CELLULOSE CHEMISTRY & BONDING IN PAPER

a Lecture Given by
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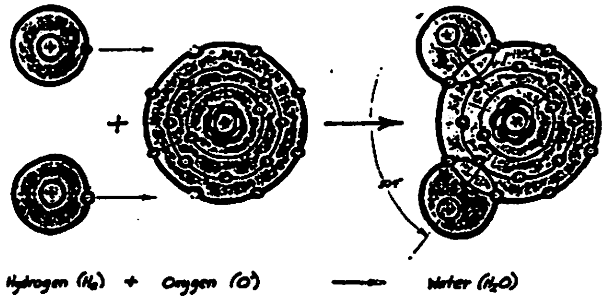
There are two important things about paper: plant fiber and water. Of the two water is by far the most crucial to its strength. Water shouldn't be what it is. It shouldn't be a liquid. I shouldn't float in it. If you look at the majority of chemicals, water is all wrong. It happens to be a bicarbonate but it isn't like one at all. Water, as you all should know, is composed of two molecules of hydrogen and one of oxygen. Oxygen has a molecular weight of sixteen and hydrogen is the lightest molecule with a molecular weight of only one. The combined weight of a molecule of water is eighteen. Carbon dioxide is, as you all know, a gas. It is composed of carbon and two hydrogens. Carbon has a molecular weight of twelve and oxygen has a molecular weight of sixteen. Thirty two and twelve is forty-four. It outweighs water two to one, yet it is a gas; and that shouldn't be possible. Anything that is naturally a liquid should have a much heavier moleculer weight than water. And you know water is a fluid. The reason is that when you form water from two hydrogens and one oxygen they don't line up correctly .

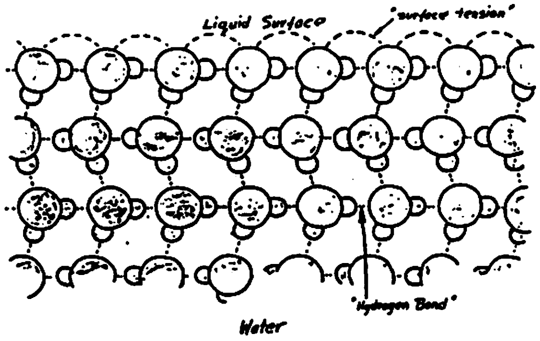
Carbon dioxide lines up with carbon and two hydrogens in a very symmetrical arrangement . But the hydrogens are so much smaller than the oxygens that they band together. So what happens is that the hydrogens join the oxygen molecules at a very fixed angle. That angle is a hundred and four degrees and it makes the molecule look like Mickey Mouse.



Formation of Water

.........So what happens is that you get an area over here of positive charge and an area over here of negative charge and it becomes what is known as a dipolar molecule. Its got two poles; it's like a magnet. And that's what makes the whole thing work. It has negative and positive areas just like a box full of magnets. And what happens is that water sticks itself together closer than it would be if it were a regular polar molecule, so, when you get a bunch of them all together it's going to look like water. All the positive areas are attracted to the negative areas and vice versa and it compacts itself. Water is a very dense liquid. Water is really quite heavy compared to most things; an awful lot of stuff floats in it.

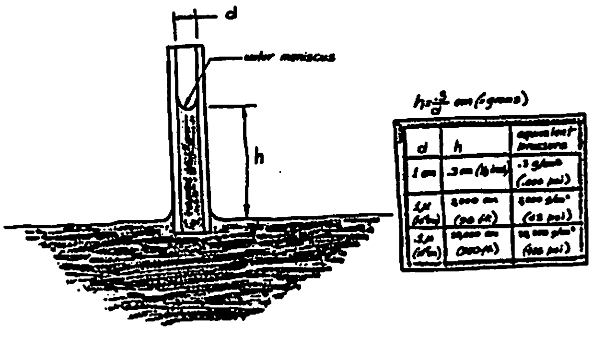
It is also because of this dipolar nature it will work it's way into stuff. It is a very good solvent. There are more things that dissolve in water than in any other solvent. So it is therefore a very powerful liquid. It is likely if some alien came here from another planet where methane was the basis he couldn't live here because oxygen and water are such virulent chemicals. It's so natural to our system that it doesn't seem that way, but compared to everything else it's really nasty, like living in a sea of acetone or something. But acetone only dissolves five or six things whereas water dissolves a whole bunch of things. Which creates problems for papermakers because every damn thing that's bad for paper will dissolve in the water; but we'll go into that later.



Hydrogen Bonding in Liquid Water

The thing is that all these forces compact the water. On the surface there are unresolved forces. That always happens in any sort of a solid or a liquid. The surface is very different from anything that happens in the middle. And this surface tension is what develops with these unresolved forces and that makes it possible for a water bug to walk on the surface of the water. It's because they're standing on the surface tension. If you put some photo flo in the water they're going to sink because that breaks the tension of the surface. Surprised a lot of bugs.

Well, there is an interesting phenomena that is really important and that is that water is attracted to glass and a lot of other things. So that when you pour a glass of water you get an meniscus around the edge. The water sticks to the side and forms a curve. Now the thing that's interesting about it is that if you have a small tube the meniscus stays about the same. The forces of the surface tension work parallel to the surface, they contract the surface, they pull on the sides. When you get a capillary small enough you find that most of the forces are pulling upwards, aren't they? Suppose two of you got a rope and you had someone hanging in the middle of it. And you hang it over a canyon or something. There you are pulling on the end of the rope. If he's up even with eye level we're both pulling horizontally; if you let him down into the canyon and we're both pulling, the forces are vertical and we can pull him up just by pulling on the rope. In the same manner, when you get a meniscus with the same shape and a small diameter too, these forces pull water up the tube. As the tubes get smaller and smaller, it becomes a very powerful force. It's what feeds every living plant.



d	h	equivalent pressure
1 cm	.3 cm (1/8 in.)	.3 g/cm² (.004 psi)
1μ ([illegible])	3000 cm (90 ft)	3000 g/cm² (43 psi)
.1μ ([illegible])	30,000 cm (900 ft)	30,000 g/cm² (400 psi)

