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Roy P. Whitney

I'm going to tell you something about the materials used in making paper and to explain why some things happen and what can be done to alter the results. If I can accomplish this, perhaps you will have a little better understanding of the materials papermakers work with. I'll try to be as nontechnical as possible, although that may prove to be a bit difficult at times.

Natural Fibers

Paper is a sheet material made by bonding together many very small discrete elements called fibers. It seems obvious that we share a common interest in fibers, so let's talk about them for a few minutes.

We say that a material is "fibrous" if its elements are slender, threadlike, and filamentous, that is, one dimension is very much greater than the other two. Fibers may be composed of animal, vegetable, mineral, or synthetic materials. All are used in papermaking, but we are concerned particularly with vegetable fibers. They are usually called natural fibers, because they grow in nature.

Natural fibers can be classified according to the manner in which they grow, as well as their location and function in the plant or tree. One class that is particularly important is the "seed-hair" fiber. Cotton is a seed-hair fiber.

I'm sure most of you have seen cotton in bloom and have seen the beautiful bolls, made up of very long staple cotton fibers. Many fibers are attached to each seed, and the fibers can be as much as 1½ inches long. These very long fibers go almost wholly into textiles and are not used in paper except as old rags, which used to be an important papermaking material.

We still hear the term "rag content" used, and rags are still used sometimes, particularly in handmade papers. But when the staple cotton is separated from the seeds in the cotton gin, shorter fibers remain and are recovered separately. These are called "cotton linters," and they are an excellent papermaking material for specialty papers such as high grade bonds and art papers, among others. Linters fibers can be up to five or six millimeters long, or nearly one-fourth inch.

Among the stem or trunk fibers are several that are important in papermaking. One is the "bast" fiber. It is found in the inner bark of numerous shrubs and trees, and it was the first fiber used in papermaking. Flax is a familiar bast fiber and was probably the first plant fiber used in textiles (linen).

Others, used particularly in the Orient, are mulberry and mitsumata.

The trunk fibers of both softwood and hardwood trees provide the principal source of fibers for the commercial paper industry today. Depending upon the wood species, they vary greatly in length, from about one-half millimeter to five or six millimeters. Wood provides a renewable source of raw material, without which the paper industry as we know it would not exist.

Straw is also a source of fibers from which excellent papers are made, but its use in this country has diminished steadily for many years.

Unfortunately, we cannot discuss fibers to any extent without getting into cellulose chemistry, which is apt to be a bit technical. I won't say much about it, but I do think you must at least be aware of cellulose and its behavior.

Cellulose is the basis of all natural fibers. It is the fundamental building block from which fibers are formed. Cellulose is a product of photosynthesis, one of the most ancient of processes that go forward on our planet. It is the most abundant organic material on earth, with an annual growth rate estimated at one hundred billion tons per year, far exceeding the growth or production of any other material.

Chemically speaking, cellulose is a polymer of glucose, which is a common sugar. Now we all know that "poly" means "many," and a chemical polymer is a large molecule made up by bonding together many smaller molecules. So, in cellulose, we have a molecule consisting of many repeating units of glucose. The process of building up a polymer can proceed in different ways. For example, the bonding may take place in a random manner in all directions, to form a three dimensional structure.

It doesn't do that in cellulose, however, which is a straight-chain polymer. That is, each new glucose unit adds on to form a chain, which can be represented much like a long string of beads. The cellulose chain may contain anywhere from a few hundred glucose units to as many as several thousand. It is dangerous to generalize, but often the longer the chain, the more resistant is the cellulose to degradation and deterioration. Cotton, for example, is a very stable and resistant fiber, and it has a very long chain length.

Cellulose and glucose are carbohydrates, which means that they are composed of carbon, hydrogen, and oxygen, with the hydrogen and oxygen atoms always present in the same ratio as in water (H_2O). This is no accident, but results from the evolutionary process on our planet. If water were not so abundant on earth, we would not have cellulose. Cellulose occurs principally in nature as the hollow elongated biological cell found in all plant life, which we call the fiber.

