. It should be remembered that a very small residual amount of water is always associated with cellulose and removal of this residue is virtually impossible without radical decomposition of the cellulose.

MR. L. G. COTTRALL: I found Dr. Gallay's paper very stimulating, indeed. He has given us some new ideas, coming as he does from the plastics industry fairly recently. Whether they are right or wrong, these ideas make us think on new lines.

When he carried out his test of removing water by solvents, did Dr. Gallay try pulp that had been beaten in a ball mill a very short time? Some years ago, there was much controversy over how we got such a very large

increase in strength in a Lampén ball mill by beating for only 2 – 3 min. and various people had different ideas. I think it was the start of the idea of internal fibrillation as distinct from external fibrillation, when the surface of the fibre or the body of the fibre itself is damaged (*Proc. Tech. Sect. P.M.A.*, 1932, **13** (1), 15), although I believe the term was originally due to W. B. Campbell. Really, I do not know whether we have at the present moment a satisfactory explanation of that very great increase in both tensile and bursting strengths with a very slight reduction in tearing strength. In the case of sulphate pulps, the tearing strength is in fact increased over this small range of beating.

Has Dr. Gallay tried testing sheets in that way and has he found that there is still that same great increase in strength when these sheets have been treated with alcohol in the ordinary way or that there is a great reduction in strength through that process?

DR. GALLAY: The direct answer to Mr. Cottrall's question is that we have been thus far using only the Valley beater in this work for strength development.

Certainly we must examine closely any unusual results obtained with specialised beating methods, since these must add to our knowledge of the potential resident in the fibres, if they are treated in better fashion. The sort of result Mr. Cottrall mentioned can be obtained by beating in a rubber-lined ball mill with rubber-covered balls. Clean-looking fibres with high bursting and tensile strengths and well-preserved tearing strength can be obtained.

It would be most interesting to examine such pulps from the point of view of separation of fibre friction and bonding.

MR. G. VAN NEDERVEEN: I think the question put forward by Dr. Gallay is one we also know in Holland. We met the problem how to beat fibres without decreasing the tearing strength too much. For beating experiments in the laboratory, we use the Lampén mill and an apparatus that is nothing but a kitchen mixer (we call it a Vimix), turning at 12 000 r.p.m. The tearing strength of laboratory sheets made from Lampén mill beatings is definitely lower than that from Vimix beatings. The breaking length is somewhat higher with the Lampén mill than with the Vimix for high freeness; but, at the end, the Vimix breaking lengths come up to the same level as those with the Lampén mill. I mean, the Vimix does really beat the fibres and is not only a disintegrator.

When you examine under the microscope fibres beaten in the Vimix, you will see that this mixer does not cut the fibres very much: the fibres are

not shortened by this beater. With cuprammonium solution one finds balloons in a few places on the fibre wall. This means that there is indeed some kind of external fibrillation proceeding in the Vimix.

With this apparatus, therefore, we succeeded in getting high tearing strength, the fibres being beaten but little damaged.

DR. GALLAY: I am very grateful for this additional contribution; it is typical of what I have noted and what may be expected if the integrity of the fibre is preserved.

As you will have gathered from what I said this morning, I dislike gross fibrillation as a component of the beating process. I wish to make my position on this matter quite clear. If the objective is to manufacture greaseproof or glassine or, in general, if permeability to gases and liquids is an objective, then undoubtedly extensive fibrillation is difficult to avoid or may indeed be necessary. If we restrict our objective to strength factors and associated properties, however, then I would wish to reduce this gross fibrillation to a minimum.

MR. P. E. WRIST: There is one particular aspect of fibre preparation that has not been mentioned so far and should not be forgotten. In practice, we are not dealing with fibres of uniform dimensions. When we form a sheet, we assemble fibres of differing shapes and sizes. The fibre length distribution influences the way in which fibres will pack together. We may get greater strength in a sheet, not by developing bonds, not by increasing the flexibility, but by adjusting the fibre length distribution in such a way that the fibres can form together better. I think this is what the papermaker is primarily trying to do with his machine Jordan. Unfortunately, he can only cut the fibre this way and that not selectively, thus he obtains the improved formation and the resulting increases of bursting and tensile strengths at the sacrifice of average fibre length and corresponding tearing strength.

Mr. Chairman, on Wednesday, you said that ten years ago there was much more beating done than today. I think this is probably due to the increasing blending of pulps, whereby some of the results of beating can be achieved without its use. I believe we should not overlook in our discussions the importance of optimum fibre distribution for optimum fibre packing.