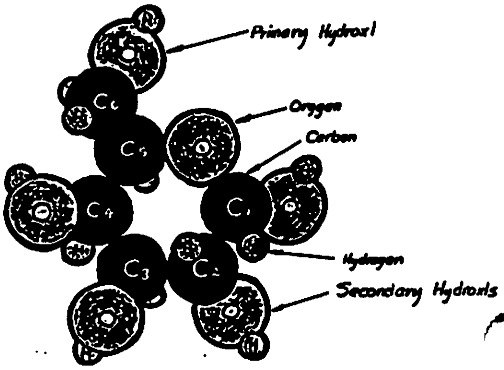
Glass Tube Dipped in Water

Surface Tension

There are trees (what's the natural height of trees, maybe three four hundred feet?) and a tree that size takes an enormous amount of water every day and it's all pumped to the top by capillary forces. The forces are really very great. In a one centimeter diameter tube it will bring the height of the water above the height of the liquid that you stick it in. Twenty three centimeters and it amounts to a force four hundredths of a pound per square inch, that much. If you bring this tube down to a micron you get 43 PSI. If you bring it down to whatever that is you get over 400 PSI, which is just incredible. You don't really get that in a plant but the potential of the pressure that could develop to move the water up into a tree is absolutely incredible.

What the plant does then is to use it's ability to make things and makes these little tubes so it can carry the water up into the plant. Now the stuff it uses to make things with is sugar. I have trouble believing that you put a seed in the ground and six months later you get an eight foot cotton plant. It's just absolutely phenomenal. The plant has changed all sorts of chemicals from the air and the ground. It does it all by little factories that come in a corn kernel. It carries all these chemicals around and builds this incredible structure in nothing flat.

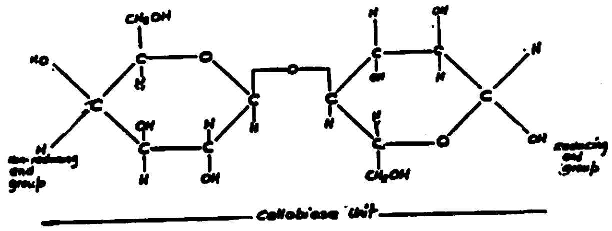
And it makes sugar. Nobody really knows how the hell it does it. Have they been able to synthesize sugar? I don't think so. But the plant does and sugar is called a carbohydrate. Now that's an old fashioned term, hydrate, actually it means a material with molecules of water are stuck to it. You take copper sulfate, it has water in it and it's blue. Heat it up and the water goes away and it's white. There are whole molecules of water stuck to it. That's really what a hydrate is so water really isn't a hydrate. In terms of the development of life they found that in any kind of an organic molecule that has oxygen in it that there's a relationship of carbon to hydrogen. Carbon, hydrogen, oxygen are always in the ratio of water. Six carbons and six waters. Six in a basic sugar molecule, sucrose. $C_6 H_{12} O_6$ or H_2O Carbon, multiply by six and that's what you get. And the plant is obviously using water and carbon to build the thing, and in a sense, as I said a while back, it is taking carbon and water and making a carbohydrate. A better term is a sacharide, but carbohydrate works. It indicates a difference between plant organic chemistry and oil organic chemistry. Oils are hydrocarbons, plants make carbohydrates. Hydrocarbons are just hydrogen and carbon, so plastics are hydrogen and carbon; there's no oxygen. Whereas things like cellulose and starch and celluloid and viscous rayon and things like that are all made with carbohydrates - there's hydrogen and oxygen and that's the whole field of organic chemistry...



Sucrose Molecule - $C_6H_{12}O_6$

This is called a six carbon sugar because there are six carbons and one of them sticks off on one side. The ring is actually five carbons and an oxygen. And the sixth carbon sticks off at one point and forms what is called a primary hydroxide which is really important . The other thing that is important is that the two ends of the molecule are pretty reactive. There's a tendency for this carbon and oxygen here to break and for this hydrogen and this hydroxyl to flip and reform again. And that makes this end very reactive; in other words, it has aldehydic properties. The sugar that happens when you flip it is a little bit different than the sugar that happens when you flip it back. When you make a solution of sugar you always have some of each.

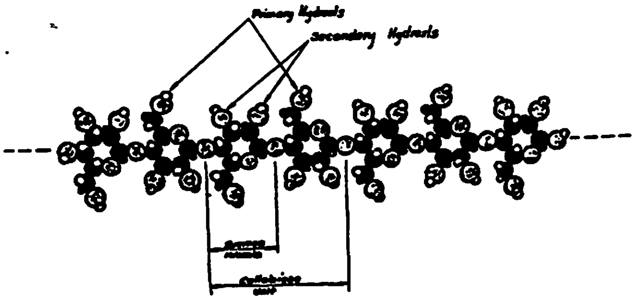
Now, what the plant does, in some unfathomable way, is stick these things together end to end. The sucrose end is reactive and so it will tend to stick them together. And it will take one type of this sugar and stick it together in a big long chain. This is called a polymer. Right, a single unit, a sugar, is a mer and when you have many mers you have a polymer. And the whole idea of polymer chemistry, which is plastics and all that, came from studying cellulose. An early plastic was celluloid which is made by modifying cellulose. Celluloid collars and all that were the precursors of the plastic universe we live in.



End to End Linking of Sucrose

The interesting thing about cellulose is that the primary hydroxyl is flipped on each molecule so it staggers it. It's like stacking up Playboy magazines...if you flip the backs each time you can make a lot higher pile than if you just stack them up one way because they tend to slip off. Well, when a plant makes starch it doesn't flip them and the starch tends to be a helix, a much shorter and much less difficult molecule to break down, so you can eat starch. You can eat cellulose all you want but it just goes through, it's fiber. You can't break it down unless you're a cow and have a symbiotic bacteria in your stomach.

What is known as the degree of polymerization is the number of mers that are stuck together. Cotton, a cotton ball, tends to have what they call a DP of 5,000 which is a really long thin molecule. Some of these cotton and linen molecules are actually plenty long enough to see without much of a microscope but they're too narrow. They're plenty long but they're way too narrow to see. What we're talking about is a real long thin molecule. Now, even in the case of wood pulp, which has a DP of maybe 2,000, it's still a very long thin skinny molecule.