Cellulose has a great affinity for water, so we say it is "hydrophilic." Cellulose molecules also have a great affinity for each other, particularly when they are wet. If two cellulose chains are brought into close proximity, they bond together very tenaciously. And this is how the fibers are built up.

Cellulose chains bond together to form sub-units called "fibrils," and these bond together to form fibers. This is all done in a very systematic way as the plant grows, and the molecules and fibrils and fibers all create a remarkably ordered system. If one dissects a cellulose fiber, he finds various layers of fibrils in the cell wall, each wound helically around the fiber. For a given plant, each set of windings is at the same angle with respect to the fiber axis.

All plant fibers are hollow. They have an empty core inside the cell wall, which is called the "lumen." In various fibers, the lumens may be large or small, and conversely, the cell walls may be thin or thick. As we shall see, the relative size of the lumen and the thickness of the cell wall is very important in papermaking.

Of course, cellulose is not the only chemical component in plants and trees. Among others, there are minerals, which provide nutrients during growth, and there are resins and gums, generally called extractives. We usually get rid of most of these before forming the fibers into paper. If we disregard them, we are left with three major constituents — cellulose, hemicelluloses, and lignin. Most chemists believe that all plants and trees contain some of each of these substances, although the proportions vary widely.

Hemicelluloses are very similar to cellulose in composition. They are straight-chain polymers of sugars other than glucose, but the chain length is usually shorter than cellulose — a few hundred repeating units rather than a few thousand. They are generally much less resistant to degradation, and to attack by chemicals or by atmospheric conditions. Hemicelluloses bond even more readily than cellulose; in fact so readily that they sometimes form sheets, which are much too dense and translucent. So, depending on what kind of paper we are making, we sometimes try to retain the hemicelluloses in the fibers and sometimes try to eliminate them.

Lignin is often called the cement that glues the fibers together in the shrub or tree and gives it the structural strength to stand straight and grow tall. Lignin is a three-dimensional polymer, it is amorphous, and it has no ordered structure. It is not fibrous. In contrast with cellulose, it doesn't love water, it hates it, just as does a petroleum product. So we call it "hydrophobic."

Unlike cellulose, lignin does not have a specific chemical composition or structure. It varies considerably among plants. So we cannot speak generically of lignin, but we should use the plural, "lignins," to indicate this. Lignins are undesirable materials in papermaking, and if we are making fine papers we try to get rid of them to the greatest extent possible.

So far, I've noted that the proportion of these three major components varies greatly among various trees and shrubs, and the following table indicates the extent of this variation. I've picked four plants which should be particularly interesting to you. It must be emphasized that these percentages are only approximate and average. Specific analyses can be found that differ appreciably.

These figures should indicate to you one reason why cotton is such a good papermaking material. It is the purest form of cellulose occurring in nature, and hence not much pulping or purification is necessary before the fibers are used. Flax and the other bast fibers are not quite as good, but nevertheless they are attractive. We can derive excellent papermaking fibers from wood, but extensive pulping and purification are necessary, and this is expensive. The great virtue of wood is its continuing availability in tremendous quantities.

Approximate Composition
(Extractive-free Basis)

	Cotton Linters	Raw Flax	Typical Softwood	Typical Hardwood
Cellulose	96%	85%	50%	50%
Hemicelluloses	3%	10%	20%	30%
Lignins	1%	5%	30%	20%

