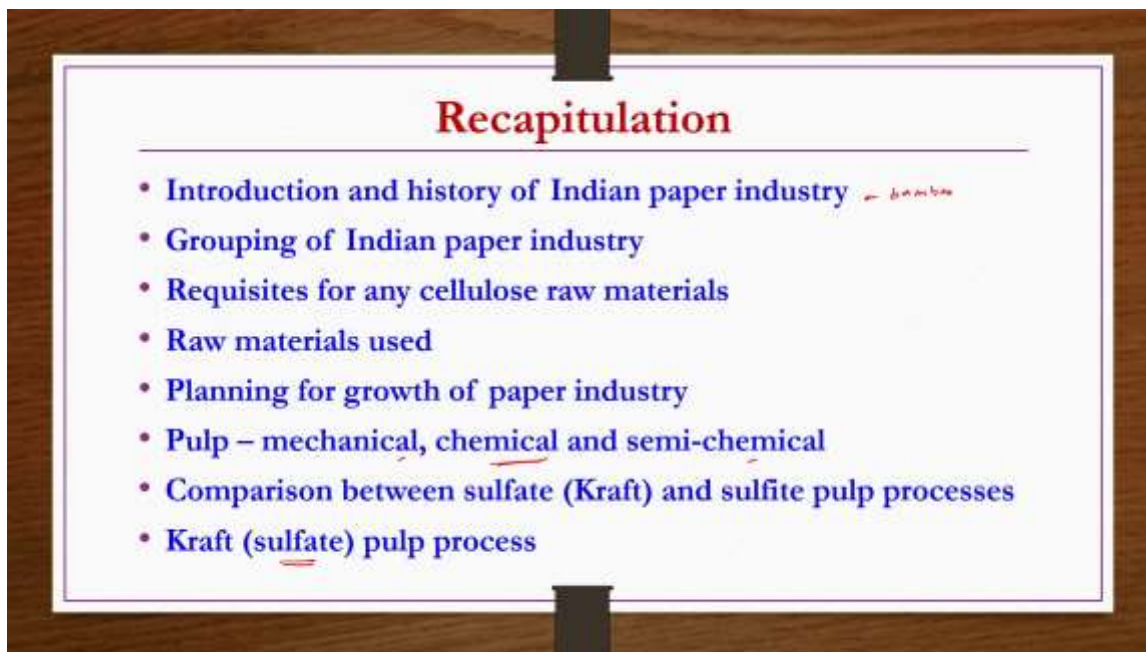


### Lec 17: Pulp and Paper Industry – 3.

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is pulp and paper industry part 3.

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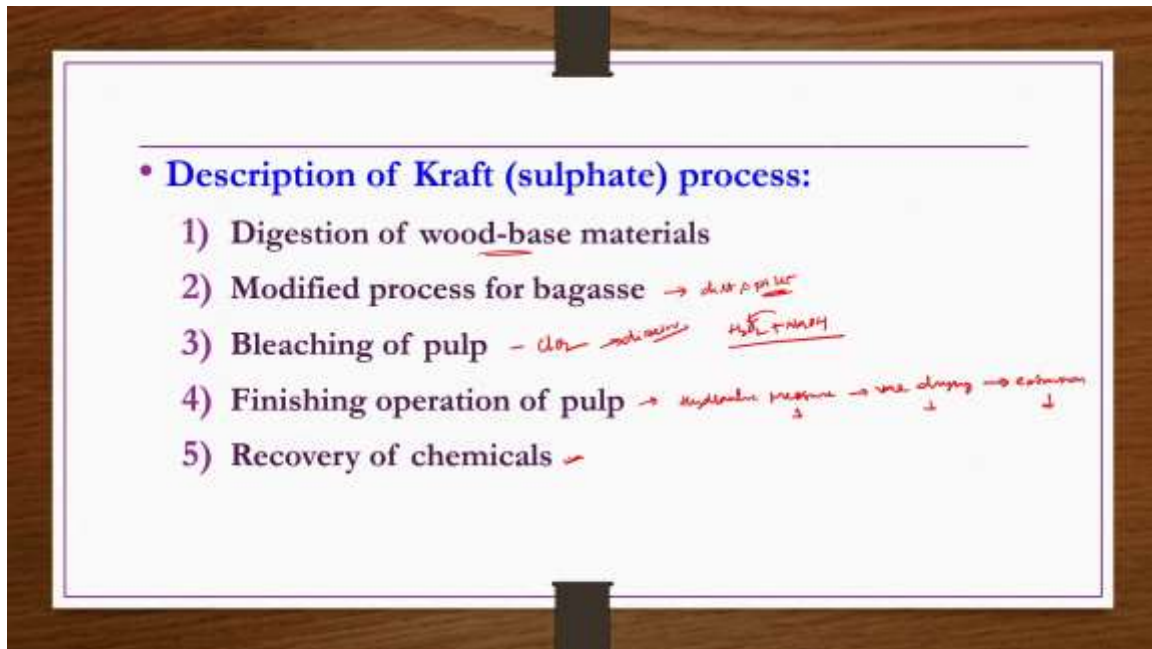
Before going into the details of today's lecture on papermaking and cellulose and its derivatives production, we will have a recapitulation on what we have discussed in last couple of lecture on pulp and paper industry. We started with introduction and history of Indian paper industries and then we realized that Indian paper industry is the first one to use the bamboo as raw material for papermaking and that is because bamboo is the one which is having the long fibers and then the quality of the paper produced from the bamboo fiber is very good compared to the other raw materials. So, then it has been realized that it is important to do the bamboo cultivation up to the demand of a paper production or the paper demand that is there in the market which is not possible.

So then other alternative raw materials has been investigated and then properly the industry has been established and then it has been found that if we blend the bamboo raw material with other wood or straw raw materials, then the quality of the paper is still going to be the better one. Then we have seen the grouping of Indian paper industry which has been done based on the size of the units and then based on the sources of material to produce the pulp and paper. So, based on that one we have done the grouping of Indian paper industries where we have seen that you know 6 different types of units are possible or groups are possible. Then we understand that cellulosic raw materials you know very important part in the pulp and paper industry.