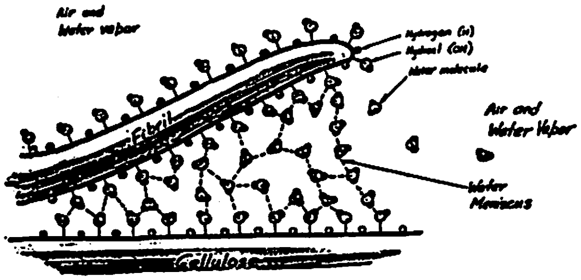


Portion of a Cellulose Molecule

This is another way of drawing the picture of a cellulose molecule. It tends to form this double sugar and that sugar gets turned into other sugar. This reducing end group on this end of the molecule, the one that's beside the oxygen, is the active one and any time that anything happens in a cellulose molecule you can bet it's going on around this end. No matter how long the molecule is, it's the end that's the reactive thing.

The other thing is that this primary hydroxyl up here is also pretty active. When a plant builds it's cell walls it works from the outside in. It makes a wall, makes another wall, and as it makes it, it layers these cellulose molecules on, one on top of the other, much like a tire. Tires are made with cloth, a layer of cloth with the grain of cloth running one way and the next one running another way and so on and so forth and they make layers and layers until it's a very strong tubular structure. A plant does the same thing. It creates a capillary. It makes it's own plumbing system by building up these layers of cellulose. Once it has formed this capillary then the liquids can move on up through the plant, up to the leaves.

Now the process of beating takes a cellulose molecule and does two things. When you thrash it the little ends get broken loose from the fibers. Fiber is a collection of fibrils and the fibril is a collection of molecules. When people talk about fiber length, this is real different from molecular length. It's one thing you have to watch out for. You have a long thin tubular structure but it's composed of all these trillions of cellulose molecules and each of those are put together into little fibrils. Some of these fibers tend to be long and narrow and they tend to fall over like this. When you beat it, you beat it into a pulp, you make a mess out of it. The ends start coming up and on the ends are these active little areas. In fact, some people say that you get a sort of partial solution. What happens is that one end is attracted to the water. It's like one end is dissolved and one end isn't. It's like having a hose in a lake. So these molecules have all these little ends.



Water Molecules between Cellulose

The other thing that happens is that within the molecule you're working water down into the structure and you're softening it. So what happens is that when you've finished beating the fiber, when you've taken it out of the beater, 90% of the fiber's weight is water. You work that much water down into the structure of the fiber. Even though it's floating in water, if you discount the fiber itself, the weight of the water inside the fiber is 90% of the weight of the fiber.

So you've got a lot of water in there and it's inside the molecule and it's in-between these ends that are sticking up and there's water all over the place. Then you make it into a sheet of paper and you start to dry it and what happens? The water molecules slowly evaporate any place you have two fibers. They're all stuck to molecules of water. You have what amounts to a meniscus and as it dries these waters are popping off into the air. It's like picking a ping pong ball out of the box; the whole thing starts to collapse in on itself. These capillary forces I talked about are no longer moving the water through the fiber because you've made a mess out of it. You've turned it into pulp and so what it does instead of pulling itself up through the fiber, is it pulls the walls together. When you get finished the fibers are much closer together than when it was cloth or when it was a tree or whatever it was beforehand. And you get an attraction between the positive and negative charged areas of the fiber; you've got more attraction than there was before you started beating.

Now back to these fibers, these long sucrose molecules, these primary hydroxyls, tend to line up with each other and you get what amounts to cross linking. Crosslinking in polymer chemistry is when a polymer and another polymer link from one to the other. This happens with these primary hydroxyls. You take an alpha cellulose fiber like cotton, or linen, or what's in the majority of wood pulp, and they'll stick together, those primary hydroxyls. You get what amounts to very much like a crystal in those areas and they call them crystalline regions.

There's a cellulose molecule and there's one and there's one and there's one and there's one and so on and so forth. The majority of the fibers will stick themselves together through these crystalline regions. The primary hydroxyls stick together. But you get areas where the ends tend to be sort of random. But because the fibers are so long they tend to line up every once in a while and you get what they call amorphous areas. You've got that active end to the cellulose in these areas. If you just laid down a bunch of sticks you'd find that you'd have areas where there are more ends than other areas and these areas are called the amorphous areas. All the action will take place there; these bonds will happen. Particularly when you make a sheet of paper and you've beaten it and you've worked the water into it and the water is squeezing everything together, you get even more crystalline areas than you had in the fiber in the first place.

You also have teased up lots of ends here and there. This creates these little ends of fiber that are these amorphous areas and so after the sheet is made and dried and the bonds are formed this is the place where pigments stick, where sizing sticks, where various thing happen. They all happen at these points. It's almost to the point that if you added an acid to the thing that's where it would break it down; that's the vulnerable part of the paper. All these amorphous areas are very active.

Anything that's chemically active is vulnerable to chemical action. You get a nice acidic environment and paper that isn't sized and get it damp and, bingo, it starts breaking it up. It's also the place where, if you put the right things on, it will prevent that sort of thing from happening. It's something that Kathy and I are continually debating; what can you do to prevent the deterioration of paper. Things like gelatin sizing and such tend to tie up these areas and they also tend to buffer the effects of acids in breaking down the fiber; so that's real good.

So what happens then, is that you take this real powerful chemical, water, work it down into the fibers; let the stuff dry, and as it dries the capillary forces pull the fibers together. It pulls them closer together than they were in their previous life. And then you've got paper. It will never go back to pulp. You've made a permanent change.

What's interesting about it is that you've made a chemical change physically, just by beating it. The bonds that hold the paper together can be broken again with water. So you can recycle it, slush it up again and recycle it. That's why you can put paper into a blender and reform it into a sheet of paper that's a pretty decent sheet of paper. But it's very different to break down fiber in the first place.