Fiber Morphology

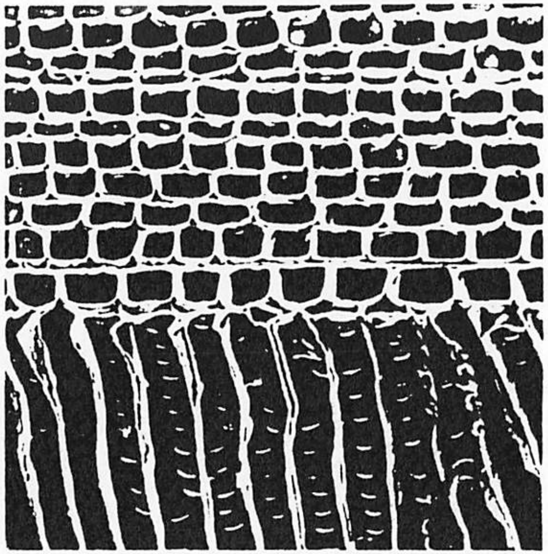
Although it is not appropriate to become deeply involved in fiber morphology, perhaps a few pictures of wood sections will illustrate some of the points I have been trying to make. *Figure 1* is a scanning electron micrograph of a section of jack pine, showing both the radial and the transverse planes. The radial plane, near the top of the picture, is cut horizontally across the tree trunk, and shows the cross sections of the vertical fibers. The transverse plane, near the bottom, is cut lengthwise of the trunk and of the fibers.

I think you will agree that this is an example of order of a very high degree. The cells are roughly square in cross section. The cell walls are very thin, and the lumens are therefore large. In other words, these fibers are mostly hollow cores.

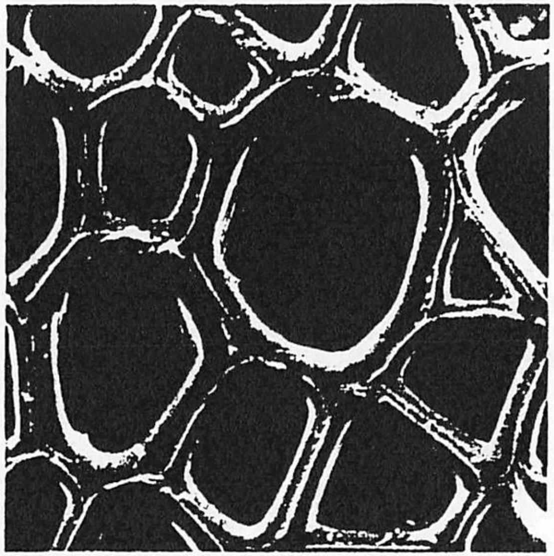
These are "springwood" or "early wood" fibers, formed in the spring of the year when the growth rate was high, and such fibers are always characterized by thin walls. In the transverse section, the pits in the fiber walls are evident. Pits are characteristic of soft wood fibers, and they form connecting horizontal passages between fibers to permit fluids to be transported up the tree through the lumens.

If these fibers are isolated and subjected to beating and violent treatment, as they are in Oriental hand beating or in a Hollander beater, it might be expected that they would collapse and look much more like ribbons than filled-out fibers. This is exactly what happens in papermaking with typical springwood fibers, particularly from softwoods.

Springwood fibers are very thin-walled as compared with thick-walled "summerwood" or "latewood" fibers. As the growing season progresses, the rate of growth slows appreciably, the fibers develop very thick walls, and correspondingly the lumens become smaller. In contrast with spring



1. Radial and transverse planes of jack pine. Scanning Electron Micrograph (SEM), magnified 160 times. (This and following micrographs are taken with permission from Papermaking Materials – An Atlas of Electron Micrographs *by R.A. Parham and Hilkka Kaustinen, The Institute of Paper Chemistry, Appleton, Wisconsin, 1974.)*



2. Fiber cross sections of aspen, a hardwood. SEM, magnified 1760 times.

wood fibers, the summerwood fibers are much sturdier, and for the most part they do not collapse on beating.

Similar sections of hardwoods show growth rings, and the same transition from springwood to summerwood. Hardwoods are more complex structurally than softwoods—they have progressed further along the evolutionary chain. They do not have pits but employ a different mechanism for transporting fluids up through the trunk. In addition to the normal trunk fibers, hardwoods have vessels, relatively large conduits that extend from the bottom to the top of the tree. As we shall see, hardwood fibers are much smaller than softwoods, and they do not collapse as readily.