Even though we are taking the wood as raw material what we are doing in the pulp and paper industry, we remove the lignin and other non-cellulosic components and then we try to have as much cellulose as possible in the pulp and then from there we are making required pulp and then paper, right? But there should be some kind of requisite otherwise you know it is not possible to make a proper paper of good quality with proper economics with you know profitable conditions. So, for that you know feasibility of the raw materials especially to the pulp industry throughout the year. Then you know quality of the paper that is being produced, at what cost it is going to be produced, all those things you know we have listed. Low cost production is required, high yield is required, all time availability of raw materials is required, those kind of requisites we have seen. We have discussed different types of raw materials required for the pulp and paper industries like softwoods, different types of grass, reeds and then straws etc. those kind of different types of raw materials are used in pulp and paper industries, those things we discussed. Then planning for growth of paper industry, obviously we understand that the supply demand gap is very high. So then in order to reduce that gap you know certain plannings are required. So, one most important is that increasing the cultivation of bamboo as per the requirement or as per the demand of the paper. Also, to see the other possibilities like using eucalyptus and then reuse of the waste paper as the sources etc. those kind of things are you know very essential for the growth of paper industry. Apart from that one having indigenous equipment for the paper industry and then continuous process production of the paper by the continuous process at the higher throughput, etc. are very essential to look in so that to make sure that the paper industry growth is sustaining. Then we have started discussing about pulp where pulp can be made by the mechanical, chemical and semi-chemical methods those things we discussed. Then we discussed out of these chemical methods you know sulphate and sulfite pulp processes are there.

So, we have seen their comparison then we have seen in detail about the sulfate or Kraft pulp process. How taking the wood base raw material the pulp has been produced by using this craft or sulphate process that is what we have seen.

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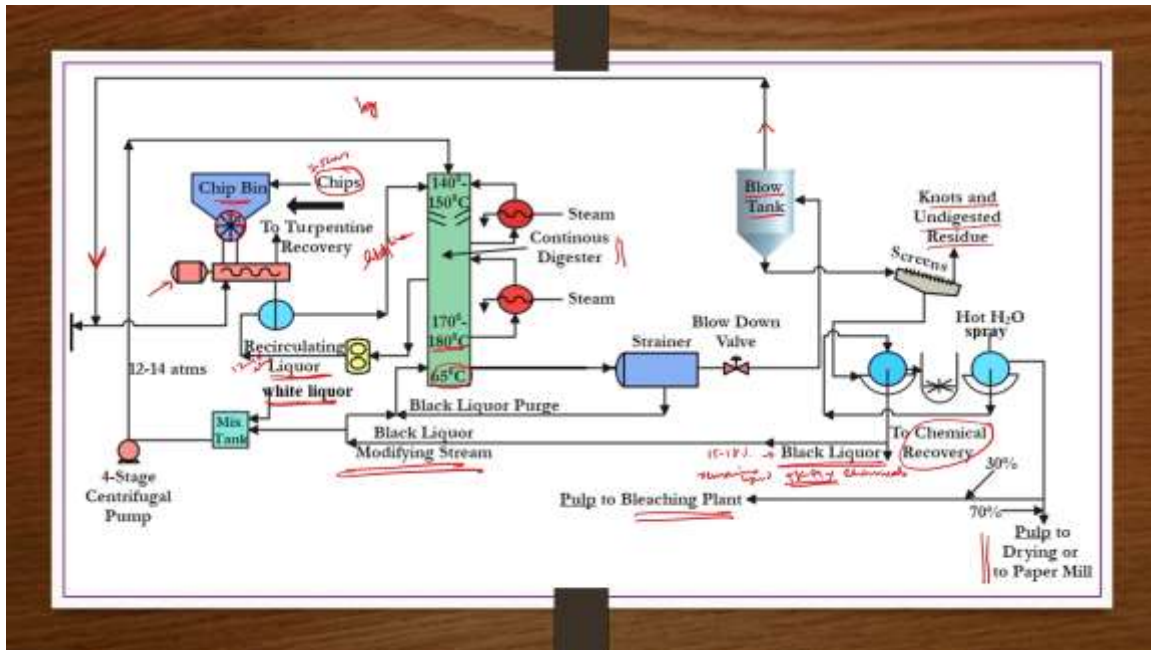
So, here in the craft process we realized that there are 5 important steps. First one is the digestion of wood base raw materials then modified process for the bagasse because the plant whatever that is available that is based on the wood base. Why because bamboo-based digester why not designed because you know bamboo is not available in much quantity whereas the different types of wood are possible.

So that way though you do not get a very good quality paper but you can continue running the plant with different materials of a wood. So that is the reason you know design has been done based on the wood base raw materials but modifications can be done for the processing of bagasse materials. So, where you know cleaning like you know in this one dirt and pit, etc. would be there. So dip within by wet grinding process etc. you can do and then remove those things we discussed. Then bleaching of pulp is very much essential to remove the color and then other impurities kind of thing. So, in general you know chlorine dioxide were used but because of using this one dioxin kind of impurities were found in the liquor which is not good. So, then people started using hydrogen peroxide individually or combined with NaOH in order to maintain the desired level of H<sub>2</sub>O<sub>2</sub> you know you need to have the sodium silicates also those things also we have seen. Then finishing of pulp operation that is whatever the pulp that you get after bleaching almost like you have to make sure that how much water should it contain based on the application based on the requirement of transport.

These processes are required they include like you know hydraulic press at high pressures like 200-300 atmosphere followed by the vacuum flash drying followed by the extrusion process, etc. is required. By this process you get water up to 60% by this process you reduce

the water content in the pulp by 40% and then by this one you can reduce it like you know solids you may be having up to 90% solids remaining only little bit of moisture or water would be there. Then last important point was recovery of chemicals that also we have discussed for the 2 options.

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So by schematic if you by flowchart if you re-see the process whatever the chips are there those chips you got by the logs of you know wood you do the debarking and then do the debarking by tumbling and rubbing action then you pass it through a chipper where you reduce the log size to the 2 to 5 centimeters chips those flat chips you take into the chip bin from here through a star wall you pass it to the deaerator and then preheater section.

So, the star wall is required for the metering of solids how many kgs per second or per hour required accordingly if you want to transport then the star wall is playing a very good role and then in the preheater deaerator required steam whatever is there that is coming from the blow tank itself. So, after this process whatever the material is there after deaerating and then preheating that is passed through the lift line then to the continuous digester. So, for this you have the tapered wall here for that purpose you know it is required tapered wall in the sense it can send you know both the solids by one side other side you know you can send the recirculating liquor also. This recirculating liquor is sent at around 12 to 15 atmosphere so that that recirculating liquor can carry the solid chips to the top of the digestion column otherwise solids alone may not transport easily through the lift line for that purpose this recirculating liquor black liquor is provided. Within the continuous digester you know you need to maintain different temperature at different elevations and

then accordingly time of the digestion you have to fix it that comes with experience or you know may be stabilized for the well-established plant.