I've mainly talked about alpha cellulose, which is a very long and slender fiber. There are other celluloses, beta celluloses, which are shorter and are usually composed of slightly different sugars. You take that basic sugar molecule and you just flip some things around and you get different sugars. There's also one that doesn't have that extra sixth sugar. When the plant starts building things with those you get a much more complicated structure. These fibers also tend to be a whole lot shorter than alpha cellulose. It's pretty hard to delineate the difference between alpha and beta cellulose. Beta cellulose has a degree of polymerization of, I think, around a thousand, let's say. And there are what they call gamma celluloses which have a DP of 15 or so, 5 to 15. These are also know as hemicelluloses.

In a wood plant, or even more so in a plant like abaca or kozo, you have a certain amount of these long skinny alpha cellulose fibers. But you also have these short sugars, really short cellulose fibers. These fibers have a lot more ends because per pound of hemicellulose you have a thousand more ends than a pound of wood pulp. You talk about cotton with a DP of three thousand, which means that it's three thousand ends long. Whereas the hemicellulose has a DP of maybe 15. You have a whole lot of hemicelluloses and a whole lot of ends and a whole lot of places for things to happen. When you make paper from hemicellulose it's much easier to beat, as some of you found out today. You can beat Kozo with a stick and actually get it to bond together. You get the same things happening that you do using a beater with a very violent action and alpha cellulose fiber.

The beating of the hemicelluloses in wood pulp, and wood pulp has a lot of hemicellulose in it, is much easier than the beating of alpha cellulose because there's so many more possibilities of things to happen that you really don't have to do much. All you have to do is sneeze at it and you can make paper out of it. And so one of the things we found out talking to the paper industry is that they're used to working with wood pulp. Because of the high degree of hemicelluloses you can beat it in these very different machines and it responds very differently to beating. So you have to be careful when you talk to paper chemists to find one that actually knows about rag fibers and long fibers and abaca, etc. They would tend to say that all cellulose is the same, which is true basically. You can beat wood pulp just as well as cotton. But there are a lot of variations that happen because of these hemicelluloses and you can imagine that this is a very different part of cellulose than alpha cellulose.

Highest in alpha cellulose are cotton and linen. Cotton in nature is a very big tube and it has a thin wall. After the plant is picked and it dies, the stuff that was inside of it evaporates and it tends to collapse in a shape like that.* It looks like a fire hose that is folded up. As is does that it tends to twist so you get a softer, more supple fiber than linen, which is a smaller tube initially with a thicker wall so when it dries out it doesn't collapse. That's why linen cloth is jiggly. It's like jello. If you compare a piece of cotton and a piece of linen, the linen will sort of jiggle. It's also why it makes a different paper.

Cotton and linen are extremely similar. As I said earlier today when we were talking about relative things, cotton and linen are more alike than they are different in relation to all the other fibers. But there is a big difference between cotton and linen in the sense that linen fibers are real long and real strong and all that but they are basically a more rigid tube in the first place. Now cotton linter, which is the fluff off the cotton seed, is a shorter fiber. Kathy says it's sort of like the down feathers of a duck. If you think of the staple feathers as the long fibers, the down would be the linter, the fuzz on the inside of the duck. It has a heavier wall. As Elaine (Koretsky) was saying earlier, you can make really nice paper out of linter but you have to beat it. Linter is very strong and very resistant to beating, much like linen. So to develop it's strength and make a good sheet of paper you have to beat it very carefully. People tend to make things out of linter fiber because it's short and it comes in these sheets of linters and you can make what resembles pulp very easily, just by stirring it up in water. But to actually get a bonded sheet of paper is very difficult.

Abaca, on the other hand, is a fiber that is sort of in-between the Oriental fibers, which are real high in hemicellulose, and the Western fibers, which are real high in alpha cellulose. So you can take a sheet of abacá half stuff and slush it up with a mixer and get a reasonable sheet of paper because you have all these little active ends that will take over for you and form a bond. The same thing is true of the Oriental fibers: Kozo, Mitsumata, and Gampi.

Any questions?

Q: Is there a relationship between the degree of polymerization and the fiber length?

A: There is, it's like cement blocks, you get a different number in a building than if you use bricks. The fibers that are high in alphacellulose tend also to be very long. It's not true across the board, and, in general, when you talk about plants those that are high in alpha cellulose tend to have long fibers. But that's not true in the case of Kozo, Mitsumata, Gampi, Abaca.. But again, we're talking about a few fibers out of the mass. The papermaking fibers tend to be those fibers which make good cloth and rope. You're only talking about maybe a dozen fibers. You cook them and all; you don't end up with mostly something else.

And they also tend to have these long fibers so that in a sense, Kozo, Abaca and all that are kind of odd balls. They do have very long fibers and Kozo and all the Oriental fibers tend to be full of hemicellulose which are very short. I mean short molecules; the DP is very small but the fibers are very long.

Anything else?

Q: What is the difference between glucose and sucrose?

A: Glucose and sucrose and dextrose are all jammed around because of the difference between chemists and the people who make food. I can't keep it straight and I used to work in an industry allied to sugar.

Fructose, and glucose, and dextrose, when you talk about food sugars this is probably the easiest way to think about it. This is a sugar molecule with the carbons and so on. If you exchange the Rh and the H here you get manos, I think, you change it here and you get galactose, if you take this out you get arbinoses. They're all real similar but they result in very different things. But if you take this glucose molecule, this aldahidic end tends to swap and you get a change with oxygen and hydrogen at this end. You get beta glucose and alpha glucose and aldahidic glucose in any solution. A little bit more of one makes fructose and a little bit more of another makes something else and it affects it if you make bread out of it or make a cake or peaches. You get different reactions from either one. And that's why in the food industry, fructose and all that kind of stuff .... It is basically all sucrose but it has these very, very slight differences. You get into the other sugars that are in hemicellulose and they are a little more different than the two types of sucrose.

Q: The main strength of paper seems to be hydrogen bonding. Then what is the significance of fiber length and how does it matter?

A: The fiber length tends to make it flexible and thin and this tends to make a stronger sheet of paper since it is less brittle. The molecules in the fiber are stronger. The bonds between the fiber are the same strength. When you have a longer fiber, you have a high folding strength. But the more beating you do, the more bonding that occurs. You increase the bursting strength or you increase the tensile strength. So usually you give up one for the other, once you very carefully beat it.