MR. G. F. GLOVER: In the first few minutes of beating, even with quite a low roll pressure, there is a very rapid increase in strength properties. I think that agrees with the idea of internal fibrillation, but the main point is that the fibre is made more flexible in those first few minutes (even seconds) and the

surface tension forces cause the fibres to bed down much more securely in the sheet, giving far more possibility of bonding. There is an increase in sheet density almost immediately in the first few minutes of beating.
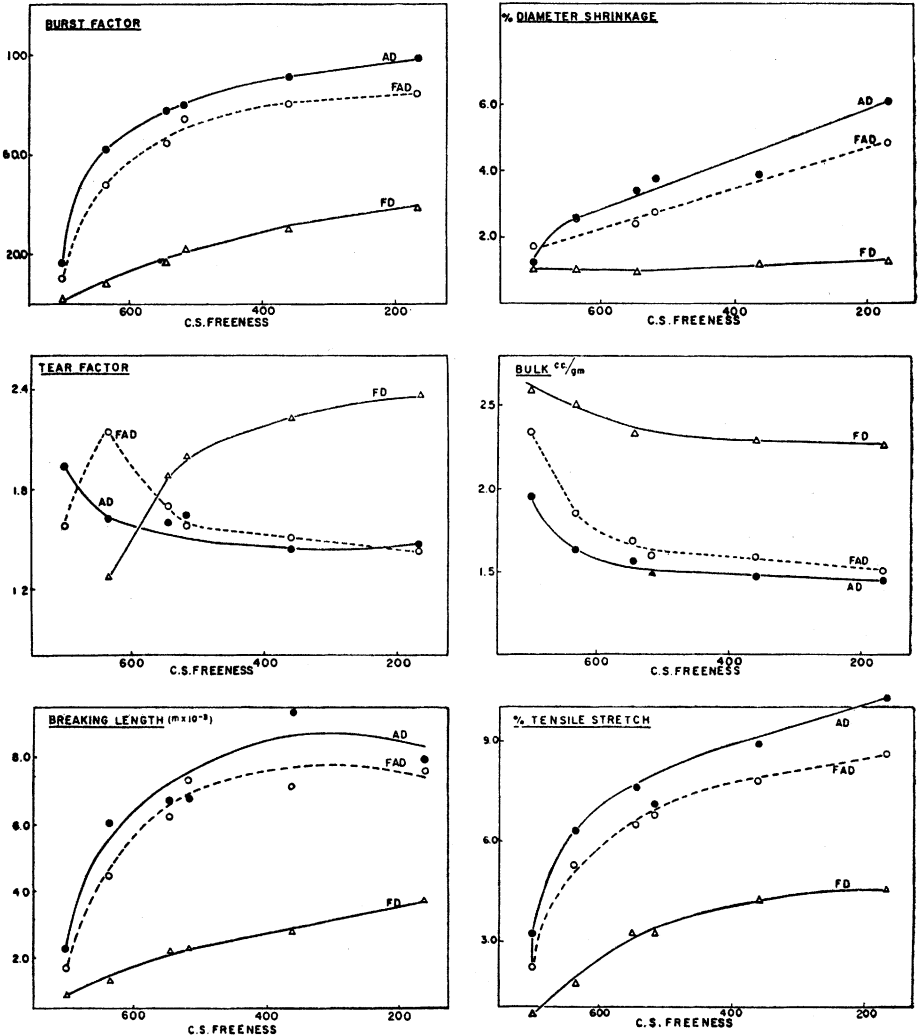

Fig. T — Variation of physical properties of freeze-dried (FD) and air-dried (AD) standard handsheets on beating — FAD designates a control series in which the wet pulp was frozen and then allowed to thaw before preparing air-dried handsheets

(From Marchessault, Lodge and Mason, *Svensk Papperstidn.*, 1956, **59**, 859)

DR. S. G. MASON: In his spoken remarks, Dr. Gallay speculated on the possibility of beating without sacrificing the tearing strength. It may be of interest to know that we were able to accomplish this by beating in the normal way in the Valley laboratory beater, forming standard handsheets and then freezing the wet sheets and evacuating them so as to remove the water by sublimation. This effectively eliminates the surface tension forces normally present when drying from liquid water. The results are illustrated in Fig. T.