So, this one to this one you also send the you know liquor to the digestion continuous digestion tank you send the white liquor as well as the black liquor along with some chemicals like you know whatever  $\text{Na}_2\text{SO}_4$  or  $\text{NaOH}$ , etcetera these things are required those things can also be mixed in the mix tank and then using the centrifugal pump you can send it to the continuous digester. After the process is over so whatever the digestion mixture is there that you have to take to the next level but you cannot take it at high temperatures of 170, 180 degrees centigrade. So, that temperature is reduced to approximately 60 to 65 degrees centigrade at the bottom of continuous digester by using the black liquor. Once the temperature is reduced to this one that will pass through strainer it will go to the blow tank where in the blow tank you know more heat is removed heat is removed in the form of the steam and then that steam is sent back to the aerator preheater purpose. After reducing the temperature further low whatever the mixture is there that you pass through a screen where you know knobs and undigested residues of wood etcetera are there they would be separated out then whatever the pulp mixture is there that you send to rotary filters where hot water is sprayed for the washing of the pulp purpose.

So, then whatever the liquor that you get from this washing finally that you call it as a black liquor. That black liquor you have to do the chemical recovery because it contains 98 to 99% of chemicals that have been used for the digestion purpose. Actually, from the solid liquid point of view it will have 15 to 18% solids and then out of the remaining liquid whatever there in the remaining liquid 98 to 99% chemicals would be there so that liquids has to be processed so that to recover chemicals and then reuse otherwise plant cannot be economical. So, whereas the pulp whatever is there approximately 30% is taken to the bleach plant so that you know from the pulp other products can be produced whereas approximately 70% is taken to the drying section then to paper mill for making the paper. Basically, almost like three fourth of the pulp that is being produced is used for the paper making whereas the remaining is used for the other cellulosic materials production because pulp is nothing but the commercial cellulose.

Chemical recovery from sulphate pulp digestion liquor:

The diagram illustrates the chemical recovery process from sulphate pulp digestion liquor. Key components and flows include:

- Inputs:** Current Feed, Copper Precipitate, Make-up Chemicals ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), Fuel, and Make-Up Lime.
- Process Units:** Six Effect Evaporator System, Counter, Copper Precipitator, Stack, Boiler Section, Combustion Chamber, Mix Tank, Pre Heated Air, Discharge Tank, White Liquor Storage, Clarifier, Causticizing Tank, Strain, Clarifier, Washing Tanks, and Lime Staker.
- Outputs and Intermediates:** 18-54% Solids, 60-65% Solids, 28-30 atom Steam, Hot Flue Gas, Air, Stack, Pre Heated Air, Discharge Tank, White Liquor Storage, Clarifier, Causticizing Tank, Strain, Clarifier, Washing Tanks, Lime Staker, and Reburned Lime.
- Handwritten Notes:** "Black Liquor (15-18% solids)" and "Sulphate" are circled in red. "To Digestors" is circled in red. "Reburned Lime" is circled in red.

Otherwise you know you cannot discard such water with such high quantity of chemicals so from the pollution point of view as well as the from the economics point of view because if you recover these chemicals you can reuse within the plant. So, for that purpose chemical recovery is very essential in the pulp and paper industry. In fact, success of pulp and paper industry depends on how effectively are you recovering chemicals. Sulphate process is dominating over sulfite process because of such reasons only because in the sulfite process different types of liquors are produced and then their chemical recovery is very much tough compared to what is the process here. So that black liquor containing 15 to 18% of carbonaceous material and then remaining liquid that would be sent to a multi effective operator 5 to 6 are required sometimes more also required depending on the size of the plant.

So here we have shown only one but multiple are possible. So, when you take this liquor into the multiple effective operator you have to supply energy so that you operate the water from the liquor. For that purpose, steam you supply and then that steam you send counter current to the liquor. So once this multi effective operation process is done whatever the

liquor that you get in that liquor you will be having solids concentration increased to 48 to 54% that is quite high from 15 to 18% solids now water is removed so much that 48 to 54% solids are there. That would be further you know heated in a rotary dryer using the hot flue gas coming from the smelter process.

So that you know the solids concentration can further increase to beyond 60%. Why to increase the solids concentration? Why not you take this black liquor directly in this melting process? If you take a liquor with only 15 to 20% of solids a combustion may not take place even if the combustion taking place that may not sustain for that reason increasing solid concentration is required by removing the water. Whatever the gas is coming out of this rotary drying system they may also contain some amount of solids in general. So, for that purpose to recover those solids you know that is passed through a cottrell precipitator. This precipitator now you know it collects whatever the solids, etc. at the bottom and then stake gases is released from the top.

So, then this liquor after increasing the solids concentration to 60 to 65% is mixed with chemicals makeup chemicals like  $\text{Na}_2\text{SO}_4$  and then sulfur. This  $\text{Na}_2\text{SO}_4$  is being used in the process that is the reason this process is known as the sulfate process. So, then this black liquor having 60 to 65% solids along with makeup chemicals fed to a smelting chamber or smelter or smelting furnace where preheated air is supplied so that the combustion can take place. Combustion of carbonaceous material takes place and then because of the combustion of carbonaceous material you get hot flue gases as well as the inorganic smelt you get. Hot flue gases would be sent back to the rotary dryer so that you know further drying of the liquor can take place.

Whereas the inorganic smelt that you get that you send it to the dissolved tank where it interacts with cold water so that to get green liquor. Now this green liquor you take to the clarifier. Now here in the clarifier whatever the solid sludge etc. are there that you separate out. After separating out the solid sludge from the clarifier before discarding it as waste you wash it with the wash water and then only solid sludge you separate out whereas the diluted wash water is there that you feed back to the dissolved tank.