A long thin fiber, like cotton, tends to cleave in long, thin areas and reform long, thin, supple molecules that withstand a lot of force. What happens if you get a thicker molecule is that it tends to be more brittle and not withstand bathing and things like that. You see, paper, the strength of paper, has to do with it's flexibility.

There was a period when they thought that when you beat the pulp it exuded some sort of glue. Just recently they have been able to get down and look at things with electron microscopes to the point where they can see that the current theories are probably a lot closer to being correct than the earlier ones.

This is in response to someone's question earlier about fiber length and hydrogen bonding. It is based on the same kind of bonding going on within the fiber as the kind that you're inducing with the beating. With the difference between short fiber and long fiber, I think the thing to remember is that you have in a naturally long fiber this naturally occurring highly ordered state. I mean you get it all. Hydrogen bonds were born in the fiber and even though there's a lot of changes going on here in the beating, in the final sheet of paper you've got this long, whole, fibrous strand that still has it's basic integrity and that's a very different thing than a short fiber. In the finished sheet of paper you've got a higher integrity, a stronger final object. Because you're starting with a stronger material. Also depending on what you're beating, as you beat, you change that raw fiber, which is more open in it's natural state. Because of the beating and the water molecules, when you form paper and it dries all of that fiber becomes much more dense than it was in the original fiber.

I think that fiber strength in the paper is higher in the longer fibered sheet.

Before I forget, some of the things I want to talk about are the things that happen in beating and the way a beater works. The roll does two things in a beater. It acts as a pump. It acts like a paddle wheel in the back of a river boat. It circulates the pulp around. Right back in the roll, there's the backfall. The reason for that is that the pulp is thick, you've seen it now, and if you didn't have a backfall, it would tend to just stir the one area and wouldn't move the pulp around. What happens is as soon as it goes over the backfall, it can't get back over it, so it has to go around and come through again. The other thing is that underneath the roll is a bed plate and the moving bars that come close to that bedplate, and they would actually contact, except that you've got fiber in the beater, and the fiber gets between the moving bars and the fixed bedplate and it gets squeezed. When you're beating something like cotton or linen the squeezing is quite violent. It's like squeezing a sponge in a bucket of water. Each time it goes through it gets squeezed and released in the presences of water and, just like a sponge, you slowly work the water down into the structure of the fiber.

Now when this happens it makes all these things I was talking about earlier possible. It also tends to shorten the fiber. As you beat, you make the fibers a little shorter because they're getting abraded and pieces are falling off and you're pounding them into a pulp.

At one extreme, if you beat fiber very lightly you will tend to have a sheet of paper that is soft, absorbent, that has very poor folding strength, but high tearing strength. I should say that the paper would be very much like blotting paper. Leave it in the beater and develop it over a long period of time, the other extreme, and you would have something like currency paper. It tends to be thin, translucent, strong, rattly, and where you actually have a much greater folding strength, bursting strength and everything else, but, surprisingly enough, you have less tear strength. The idea of that seems to be that the fibers themselves are very strong and they resist tearing. In a natural state, when you try to tear a piece of cotton fiber, it's difficult. When you grab a piece of paper, you tend to spread your force out among the fibers. When they are more bound together, they tend to localize, and so it makes it more possible to tear them. I don't know if that makes any sense to you.

The only strength factor that reduces as you beat the fiber is tear strength; everything else goes up, fold strength and so on. The paper gets more translucent. And because you've worked more water into the fiber you have all these bonding sites and all these capillary forces tend to pull everything back together again. It's going to shrink a lot. The higher the degree of bonding you get, the stronger your paper will be and the more it will shrink. And because it pulls itself together, cotton fiber is translucent, it won't pass light. The closer the fibers are stuck together, the easier the light gets through it. So, as you beat, you tend to get a more translucent sheet of paper. A cotton fiber will pass light. You hold a piece of cotton cloth up to the light and the light comes through. It is a translucent fiber already. If you get those fibers closer together you get less bending of the light beam as it goes through it. It has less to go through and therefore it becomes easier for the light to get through it. It becomes more transparent.

Well, that was a real problem in the old days because if you wanted to make a thick book like a Bible and have it so that you could carry it around, it was a very difficult thing. Of course, the easy thing to do is make the paper very thin. If you make very thin paper, it's very translucent and so you see the next page through the page you're trying to read. It can get a little confusing. Somewhere, probably in Japan, they came up with the idea of adding clay to the sheet. Clay breaks up those light beams. They called it India Paper or Bible Paper and things like that; they are clay filled papers, which aren't very common. But that breaks up the light going through and makes it opaque. So a lot of thin papers are opaque but they're opaque because they put something in it to make it opaque. And, of course, when you put pigment in the paper you do the same thing.

Q: What about the draining force itself?

A: Oh yes, freeness, that's called freeness. A pulp that's not beaten very much is very free. Water is not stuck into it very much and so for that reason it doesn't shrink much as it dries and so on and so forth. You might get blotter sheets. Water drains through it very quickly so when you form a sheet of paper of very lightly beaten pulp you have very little time to shake it. Bingo, it goes right through.

Whereas, if you have a good currency pulp, let's say, you stand there for five minutes and you get so bored waiting for it to drain that you loose track and mess up the sheet. Now there are ways to get around this. In the old days in the paper industry they heated the vat and that makes the water less viscous and the pulp goes through quickly. So if you're making a very strong book paper, if you heat the water it'll go through faster. But it's kind of hard to heat the water without the proper equipment.

In Oriental papermaking, they have just the opposite problem. It's so damn free that you haven't any chance to form a sheet. So you put tororo-aoi in the pulp and it slows it down. You do that first dip and cover the mold and it will slow down the water getting through. If you didn't slow it down you'd just barely get the fiber to hold the water and it would drop right through and you'd have a very difficult time getting a smooth sheet.

As you dip, if there is very little attraction between the water and the fibers, it just goes through very quickly. The more you beat it, the more the fibers in the water are attracted to each other and the slower the water is going to go through the mold.