We spoke a moment ago about the three major components of all trees and shrubs, but we said nothing about their location in the structure. *Figure 2* is a radial section showing fiber cross sections in aspen, which is a hardwood, at a much higher magnification. As you see, these are typical springwood fibers, with very thin walls and large lumens. Essentially, all of the cellulose and the hemicelluloses are in the cell walls. But I'd particularly like you to look at the boundaries between the walls of adjacent fibers and the rather ragged and ill-defined material located there. This is lignin, and this area is the "middle lamella." This lignin indeed serves as a cement to stick the whole structure together, but unfortunately, not all of the lignin is located here. About half of the lignin is in the middle lamella, and the other half is interspersed throughout the cell wall. I say "unfortunately" because the middle lamella lignin is relatively easy to remove in pulping. The cell-wall lignin is very difficult to remove and cannot be taken out without some degradation of the cellulose.

It has been noted that fibers vary greatly in size. Indeed, they range from five millimeter cotton linters downward through the hardwood fibers, with the maple fiber being one-half millimeter in length. It seems evident that these great differences in size should cause differences in the properties of papers, and that is indeed the case. Many grades of paper contain blends of fibers in order to take advantage of the contributions of each.

Most natural fibers are tapered at both ends. An exception is cotton, which has its greatest diameter at the end that was attached to the seed, and it tapers over its whole length to the tip.

3. Cotton linters fibers. SEM, magnified 115 times.

Pulping and Bleaching

I think it is not necessary to spend a great deal of time on the papermaking process, as it is well-illustrated elsewhere in this book. I'll try to confine myself to showing you what happens in the various processing steps.

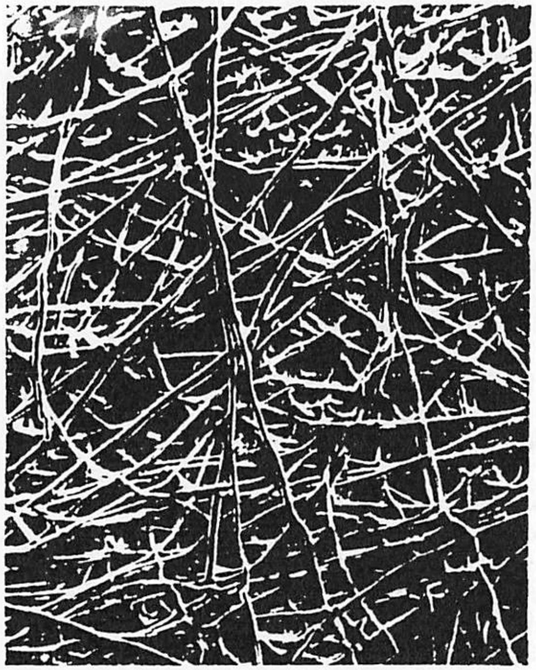
We start with a source of fibers, which might be raw cotton linters, the inner bark of the mulberry tree, or part of a tree. With all materials except cotton, we must liberate and separate the fibers, and this is one of the major objects of pulping. All fibers are pulped, either mechanically or chemically or both. I sometimes get the feeling that this is not generally realized, and that there is an impression that pulping is detrimental and to be avoided. It may be detrimental if not properly done, but it cannot be avoided.

If the pulping is solely mechanical, as in making groundwood, all of the lignin remains in the pulp, and the resulting papers are of very poor quality. They have poor strength, they yellow rapidly on aging, and they are used in products where quality and long life are not important, such as in newsprint and the groundwood printing paper used in most paperback books.

In chemical pulping, the object is not only to liberate the fibers but to purify them. Numerous chemical reagents are used, and the pulping can be mild or quite drastic. The cotton linters that you buy have had a mild alkaline pulping to remove gums, waxes, and some other noncellulosic materials. Pulp used in Japanese hand papermaking is steamed to release the inner bark from the other components, and then pulped by boiling for two hours with sodium carbonate, an alkali, to liberate the fibers. Wood, because of the high lignin content that must be removed, is subjected to more drastic chemical pulping treatments.