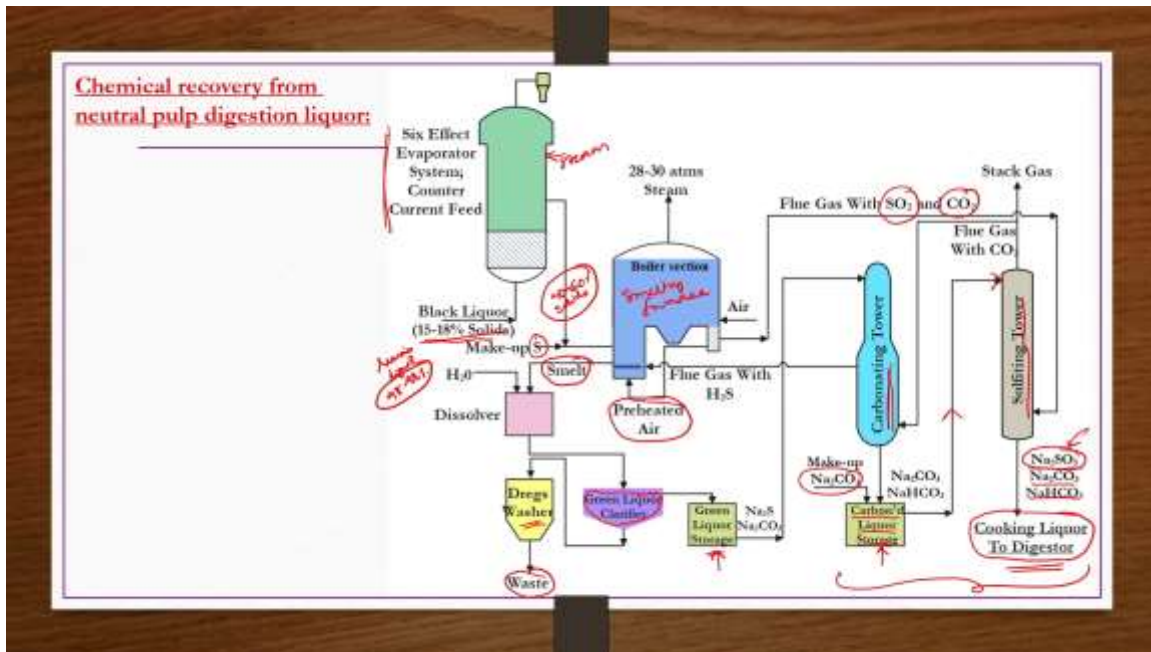
Whatever the filtrate from the clarifier is there or clarified liquid is there that you do the causticizing in a causticizing tank using the lime. After that you know what you get you have primarily carbonated mud and then white liquor only would be there in the mixture after causticizing. So that you can separate by the clarifier. Again, another clarifier here you use to separate out the white liquor and then that white liquor you can reuse to the digestion purpose. Digestion whatever you know continuous digestion of wood chamber is there to that one you can reuse as shown in the previous slide.

Whereas the carbonated mud whatever is there that would be passed through a rotary vacuum filter to remove more liquor from it if at all it is having and then that liquor is fed



back to the dissolved tank. Whereas the almost like dry carbonated mud is there that is primarily having the lime deleted thing. So that would be passed through a lime kiln and then dry it using the fuel and then reburned lime whatever is there that you take to the lime slakers for the re-causticizing purpose. This is the chemical recovery from sulphate pulp digestion liquor.

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Whereas we have also discussed chemical recovery from neutral pulp digestion liquor. Here most of the steps are same. Whatever this neutral pulp digestion liquor is there that is coming from the neutral sulfite process not sulphate process. So, if you have a neutral sulfite process then chemical recovery if you wanted to do from its liquor so this is the process. Mostly the process is similar like you know whatever we have seen for the recovery of chemicals from the liquor that is obtained from the craft process. But only thing that there we have causticizing step now here rather causticizing you have the sulfiting and carbonating towers. Before that whatever the steps are there they are quite similar.

So, whatever the liquor that you get here also roughly 15 to 18 percent solid should be there and then remaining liquid whatever is there that liquid would be containing 98 to 99 percent chemical here also. So, these chemicals has to be recovered both from the pollution concerns point of view as well as from the economics of the plant. You cannot afford to have the so much of chemicals losing every time. So, for that purpose of recovery this flowchart is here. Now the starting point is you know here also multi-effective operator is used so that to increase the solid concentration in the black liquor from 15 to 18 percent to 50 to 60 percent roughly or 45 to 55 percent that can be done by evaporation of the liquid



that is present in the liquor and then that evaporation of liquid can be done by heating and then heating is done by the steam.

That steam and then liquor are you know entering the multi-effective operator in the countercurrent way. After this multi-effect evaporator process whatever liquor, you get that would be having you know roughly 50 to 60 percent solids only 40 to 50 percent liquid should be there. So now after improving the solids concentration in the black liquor by evaporating the water you know what you do you mix with the makeup chemicals like sulfur, etc. If required you know sodium, sulfite, etc. may also be added and then that liquor would be sent to the smelting furnace.

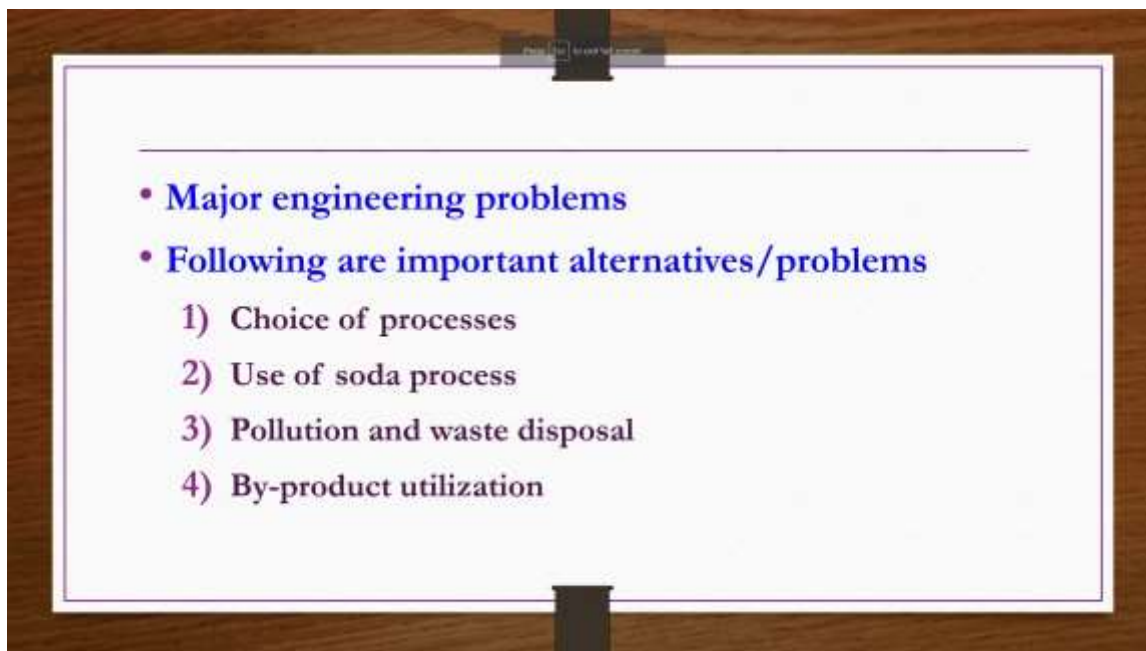
In this smelting furnace what happened carbonaceous material would be combusted, right? For that purpose, preheated air is being supplied. When this combustion takes place you get the flue gas as well as the inorganic smelt, right? So, the flue gas what you do? The flue gases having  $\text{SO}_2$  and then  $\text{CO}_2$  would be sent to a sulfiting tower where whatever the chemicals that are present in the black liquor liquid. So, you know mostly they will be converting into the sodium sulfite, sodium carbonate, sodium bicarbonate these kind of chemicals. Of course, they will not be in pure conditions but still in the liquor condition. So that you can collect as a cooking liquor and then take it to the digester if required.