What some of you experienced today in pulling a sheet of paper was getting the front edge of the mold under the water and having to pick it up because of the suction. Your mold goes under the surface of the water. As you pick it up all you have is wet pulp lying on the surface of the mold. Water is draining through. The surface tension that's making the water stick to the water is slowing it down. But if you go underneath the surface, as you come up, you've got a meniscus. As you pull it out, you get a great suction that is pulling back. It feels like there's somebody in there that just grabbed your mold. As you're pulling out of there, it just sucks the water out of your mold and you don't have time to shake it. The other thing that can happen is that if you pick your mold up out of the water and it's not level the water all runs to one end and runs out and you don't have time to shake it. So you can influence the freeness by the way you pull the sheet. In other words, if you have a very free pulp and you're trying to make a thick, soft paper, if you don't come out level or if you get the mold underneath the water, it's going to be a lot of work. The only thing that is bringing the water through the paper is gravity. You're not talking about the water that has been bound into the fiber through beating because you can't touch that in the sheet forming stage. All the other water is what you have.

If you walk away from the vat for a while, all the fibers sink to the bottom. So while you're forming the sheet you stir it up in the water so that you get time to shake it and get the fibers in a nice even layer. If the water goes away you don't have time to do that. And there's nothing particularly holding the water there. It has no real tendency to want to be there and the freer the pulp, the less tendency there is. What happens in Oriental papermaking is that you add something to the water to make it thicker, more viscous, and so it tends to slow down the rate at which it goes through the screen.

You can still be misled by Japanese papermaking. One of the reasons it seems that no drainage is going on is because the stuff is so thick. But what's fooling you is that because it's draining out in those long stringy drops, it's not splashing. You just don't hear the drainage because the water isn't making any noise.

The first time I saw Japanese paper being made it was hard to believe. It didn't look like they were using water. It looked like water, it felt like water, but it sure didn't act like water. It's so much thicker, it's like oil, cream, compared with the stuff we use.

Q: How does fiber distribution, forming the sheet of paper, effect the strength of the sheet of paper?

A: Once you've beaten the pulp, whatever kind of fiber it is you're preparing, once you've made it possible for bonds to happen, there are a lot of ways you can miss the boat from then on. If you don't distribute the fiber evenly on the sheet, you have various areas of thick and thin so you have differences in bonding. And as the sheet dries you have unequal forces and all sorts of funny things happen. You have weak areas and strong areas.

One of the main things that happens in the vat in sheet formation doesn't really have to do with pure strength of the sheet but with uneven strength. If you had a sheet that had good formation, good distribution, but you shook it in one direction so that you have a strong grain, it would seem that you would have tear strength against the grain but not much with the grain. You might want less grain and more random lining up of the fibers.

Q: How would that effect folding strength?

A: You don't really loose with a paper with high grain. When they make something like carpet tubes, they actually want paper with a high grain. they layer it up and wrap it spirally so that each layer has the grain going in a different way because you get less strength in one direction but more in the other. Your net result is about the same. But you're getting more strength in one direction and you can use that property in certain ways. Japanese paper has a very strong grain because you pull and shake it sideways hardly at all.

When you pull a sheet, and you give it a shake one way and then a shake another way, it's not just a matter of making the fiber random. You're actually creating cross grains within the sheet of paper. The shake helps counteract the fact that you're making the paper in this fashion.(demonstrates) You can counter it a little bit by shaking it. They have tried to do that in a paper machine by shaking it sideways but they gave up on that.

If you go into the vat facing vertically and then pivot, you pick up a lump of randomly oriented fibers. Say you work in a traditional mill with a hog and it really creates a strong current in the vat, then the mold is put into the vat at an angle. The pulp is flying up on top of the mold because of the current the hog creates. The pulp is really just thrown up on the mold. Then there is almost no dipping. If you go in at an angle, you create very strong grain in one direction; but if you dip the mold straight down and then pivot, the pulp will just plop on the surface of the mold.

There's another factor involved here and that is the press. The press is really important to papermaking because the fibers are 90% water. After you have made the sheet of paper, you drain the excess out. Because of the large amount of water in a sheet, if you just let it dry, you'll have a much softer sheet than if you press it. Because when you press it, these capillary forces are tremendously powerful but they only work when you get down to very small dimensions. So one of the things that really helps is that in pressing you squeeze out the excess water and get the fibers closer together and make those potential bonds that you spent all that time in the beater working on.

One of the things that happens when people caste pulp is that it doesn't get a chance to form these bonds. So in the case of casting we always put something in there, methyl cellulose is a good one. You use an adhesive to stick these things together because you're not going to get hydrogen bonding like you would with a sheet made with a mold and a press.

The other thing is that usually people who are casting pulp are bothered by shrinking. The stuff shrinks; it tends to have problems with warping. Some people, Frank Gallo for instance, know how to make a mold so that when it shrinks it works out OK. When you caste metal, and a lot of other things, as you caste and it cools, it shrinks and so you make the mold in such a manner that when it shrinks it's OK. It's the way you want it. But a lot of people who make molds for casting paper don't know how to do that and I sure as hell don't know how to do it. They don't want the paper to shrink and when it does a lot of funny things happen that they didn't intend to happen. They don't want a pulp that's very well beaten. When you combine no press and fiber that you've not beaten very much, you can wind up with a very spongy sheet of paper.

One of the things that happens in papermaking is that the paper is never stronger than when you first make it. Because paper is very hydroscopic; it picks up moisture. As the temperature and humidity change it gives it off and as the moisture gets in there it breaks some of the bonds and other stresses work their way out in the sheet of paper. But you actually lose a little bit of strength, not much.

In terms of a normal sheet of paper you've got so much strength by making it properly in the first place that it's insignificant. But you take something like a caste piece where you've got a marginal situation already and then let it sit in the environment for a while, it tends to lose a lot of strength relative to it's initial strength. There are some caste paper pieces by well known folks that are falling apart on walls and it's because there seems to be a hesitancy to put any sort of glue into it. They were concerned that they might make paper mache. And paper mache is not an artistic medium....

Q: Can you add just a little methyl cellulose, not too much?

A: You can add... what is it, 2 percent. You have to experiment with it but you can add a lot of things. Any kind of glue will do the job.

Q: But wouldn't that make it stick to the mold and not release?