So, all of our fibers have undergone a pulping treatment, of greater or lesser severity, and with more or less degradation of the cellulose fibers. Properly conducted, the pulping need not seriously degrade the fibers.

Bleaching can be considered a continuation of pulping, to purify further and to whiten the fibers. Particularly with wood



Bleached mitsumata *fibers. SEM, magnified 15 times.*

leaching is effective in removing much of the lignin in
wall. Most bleaching today is conducted with chlorine
nds, and it must be done very carefully to avoid cellu-
radation. Like pulping, bleaching is a necessary opera-
t it must be conducted with care and understanding of
going on.

tton linters are shown in *Figure 3*, another scanning
micrograph. Cotton fibers are thin-walled, with large
and they collapse readily into ribbons. They also have
ncy to twist about their long axis, as some of these fibers
ne.

ure 4 shows *mitsumata*, a bast fiber, at the same mag-
n. As you see, these fibers are much more slender than
ers, and this makes them more flexible.

Beating, Sheet-Forming, and Drying

After pulping and bleaching, the next major process step is beating and refining. Beating is always necessary to make good paper. The dimensions and the surface of the cellulose fiber must be controlled to obtain the desired properties.

Two major effects of beating are cutting and fibrillation. Cutting results in shortening of the average fiber length and is necessary particularly with long fibers to obtain good sheet formation. Very long and very flexible fibers give sheets with "wild" formation. That is, the fibers agglomerate or flocculate into clumps that show up as thick places in the sheet, with thin areas surrounding them. I'm sure you have all observed the mottled appearance of some papers when viewed against a strong light. This tendency toward flocculation is controlled largely by adjusting the fiber length. Of course, cutting can be carried to the extreme of impairing the fibrous nature of the pulp and ruining its papermaking qualities.

Fibrillation involves altering the surface of the fibers by macerating, fraying, brooming, and generally causing the intricate fibrillar structure to be disrupted. This creates much more surface, which is then available for bonding in the papermaking step. Beaten fibers are much less well defined than unbeaten ones, but they bond together much better and produce stronger, smoother, and generally better paper.

Figures 5 and *6* show the same softwood fibers before and after beating. The beaten fibers are more collapsed, more transparent, and they form a more compact mat with less void space.

Most of what I have said about beating is summarized in *Figure 7*. The development of surface, the freeing of the surface fibrils, and the interfiber bonding which results are strikingly illustrated. The old papermakers were certainly right when they used to say that "paper is made in the beater."

The next major process steps are sheet forming and drying, and these have been covered in detail elsewhere in this book. You know that essentially all paper is made by a filtration process. A very dilute slurry of fibers in water is prepared and caused to flow onto or over a porous screen. The water drains through the screen, depositing the fibers as a mat. This wet mat is removed from the screen, water is pressed out, and the

5. An unbeaten kraft softwood pulp. SEM, magnified 47 times.

6. Same pulp as Figure 5, *after beating. SEM, magnified 47 times.*

7. Interfiber bonding. SEM, magnified 2250 times.

sheet is dried. The equipment used has been developed considerably over the past 18 centuries, but the basic process remains the same.

Since about 1800, two types of continuous paper machines have been in commercial use. These are the cylinder machine and the Fourdrinier. The cylinder machine consists essentially of a wire-covered cylinder rotated in a vat containing the fiber slurry. The sheet is formed on the cylinder surface, couched off, pressed, and dried. The Fourdrinier comprises an endless wire screen, with the pulp slurry flowing onto it at one end and the wet sheet couched off at the other. The pressing and drying operations are essentially the same as in the cylinder machine.

The cylinder machine has serious limitations as regards control of sheet properties and speed, and is essentially obsolete for commercial purposes. It is still used in special situations, one such being the production of art papers. The Fourdrinier is much faster and more versatile, and it dominates the commercial scene. However, it shows signs of obsolescence, too, and other forming devices are coming into use. They still, however, employ the original concept of drainage of water through a porous screen.