It should be emphasised that by freeze-drying we have not completely eliminated interfibre bonding — that is, the freeze-dried sheets are not held together by frictional forces and fibre entanglement alone. In these experiments, sublimation was carried out at about $-10°c$; however, once we get below a certain moisture content, which depends upon the water sorption isotherm, the 'freezing point' of the water associated with the cellulose is less than $-10°c$. Thereafter, we may consider that the water is removed from a solution of 'liquid water' in cellulose; thus, the last stages of freeze-drying are basically no different from those in evaporation drying.

DR. GALLAY: I fully agree with the statement made by Mr. Wrist on fibre distribution. It would certainly appear logical that some filling of voids with fibres of suitable length should enhance entanglement.

I am reminded of the excellent work carried out by Prof. Brecht on the wet strength of mechanical pulp, from which he concluded that the highest possible wet density was required for maximum tensile strength.

I agree also with the remark by Mr. Glover and I interpret that by concluding that there simply has not been time for appreciable damage to occur during the first portion of the beating curve.

With regard to Dr. Mason's remarks, we have not made a study of the freeze-drying method. I am rather surprised at the relatively small loss in tensile strength shown, but hesitate to comment further in a field that is unfamiliar to me.

MR. G. F. UNDERHAY: I have two points. One is that I thought Dr. Gallay's unbeaten strength figures with which he compared the strengths of his pulp after the alcohol washing were very low indeed. It seemed to me that for that reason the ratio was rather higher than it should have been.

The other point was that I heartily endorse and agree with what Dr. Gallay said about the incidental properties that arise when you are beating pulps. Once again, does it not underline the fact that wetness development is not only an incidental property that you may not want, but that, if you do want it, it is very badly measured by the Schopper-Riegler instrument?

DR. GALLAY: The last part of Mr. Underhay's remarks I agree with heartily, but his first point requires clarification. The pulp used was a normal sulphite pulp of average strength. Due regard must be paid to the fact that these sheets were air-dried and not pressed after couching. The published paper will deal with this further.

THE CHAIRMAN: I think we must end the discussion on Dr. Gallay's paper; time is up. Mr. Cottrall, you wish to say something?

MR. COTTRALL: Dr. Gallay is assuming that filling in the spaces in the paper with little bits and pieces increases the strength of the paper. We heard, the other day, that fines in paper add nothing to the strength of the paper.

THE CHAIRMAN: Summing up this discussion, it shows that there is much more to it than is apparent. Personally, I think the important points that have been brought out by Dr. Gallay's paper can be stated in the following way.

In the last few years, we have had a deluge of hydrogen bonds over the paper industry; everything in paper is suddenly hydrogen bonds. This is probably due to the fact that so few people in the paper industry and in research really know what a hydrogen bridge is. There are many types of hydrogen bonds. We certainly know that the hydrogen bridge can be quantitatively calculated only in very few extremely simple circumstances. It is a nice concept, however, because it is easy to understand and to apply qualitatively. Thus, everybody jumps to it.

MR. HUNGER: I am afraid we have now built up a Tower of Babel in the nomenclature of the cell walls. According to the classic terminology of Kerr and Bailey, we have a primary wall and secondary walls nos. 1, 2 and 3. Bucher has reintroduced the term tertiary wall and Meier has introduced that of a transitional lamella. Today, it seems that the primary wall Prof. Giertz spoke of corresponds to the outer secondary wall referred to by Mr. Emerton. I strongly support Mr. Emerton's proposal published some time ago that, until there is definite proof to the contrary, we should use the terms of Kerr and Bailey only.

MR. VAN NEDERVEEN: I want to thank Prof. Giertz for this lecture, because I found most of our own experiences embodied in the ideas he put forward.

My interest, too, was aroused by J. d'A. Clark's article in the book by Ott, *Cellulose and its derivatives*.

At the Fibre Research Institute in Delft, our observations indicate that the values obtained with the Schopper-Riegler instrument are composite values, in which the influence of more than one property of the pulp suspension is hidden.

Swelling, fibrillation and shortening of the fibres are three phenomena that contribute to the beating degree found with this apparatus. We therefore use the Jayme swelling measurement and that of fibre length distribution with the HS apparatus. An impression of the fibrillation is obtained by determination of the specific surface of the fibres with the Robertson and Mason apparatus. In this way, the three factors that each contribute in their own way to the ultimate value of the beating degree are measured separately.