A: Yeah, if you put too much in. What most people who caste paper do is put pulp into a mold and work the water out with a sponge. What you all do is pull a sheet, and place the sheet into the mold and, even if you didn't press, what you're getting is a product very similar to a traditional sheet of paper. So you're creating the kind of bonding that holds the sheet of paper together. So you don't need glue. And you don't have trouble with the adhesive sticking things together. You only need methyl cellulose to keep the separate sheets together on the edges.

Another good trick is to use a vacuum table. You have a flat board and you put down a felt and couch a sheet on top of that. Put a thin film of plastic over the whole thing and pull a vacuum underneath the plastic. The pressure of the atmosphere at sea level is 15.7 pounds per square inch. So what happens is that if you pull the air out from under the paper the atmosphere tries to push it down with a maximum pressure of about fifteen. But you get additional help from the fact that as you pull the vacuum on, you tend to suck water out of the thing, so you get an equivalent of maybe 30 PSI. That's pretty damn good. Plus you can lump the plastic to form it. You get a similar effect to pressing. And it's pretty decent.

What we recommend to make a traditional sheet of paper is about 60 PSI. Sixty pounds per square inch of paper. When you do that, after you finish and pull the felt off, the paper will stick to the felt below rather than come off with the one being peeled off. You'll have enough water out of the sheet so you can handle it and so forth. And that will create good bonds and so on. But you can get away with less. It all depends on what you are trying to do.

When we first tested the paper we were making on the MIT fold tester, we weren't making paper for anybody who was making books. Because they didn't want it. Anyhow, it didn't do very well at all. What we found out later was that you don't use a MIT fold tester on thick paper and get anywhere near the same results. You have to use a different drum and different weight and all that kind of stuff and it still doesn't mean much. The reason is that a very thin material can bend without a lot of internal stress. When you take a much thicker piece and bend it what happens is that you've got a classic engineering problem in that this area (demonstrates) is under great compression, and this area is under great tension. The middle might survive but because everything else is gone it tends to break. Whereas you take a paper which has less inherent strength in the first place but if it is much thinner you can bend it without any problem. When you get something really thick you get compression at the bottom and tension at the top. If you do a fold test on a thick sheet of paper, you'll find that it does get a lump at the top. It's also why, when people make books from thick paper, even though it's good, strong paper, they have troubles. It won't bend, you pull it open and it springs back so you force it open and you break the paper. It's because the paper might be plenty strong but it's too thick for the job.

The folding strength of the paper goes up as your beating goes up. The tear strength drops off a little but the folding goes up. If you get to glassine, you've shortened the fiber and you've made it translucent but you've lost some of your strength characteristics. Something like currency is incredibly strong. They estimate six thousand folds.

The original fiber is very important and how unabused it has already been. For instance, we make paper from a cotton that is natural, not bleached at all. So that we can cook it ourselves in a very mild caustic and beat it carefully and end up with a paper that has high folding strength and relatively high tearing strength, both. Old rags, forget it, subject them to bleaches and washes; they're abused. The cellulose is abused.

Russian hemp is a wonderful fiber because it's very long and we get it totally raw. You start with the raw fiber and can completely process the fiber yourself.

When we first started making paper in San Francisco, we got rags, cotton rags. The only cotton rags you can get anymore, that don't have synthetics in them, are from restaurant linens and hospital sheets and doctor's gowns and that sort of thing. Because of the cleanliness they're after the fibers are abused. We couldn't figure out why we couldn't get thin, rattly paper. All we got was this soft, spongy stuff. It's because we were starting with gutless fibers. I read somewhere that even in the old days they made watercolor paper and good paper from new garment cuttings and never used old rags to get a strong paper. Old rags are no longer a source of fiber because of synthetics, There is just no way to check for synthetics that's going to be worthwhile.

Here are two pieces of paper- one that is loft-dried and one is not. You've got a very different surface on here and on here. Ink absorption is a surface phenomenon and when you have a very different surface, you have a very different reaction. What happens is that with all those little beads and bumps it's going to react very differently with the medium. The gelatin tends to be more absorbent given a certain situation. It's just like if you want to dissolve something. You grind it up first, it'll dissolve faster because you've given it more surface area and that sort of thing.

One of the things I want you to go away with is the idea of how bonds get developed. Whether you're beating them with a stick, in the case of hemicellulose fiber; or with a beater, in the case of an alpha cellulose fiber. And also what happens in beating. On one end of the scale you have soft, weak, opaque, absorbent paper, and on the other end you have thin, rattly, hard, strong paper, that's not nearly so absorbent. And it has to do with stresses. You're always dealing with the range in-between. You're picking somewhere in the middle.

Q: What happens when you put different fibers together?

A: You get a combination of effects. It's a really good way to get what you want. The other thing that adds a great deal of strength is sizing. It adds strength in several different ways. The stronger the paper is initially, the less the effect of the sizing is going to be. When you size a relatively weak sheet, the net change is going to be greater. One of the things it does is to tie up these areas where moisture can enter the sheet. It adds strength in the non-chrystalline areas in the fibers, which are the weaker areas of the fibers. What you're doing is bridging the crystalline areas. I think that where the paper is going to rupture is in those amorphous areas because those areas are less strong. There's less bonding and so on. So when you bridge them by tying up those areas with sizing, you add strength.

Tim Barrett did a really interesting test where he added a very small amount of gelatin sizing to paper and got the same strength that you get with a large amount of sizing. Now he didn't get any other things; it didn't hold out ink better, but he got the strength increase. So it tends to indicate, as we were talking about in Washington, that bridging those amorphous areas, that's the only place that sizing is going on. Because the paper is not changing it's absorption to inks and water.

It's like little magnets. All the action that happens at those amorphous areas. The crystalline areas are almost inert. Anything that's going to happen, whether it's sizing, whether it's degradation, whether it's coloring the paper and so on and so forth, is going to happen where one of those fibrils is sticking up and at one of those amorphous areas. It's because you've got charges there. Bonds that won't change. Chemically active areas. Chrystalline areas tend to be inactive in that not much happens there.