Chemical Additives

It would be difficult to overstate the importance of chemical additives in papermaking. It is safe to say that a large fraction of the 60 million tons of paper produced annually in the United States could not meet the varied end use requirements without the additives which impart the desired sheet properties. Paper can be made water-absorbent or water-resistant; it can be filled, dyed, coated, impregnated; it can have remarkable wet strength or almost none at all. These and many other characteristics are made possible through the use of chemical additives.

Internal sizing has long been employed to control wetting of the sheet and to permit the paper to accept ink and other aqueous fluids without undue feathering or spreading. The principal internal sizing material is rosin. The rosin is cooked with an alkali, or otherwise treated, to form a paste that is added to the furnish before the paper machine. Alum is then added, to precipitate very fine rosin particles on the fibers and render them water-resistant. However, a difficulty arises in that alum is a very acidic material, and the whole papermaking system as well as the finished paper becomes acid as a result.

This may be a good point to digress and to speak briefly about acidity and alkalinity and pH. Water ionizes into what are called hydrogen ions and hydroxyl ions. By some mathematical manipulation and by knowing the ionization constant, we can show that the sum of the logarithms of the reciprocals of these two ionic concentrations is constant at 14. The hydrogen ion concentration is a measure of acidity, and the logarithm of the reciprocal of the hydrogen ion concentration is the pH.

If this all sounds pretty complicated, just remember that pH is a measure of acidity on a scale of 0 to 14. At a pH of 7, the solution is neutral, with equal numbers of hydrogen and hydroxyl ions. As the pH moves progressively below 7, the solution becomes more and more acidic. Conversely, as the pH moves above 7, the solution becomes more alkaline. But remember also that this is a logarithmic scale, and therefore very sensitive. A solution of pH 5 has 10 times the acidity (hydrogen ions) of one at pH 6. At pH 4, the solution is 100 times more acid than at pH 6.

Most rosin-sized papers are made in the pH range of 4½ to 5½. We know now that this is much too acid for the papers to show any great degree of permanence, and they will deteriorate significantly in a few years. Papers of archival quality must be made at essentially neutral pH. In fact, they often contain alkaline materials that neutralize any acids that may form over years of storage.

Fortunately, other internal sizing agents are now available that can be used under neutral or slightly alkaline conditions. One particular agent is called Aquapel. It is a synthetic material and a good sizing agent. So, if you want your papers to last a long time, you should be careful about rosin sizing and particularly about the amount of alum you use.

Surface sizing is applied after the sheet is formed and dried, and it is therefore mostly on or near the surface. It is used to impart surface finish and to control surface properties. Quite different materials are used - materials such as glue, gelatin, casein, and starch. Most bonds and writing papers, and many art papers, are surface sized.

Filling and loading are also practiced extensively with many papers. Fillers improve the opacity and also provide further control of surface properties. Most fillers are minerals that have been very finely ground. Kaolin clay is the most common filler. Calcium carbonate (ground limestone, precipitated chalk) is also used extensively in alkaline papers. Titanium dioxide is a preferred filler, but it is also about the most expensive. Some synthetic materials are used.

Fillers always weaken the sheet. Retention of fillers is also poor, since they have no affinity for cellulose and wash out readily during the sheet forming process. A well-closed white water system is essential for good filler retention.

Coloring or dyeing is an essential part of papermaking. Practically all papers are dyed, even all white papers. In fact, white papers are just about the most difficult to match.

Most paper dyes are synthetic, organic, water-soluble materials. Some pigment dyes are used, and they behave like other fillers. There are three classes of dyes in use commercially. These are direct dyes, which have a strong affinity for cellulose and are probably used the most; basic dyes, with a strong affinity for lignified (and therefore unbleached) fibers and are used widely in groundwood papers; and acid dyes, with no affinity for cellulose. Acid dyes require a mordant to set them, and the usual mordant is rosin and alum, which we have already discussed.