Our investigations on beating have been carried out with various laboratory instruments — a Lampén mill, a Jokro mill, a Valley beater and a modified Turmix (kitchen mixer). Applying these methods and also checking the effects of beating with the phase contrast microscope, we found the largest divergency in beating effect between the Lampén mill and the Turmix. We think it useful always to use these two instruments in studying the beating behaviour of an unknown pulp, just because of the very different effects they have.

For mill control, the determination of swelling, the fractionation with a classifier and the measurement of specific surface would take too much time. Now Ivanov (Leningrad) and Imset (Oslo) have developed rather simple instruments for getting a quick impression of the fibre shortening and the swelling separately but in one operation. We think both of these instruments would be very valuable tools in mill practice.

Has Prof. Giertz had any experience with these two instruments?

PROF. H. W. GIERTZ: I can very rapidly answer the question about the different apparatus. I do not know about the Ivanov apparatus, but I am fairly familiar with the Imset one, which measures the shortening of the fibres and at the same time the swelling degree of the long fibres. I say swelling, but, as the method is based on centrifugal forces, it is more or less the same kind of retained water that is measured with Jayme's method. As I know that only a small part of such retained water has to do with swelling and that the main part more accurately ought to be called entrapped water (held by the fibre in the lumen and other pockets), I do not think it is a suitable instrument for laboratory work. Whether it is a good apparatus in the papermill, I do not know.

MR. COTTRALL: I would really like to know something about this swelling. In his paper, Prof. Giertz makes a reference to me in relation to the considerable importance I attach to swelling. I certainly do, so far as the unbeaten part is concerned, but I am not quite clear how to get information on the amount of swelling when the fibre is beaten. Let us take a dry fibre: put into water, it swells considerably. I think you will all agree with that. Then you beat this fibre, either by internal fibrillation by breaking the bonds between some of the cellulose fibrils or by external fibrillation by taking pieces off the surface or by splitting the fibre or by all three methods. My point is, if you add the volumes of all these pieces together, is the sum of these very much greater than the volume of the soaked, unbeaten fibre — or are you, when you are considering swelling, taking the external boundary of the fibre, including all the voids derived from the internal and external fibrillation of the fibre? Assuming the length of the fibre is unaltered, is the volume of the fibre (obtained by multiplying the length by the average cross-section comprised of the sum of the body of the fibre plus the sum of the areas of all the external fibrils) any different or very much greater than the volume of the soaked, unbeaten fibre (*cf.* Kress, O. and Bialkowsky, H., *Paper Trade J.*, 1931, **93** (20), 42)? It is indicated in Prof. Giertz' paper and in other papers that the volume is very much greater and I should like the point to be clarified.

Another point in connection with the effect of hemicelluloses referred to in Prof. Giertz' paper, is what would happen in the case of a fibre that contains no hemicellulose, such as a rag fibre?

I am not suggesting that external fibrillation is an advantage for most papers, but most swelling measurements have been made when the fibre is appreciably beaten and there is considerable external fibrillation. It is when there is appreciable external fibrillation that we get the high figures recorded for so-called swelling. I do not regard these as representing measurements of true swelling.

PROF. GIERTZ: But you get this fibrillation at such a very late stage of beating that it cannot play any role for ordinary papers. If you make a bond paper or a greaseproof paper, however, it may play quite an important part. I have explained this in my paper.

MR. H. W. EMERTON: In his paper, Giertz says, "the fibre splits in the longitudinal direction and forms fibrils." I should like to underline a fact that I have repeatedly emphasised, that, to a much greater extent than is realised, external fibrillation is not in the form of longitudinal strings, but is in the form of sheets or membranes.

The bulk of the cellulose in mature fibres is in the middle secondary wall in the form of co-axial layers of microfibrils, the tangential surfaces of which are encrusted with hemicelluloses. Such lignin as is present in the cell wall occurs between these co-axial polysaccharide layers. Thus, the removal of lignin by cooking predisposes the structure, when mechanically treated, to disintegrate into thin membranes. It is, to a large extent, the effect of surface tension drawing these together, also folds and turned up edges, that lead to the impression that long, thin fibrils are seen.