The fibers tend to be negative with an overall negative charge, which has to do with the way water is stuck on the outside. Retention agents are attracted to these areas as retention areas. They are in return attracted to a chunk of pigment. It's also true, as Kathy was saying, that if you use sizing as a retention agent, you're going to find that the sheet is much more absorbent. So you might want to add more sizing. What happens is the sizing isn't working to prevent water entering these amorphous areas. It's holding pigment to it. So you need to add a little more sizing on top of the pigment. The action is between the amorphous areas and the sizing and if the sizing is all pigmented then you're loosing some of the resistance to absorption.

Q: Have you ever experimented with overbeating pulp and coloring it with a pigment? This is something I have been meaning to try because I think you can get a very translucent paper made with overbeaten pulp and still load it with a lot of pigment. Every time I think of this I start beating a load of pulp and then something happens that takes me away from it and then my daughter eventually throws out the pulp. So I've never done it. So, I'm wondering if you've ever tried it.

A: No, the only time we've ever overbeaten pulp is to try to get it transparent. You start loosing strength and stuff but you pick up translucency, and it's glassine. Of course, they tend to use really weak fibers to make glassine so it doesn't take so long to beat it. Well, Bennett has had really good experience with that. His set-up tends to overbeat the fiber and all sorts of weird things happen. It tends to be a lot more translucent. But if you loft dry it, it'll just crepe like mad and you loose the translucency because it's all wrinkly. But if you can overbeat it and restrain it, it'll be quite transparent. That's one way to do it. In industry, of course, they don't want to beat long because it takes a lot of energy and it's expensive and so they use a weak fiber like straw, which makes the fiber more translucent.

One of the reasons the paper industry is switching to alkaline pulp is not for the long-term use of the paper but the fact that they can add calcium carbonate filler to the sheet. Most commercial papers now have fillers in them to make them opaque. Calcium carbonate is a lot cheaper than titanium dioxide and it has the added effect of being an excellent buffer to acids. Pollution tends to be acidic and the acidity in the solution tends to cause hydroxyles in the fibers at those active amorphous areas, causing them to break down. The calcium carbonate doesn't interact much with the fiber, but it does absorb acidity and it helps keep it away from those amorphous areas.

But there's a problem in adding calcium carbonate. It doesn't want to dissolve. It's like a pigment; it's hard to make stick. And so, you have to use retention agents to make it stick well. I think if you have some in your water, you already have some built in buffering and it's already well dissolved and you don't have trouble with it. One of the real problems when you're dealing with wood pulp and putting acid sizing in it is you're taking a bad situation and making it worse.

Don't you add it in the beater, Tim? (gets a positive nod) If you're adding a buffer you add it in the beater.

My main objection to calcium carbonate, even in low percentages of about two or three percent, is that even in those low amounts the paper looks chalky. I think it does probably make it longer-lasting, but there's the question of what a papermaker's obligation is, what the librarian's obligation is. You can buffer it and in the atmosphere of the typical city you're still not going to do any good. Archival paper is starting to get into the realm of scrubbing the air coming into the collection.

Q: If you have an unbleached linen and you're getting a translucent brown paper, you add no more calcium carbonate say, than if you were pigmenting a cotton pulp. Then you get not only a buffer, but opacity that brightens it up a little bit.

A: And it looks like paper that has had calcium carbonate added to it, to my eye. I object to it aesthetically. I think that if you deal with a short or weak fiber and an acid sizing and all that kind of stuff and all the problems you have in a papermill, it's a good idea to put calcium carbonate in it. But I think that when you're dealing with the kind of fibers that we are, you've got so much strength in those fibers that I think you've got the strength that you need. It's as good as anything.

Q: The cases where it is really evident that calcium carbonate did some good are cases where they put in 30% calcium carbonate and then did an experiment. But there's almost no evidence for it's effect naturally.

A: And we can live with books that were printed in the fifteen hundreds with nice white, supple paper and there's no alkaline reserve and it's made it. Conservators like calcium carbonate, I guess.

Q: Is the paper ruined by washing, like in old books?

A: A lot of interesting things happen when you wash old papers. Whether it's good, I'm not so sure. You tend to wash away sizing and the sizing is what's kept it good all these years.

Q: If you wash, you probably resize anyway.

A: But there are things that happen when you wash. Sometimes you actually get a strength increase. There's evidence that says that you do get a strength increase after washing, but it tends to fall off.

Gary Frost: This has been a magnificent talk in bringing out the composite of givens with the achieves. In other words, if you're given a sheet that has good fiber and you wash it, you could diminish the tear strength. However, if you had a poor sheet that had sizing relative to the amount of flexibility that you would achieve at a given strength might be better as a result.. This is such a floating scale of phenomena and such a magnificent presentation because if you keep a constant accumulation on factors that do the strength...

Howard: Yeah, we were talking with Elaine this morning about unbeaten abaca being soft and beaten abaca being hard, But we were saying that this is relative to a hard choice of beating and not beating abaca. Unbeaten abaca relative to unbeaten linters is relatively rattly and hard. There's this relative thing you always have to think about when people are talking about conservation and longevity and all that stuff. It's relative to what? If you're dealing with a real short fiber and you've acid-sized it and all that kind of stuff, you're dealing with something that's real marginal in the first place and some relative things that can happen to it are much greater. With weak fibers you wash, you're doing some really good things to it because you may wash out things that are causing trouble.

Don Farnsworth was trying to make some conservation pulp for people patching things. He took pulp and he beat it, let it dry, slushed it up again, and let it dry, slushed it up , and let it dry, and it worked like a charm. And he got a very stable pulp in a very short period of time. When you first make the paper, it feels stronger because you've got residual stresses in it; but humidity only makes those things relax. So when you get a more stable sheet, you loose some strength, but it's more stable.

Q: So what would you say, should you wash books or not?

A: One of the things that bothers me is the aesthetics of the thing. There are two Nurenberg Chronicles in a show at the National Gallery that Slasser and another curator put together. And one had been washed and one hadn't. And the one that hadn't been washed looked so much better than the one that had been washed, even though the other one was nice and clean.

Gary: Add a couple of decades too, and I'll bet you the deficiency will be enhanced. Because of what you say about all those sight effects and the fact that you've loosened the sheet in terms of the density of the whole text block...

A: If you were restoring comic books or thirties pulp westerns, it probably would help.

Gary: I think we're getting into the third week.