Among other chemical additives are beater adhesives, such as starch, natural gums, modified celluloses, and wet-strength resins. Some of the natural gums and mucilages have remarkable abilities to control fiber flocculation and sheet formation. I've only scratched the surface of what might be said about additives, and if you are a papermaker, this is a fertile field to explore.

Paper Properties

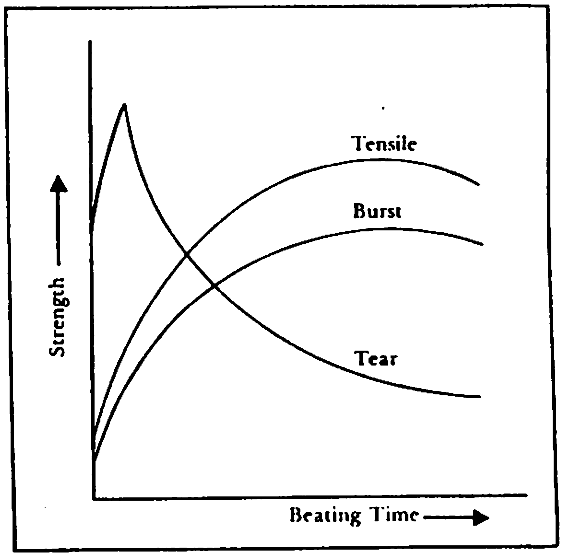
Let's wind up this rather long discourse with a few comments about paper properties. We have not yet discussed the strength properties of paper, for example. I doubt that paper strength is of major concern to you, but nevertheless, you should be aware of the effect of processing variables on strength.

In *Figure 8*, I have plotted three common strength properties against the degree of beating. As you see, the sheet tensile strength increases with beating time until a maximum is reached, after which further beating is detrimental. The bursting strength, which depends upon both tensile and stretch, shows about the same pattern as does tensile. The tearing resistance shows a quite different trend, however, and generally decreases as tensile increases. Usually, increasing tensile and burst indicates greater bonding of the fibers, and this usually decreases the ability of the sheet to withstand tearing.

Sheet density is also heavily dependent upon the degree of beating. The greater the extent of fiber bonding, the more compact and dense will be the sheet. Extremes in density might be a sheet of blotting paper, which is very lightly bonded, and a glassine sheet, which is so thoroughly bonded as to become translucent.

Some sheet properties depend upon the paper machine and the way it is operated. An example is two-sidedness. All sheets have a wire side and a felt side. The difference is quite pronounced in some instances. Also, machine-made papers show uneven fiber orientation, with quite different properties in the machine direction and the cross direction. Handmade papers should show little, if any, directionality.

Certain sheet properties also depend significantly on the moisture content, which in turn is governed by the relative humidity of the air in which the paper is stored. The moisture content of paper may be almost zero in very dry air and as much as 30% at close to 100% relative humidity. Paper also changes dimensions with moisture content, a property called hygroexpansivity. Fibers expand and contract principally in cross section rather than length. So if the sheet has a high degree of directionality, the dimensional change will be greater in the cross direction than in the machine direction.



8. Development of Sheet Strength with Beating.

Let me close by saying that I think it is wonderful that so many people have rediscovered an old art, and are enjoying it and finding it useful. However, I have a few words of advice to those involved in hand papermaking:

Please don't fail to take advantage of all that has been learned about papermaking in the last century or so. Don't focus your attention exclusively on cotton or flax or any other single fiber, but learn about the flexibility and versatility that can be achieved with blends of fibers. And please remember that you must do more than start with fine fibers. You must process them in such a way as to enhance their potential and avoid damaging them.

Dr. Roy P. Whitney, a chemical engineer, has served on the faculties of the Massachusetts Institute of Technology, the University of Maine, and The Institute of Paper Chemistry. He has published numerous papers and is currently assistant to the president of the Institute of Paper Chemistry, Appleton, Wisconsin.