If the more purification is required then what you do? Whatever the flue gases with  $\text{CO}_2$  only because in the sulfiting tower you do the sulfination so that you get the sulfites etc. So, after that primarily flue gases would have  $\text{CO}_2$  only. Those things you take to the carbonating tower where carbonation takes place and then you get sodium carbonate, sodium bicarbonate, etc. So, if required sodium carbonates make up chemicals may be added so that you get a carbonated liquor storage. This liquor what you can do? You can send back to sulfiting tower so that whatever the carbonates, etc. are there, they will be forming sulfides like  $\text{Na}_2\text{S}$ ,  $\text{SO}_3$ . Whereas the inorganic smelt whatever is there that is taken to a dissolver where cold water is used to dissolve the inorganic smelt then you get a green liquor. That green liquor would be having the solids as well as you know liquor. So, the waste solids you have to separate out by a clarifier. Whatever the solids that you get, the waste slurry you get that you further wash it with water and then wash water you may be reusing into the dissolver whereas the sludge you know almost like a little water or no water that would be taken as a waste.

Whereas the clarified liquid from the liquor clarifier whatever is there that you take it to the green liquor storage which would be having  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{CO}_3$ , etc. Since  $\text{Na}_2\text{S}$  is there so that you send it back to the carbonating tower and then from there you get the carbonated liquor storage that liquor again you send back to the sulfiting tower so that  $\text{Na}_2\text{SO}_3$  you get and then that liquor may be reused to the digester. Remember only this liquor is reused in the digester for the sulfite process whereas these things you have to do separate processing otherwise you know you have to do the process continuously until there is no green liquor

or almost all chemicals have come into the cooking liquor. So that cooking liquor you can use or reuse into the digester of a neutral sulfite pulp process.

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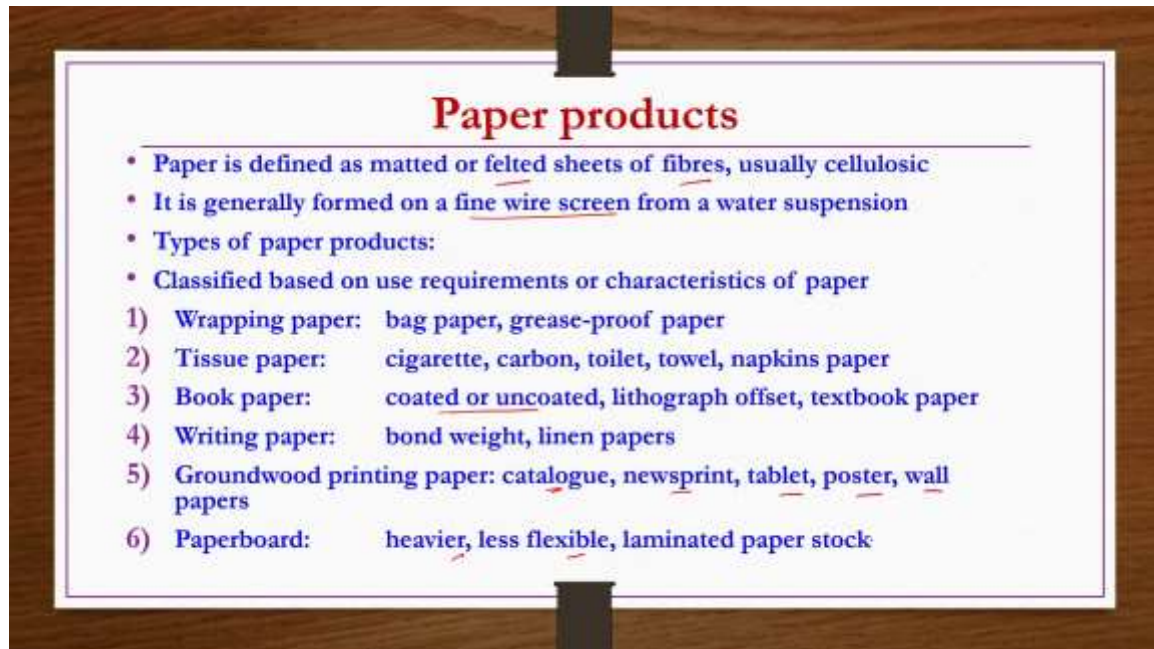
Then we have also discussed about major engineering problems which include like choice of processes like whether should you go for the sulphate process or sulfite process.

Obviously, sulphate process is better compared to the sulfite process because of the environmental concerns and then more economics or more funding required for the purification of the liquor. For those reasons sulfite process is not preferred, sulphate process is preferred. But however recent developments have made advancements in the sulfite process where now the cleaning of the liquor is efficient and then economic. So sulfite process is also used on par with the sulfate process nowadays. Then use of soda process, small batch operation pulp produced by the soda process which is effective, but it produces the low yield and then low-quality paper.

Economics also not good because it is a batch process you cannot use for the continuous process. So, use of soda process is almost not in use nowadays. Then pollution and waste disposal problems like how to dispose the water, etcetera or liquor, etcetera those things will always be there with pulp and paper industries. So, one should be very careful by recovering the chemical that you know discharging can be done. Byproduct utilization also lignin resins and latex, etcetera, gums, etcetera may be there in wood.

So, they should be recovered and then properly processed so that the byproduct utilization may also support the economics of the overall plant.