THE CHAIRMAN: On Mr. Emerton's paper, I must say that in transmission electron micrograph experiments carried out in Stockholm by Dr. S. Asunmaa on bonding in paper — studied by the serial cutting of pieces of paper to about 100 Å thickness — you can see that quite large bonding areas occur. You can also, because of the osmium penetration, easily identify the S1 layer. Consequently, it is frequently possible to identify the part of the cell wall in such fibre-to-fibre contact areas. We only consider electron-optical contact areas. Whether such contacts mean bonding or not is uncertain, but the fibres frequently appear welded together even in high resolution micrographs. The probability that we are here dealing with bonds is much higher of course than in the experiments of Nordman discussed yesterday. Such welds are found between all the layers. We have observed such areas between S1 and S1 layers; we have them between S1 and S2 layers; we have them between S2 and S2 layers. We also frequently observe a collapsed lumen when it is impossible, even at high resolution, to observe anything but an electron-optical contact.

Consequently, I think it is an oversimplification to say that we want to take away S1 in beating to have the benefit of S2 bonding. I think there is no evidence that bonding is better between S2 and S2 layers. I think that all types of bonding occur between all the variables and, after all, if we still believe in the hydrogen bond, all surfaces are profuse with hydrogen bonds, so there is no reason from that point of view to assume that bonding could not occur between all layers.

Furthermore, I think Mr. Emerton does not intend to say what could be read into his paper, that you can carry out beating so nicely that you remove just the S1 layer. As a matter of fact, in micrographs of all beating products, sheaves or flakes, loose fibrils or whatever they are named are formed by splitting fibres more or less at random. Only seldom does the split occur at or near the S1/S2 boundary.

That brings me to the second point about the fibrils. All fibrils discussed in the papers are the fibrillar portions of a fibre. This is what you first see in

the microscope, because, when you focus, you will focus on the fibre, but not on the slide below it. On that slide, you would see loose fibrils, also separate entities that I will call chips (or sheaves or something like that), which are free. Many fibre microscopists never see them, especially when using Herzberg staining solution, because this agent swells these loose particles so that they are practically dissolved.

By pouring pulp into a shallow trough with a bottom made of teflon foil and allowing the water to evaporate at 60°c, examination under the light microscope shows a great quantity of fine material, woolly and hairy — just like the hairs in a horse's tail — all over the picture. This material was lost in the whitewater in the process of making a sheet of paper from the pulp.

I think that Mr. Emerton may be right. He thinks that the material coming off the fibre in the beating process is flakes — the material looks hairy to me. It may, of course, be possible that the flakes have rolled up into bundles in drying, owing to surface tension forces. Cross-sectioning of such material has, however, not forced such a concept on us.

If we take the whitewater from the sheet made on the wire and evaporate it on the teflon foil, we see it is a mass of small particles intermixed with a few long fibres that have passed through the mesh.

The point I have tried to make is that, in beating, even at its early stages, a great mass of fibrils is torn off the fibre. Very probably there are more loose fibrils than those still adhering to the fibres. Van den Akker's paper on the forces required for tearing loose a fibril makes it understandable that the probability may be higher for the particle to be completely torn off than left partially intact, once the tearing process has begun.

If we discuss fibrillation in beating and paper properties, we cannot ignore this material.

MR. EMERTON: I think there is no real disagreement between us — just a question of emphasis — on this matter of longitudinal fibrillation. We must not accept too readily the idea of fibrillation being in the form of long, thin fibrils.

I did not mean to imply that it is desirable during beating to remove S1 in order to get bonding between S2 layers in adjacent fibres: that may or may not be so. My argument was that it may be desirable — I do not state dogmatically that it is — to remove S1 simply to enable the fibre to imbibe plenty of water and become more plastic.

THE CHAIRMAN: I think I was not the only one who thought that you stressed the point too much, so I just wanted to give you a chance to put it right.

DR. H. MEIER: I do not quite agree with Mr. Hunger that the primary wall of Prof. Giertz has become synonymous with the secondary wall of Mr. Emerton. As far as I understood it, Prof. Giertz really meant that only the primary wall is removed during beating, whereas Mr. Emerton meant that S1 is removed, too.

Probably, the only technique with which to resolve this question is that of metal shadowing used by Mr. Emerton. It is possible by this means to distinguish clearly between the crossed fibrillar structure of the primary wall and the parallel structure of S1.

DR. B. G. RÅNBY: Firstly, I should like to say that the S1 layer in the cotton fibre is called the *winding layer* and that term is used rather extensively in the U.S.A.

Secondly, I should like to fulfil an intention of two days ago and speak this afternoon about recent work on hydrogen bonds, especially in cellulose. What we know now about them gives some explanation how it is possible at all to beat a pulp containing no hemicellulose and to make such strong paper from it. I should also like to show how amorphous cellulose can react with water in the same way as hemicellulose.