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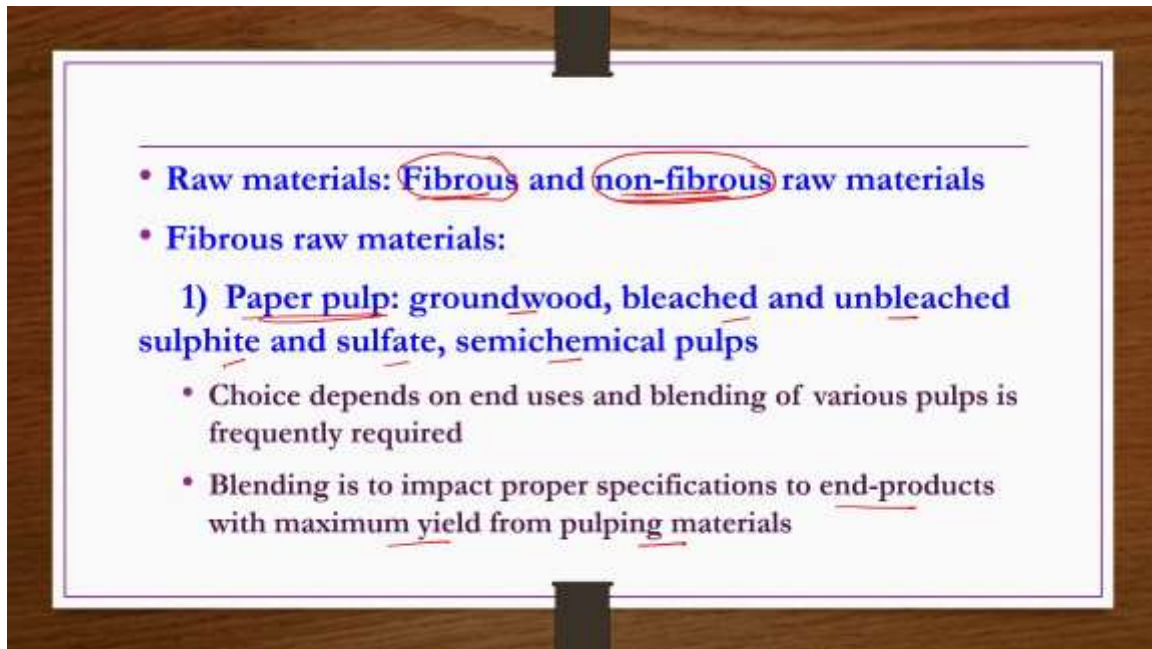


Now in this lecture we will be discussing more about paper products. Paper is defined as matted or felted sheets of fibers. These fibers are usually cellulosic. So how do you get papers? It is generally formed on a fine wire screen from a water suspension.

Types of paper products. These are classified based on requirements or characteristics of paper. Like you know wrapping paper, like something like bag paper, grease proofing paper, etcetera are called the wrapping papers. Tissue papers, cigarette papers, carbon toilet, towel, napkin papers, etcetera all of them are known as the tissue papers. Book paper coated or uncoated, lithograph, offset, textbook paper, etcetera called as book papers. So sometimes some papers are coated with polythene lining, etcetera glassy lining, etcetera some kind of coating is also done.

So, they are known as the book paper. Writing paper like bond weight, linen papers, then ground wood printing paper whatever the pulp that you get from the mechanical process they are used to make a paper for the catalog, newsprint, tablet, poster, wallpapers, etcetera all of them are known as the ground wood printing paper. Paper board like heavier, less flexible, laminated paper stock etcetera are known as the paper board.

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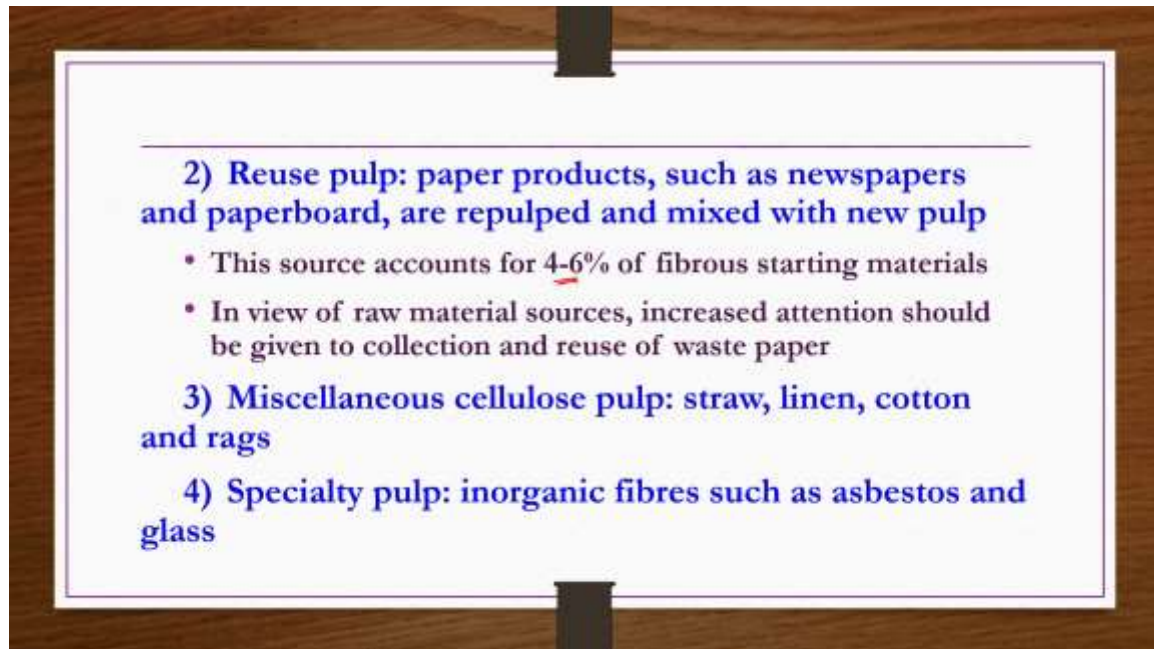


Raw materials for the paper production, fibrous and non-fibrous raw materials are there. Actually, pulp is used to make the paper and then pulp is mostly cellulose, then that cellulose is fibrous. So then why are we calling it requirement of non-fibrous raw material because some fillers sizing kind of thing and then some additives would be there like you know to provide the strength or flexibility, etcetera.

So, some inorganics are being used which are non-fibrous. So that is the reason those things are grouped as non-fibrous raw materials. Under fibrous raw materials, we have the paper pulp as just we discussed as well as in the previous couple of lectures we discussed a lot about pulp. Such pulp whether you get by the groundwood methods, whether it is bleached or unbleached, whether you get it by the sulfite or sulfate process or semi-chemical pulp. So, any pulp can be used for making papers, but only thing that depending on the nature of the pulp, your quality of the paper would be there. So, choice depends on end uses and blending of various pulps is frequently required, unavoidable.

Blending is to impact proper specification to end products with maximum yield from pulping material. Yield as well as the specific requirements of the end products can be met by this blending.

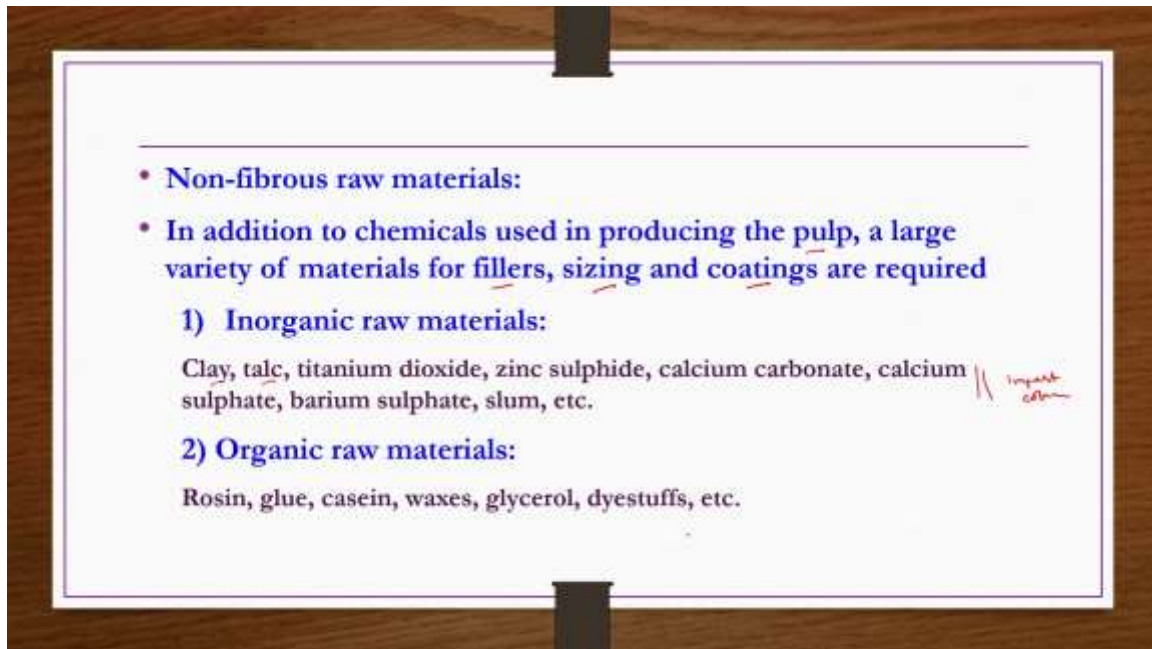
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Second one is the reuse pulp. Newspapers, etcetera are considered as a waste paper after sometimes, right? Like that other office papers, academic institution papers as well as the business paper, corporate papers also, some papers may be there which may not be useful in future. So, such papers are considered as the waste paper and then considering the environmental concerns as well as the not having enough forest resources to get the new raw material for the pulp making so that to make the paper from that pulp, it is better to reuse such kind of waste paper.

It is very essential in the today's context definitely, okay? This source accounts for 4 to 6 percent of fibrous starting materials. In view of raw material sources, increased attention should be given to collection and reuse of waste paper because not enough forest resources are remaining to make pulp as per our wish. So, we have to learn how to reuse the waste paper and then make a new paper from the waste paper. Miscellaneous cellulose pulp like straw, linen, cotton, and rags, etcetera are also used and then there are some specialty pulp like inorganic fibers such as asbestos and glass papers are also available.

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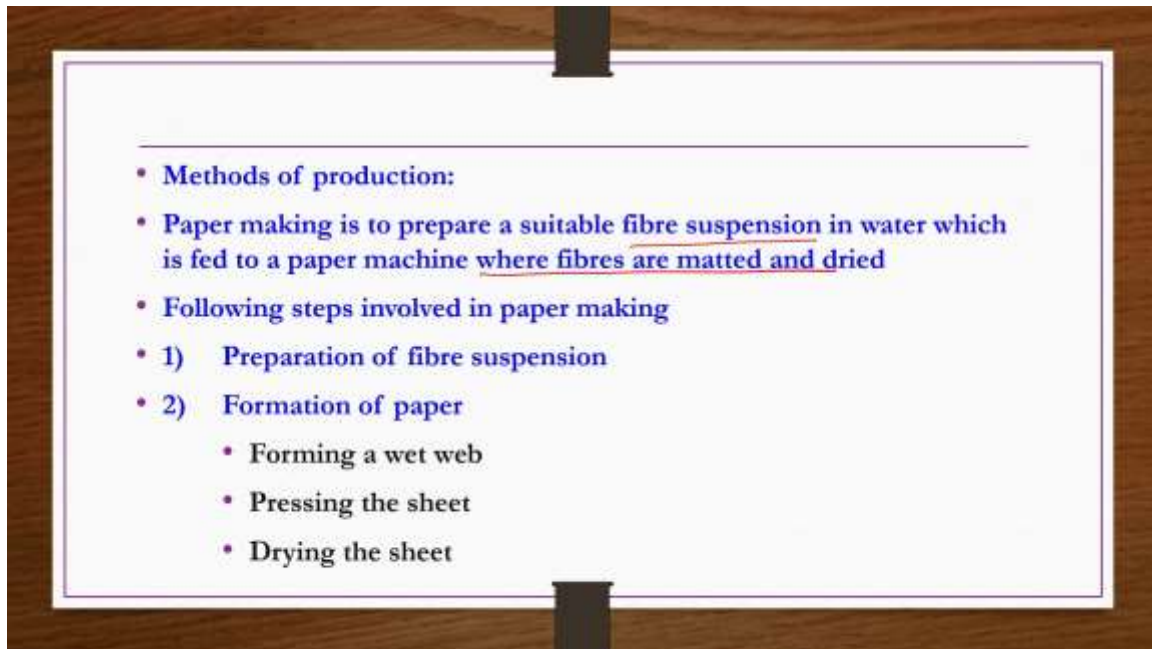


- **Non-fibrous raw materials:**
- In addition to chemicals used in producing the pulp, a large variety of materials for fillers, sizing and coatings are required
- 1) **Inorganic raw materials:**  
Clay, talc, titanium dioxide, zinc sulphide, calcium carbonate, calcium sulphate, barium sulphate, slum, etc. // Impart color
- 2) **Organic raw materials:**  
Rosin, glue, casein, waxes, glycerol, dyestuffs, etc.

Coming to the non-fibrous raw materials, apart from the pulp, there are some kind of fillers and then sizing material, etcetera required. In addition to chemicals used in producing the pulp, large variety of materials are used for fillers, sizing and coatings also, right? They bring some kind of strength or flexibility or colorness or opacity, these kind of different requirements may be there from the end product point of view. Accordingly, the fillers, sizing materials and coatings changes. So, they are both inorganic and then organic type are there. Inorganic non-fibrous raw materials like they include clay, talc, titanium dioxide, zinc sulphide, calcium carbonate, calcium sulphate, barium sulphate, slum, etcetera. Most of them you know impart color, these are you know for imparting color, they are you know some kind of pigments, they are used as pigment to bring some kind of colors for the paper or special kind of appearance to the paper. Inorganic raw materials like rosin, glucose, in waxes, glycerol, dyestra, etcetera are in general used.



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Coming to the methods of production of paper, paper making is to prepare a suitable fiber suspension in water which is fed to a paper machine where fibers are matted and dried that is what happens in the you know paper making. Actually, pulp making is a tough process, once the pulp is there, you know if you have efficient paper making machine, so then work is less in the paper making, okay? Or the plant size wise if you see you know more involvement towards the pulp making is there whereas the paper making side only you know pressing machines are required. So, we are going to see those details from the flow chart anyway. Following steps involved in paper making, preparation of fiber suspension is very important.

Whatever the pulp that you have you know that is insoluble in water actually and then when the material is insoluble in water and then but that water must be used so that to make paper, right? So, this pulp is mixed with water and then made a very dilute pulp mixture and then from there you make the wet paper and you do the drying kind of thing. But the pulp is not miscible with the water, so then proper mixing and then a agitation, etcetera, high shearing kind of action should be provided so that you know uniformity of pulp and water mixture take place. Actually, in the pulp and water mixture 99 to 99.5% is water only, okay? Less than 0.5 to 0.75% pulp is there, okay? Cellulosic pulp is there, okay? For that purpose, preparation of fiber suspension is very essential. How good are you making? How uniform and then refined fiber suspension are you making? Accordingly, that good paper quality you are going to get. Once having the fiber suspension making paper or formation of paper from the fiber suspension is the second step. Within the second step we

have forming a wet web, pressing the sheet, drying the sheets like sub steps are there. So now we are going to see all of them in detail.

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The slide is titled "1) Preparation of fibre suspension". It contains a list of bullet points describing the process. A diagram in the top right corner shows a mechanical disintegrator with a rotating drum and knife attachments. Handwritten red notes are present: "beater" in a circle above the diagram, and "50-60% water" and "10-15% fibre" written next to the list items about slurry composition.

- 1) Preparation of fibre suspension
- Pulp is water slurred to  $\frac{1}{2}$  -  $\frac{3}{4}$  % fibre content by mechanical disintegrators of various designs
- These usually consists of rotating drums with knife attachments or rotating stationary disks to produce viscous shear
- Such operations are called beating and refining
- Fillers are added to the slurry to increase brightness, bulk, flexibility, opacity, softness, and weight of finished paper
- Sizing is an important ingredient often added to the slurry to reduce water of other liquid penetration into certain paper products
- Colouring agents are also mixed into the slurry before processing
- These are generally synthetic organic dyestuffs, but some colouring is done by water-insoluble pigments

Preparation of fiber suspension. Pulp is water slurry to half to three-fourth percent of fiber content by mechanical disintegrators of various designs. Various designs are there. One of the designs usually consists of rotating drums with knife attachments or rotating stationary disc to produce viscous shearing, something look like this.

So, we have a rotating drum to which metal blades etc. are being attached and then once the mixture of pulp and then water comes here, so rigorous mixing takes place because of this rotating drum and then this mixing whatever is there that will provide high viscous shear which is very essential to make a uniform fiber suspension. So, once you make the uniform fiber suspension further refining can also be done by some kind of conical refiners are there. So that will be shown in the flow sheet. So, you use the conical refiners, etc. to make it more refined and uniformed fiber suspension. Such operations are called beating and refining. So, this is an example of a beater. Various designs are there. One design is shown here. Fillers are added to the slurry to increase brightness, bulk, flexibility, opacity, softness, weight of finished paper as per your requirement.

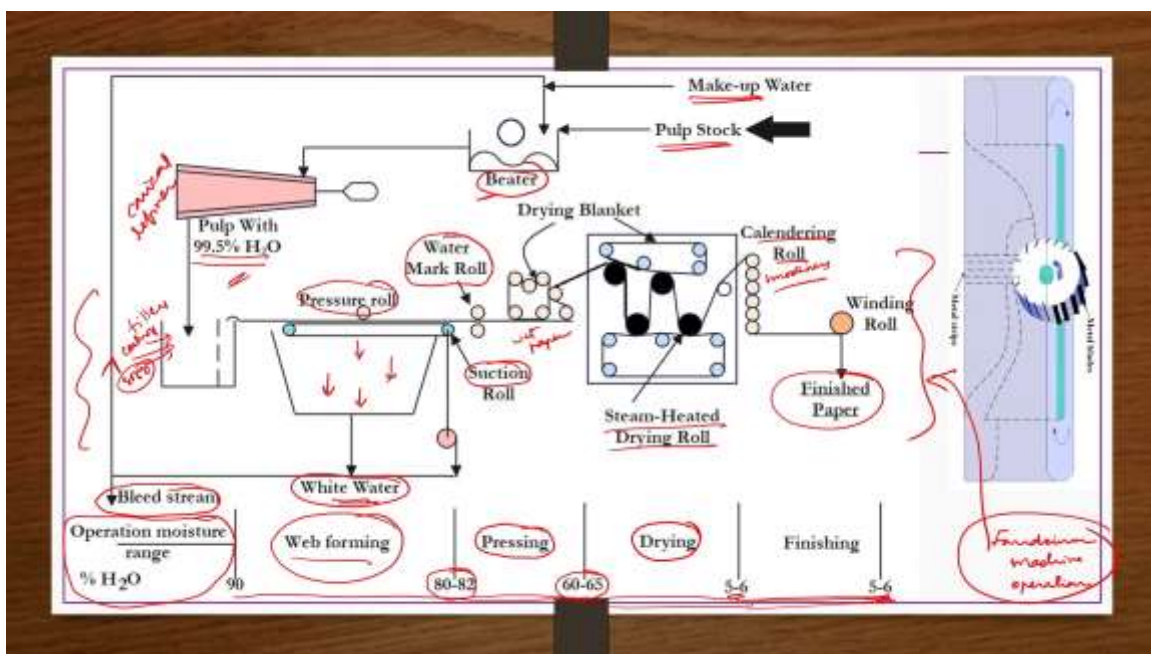
As per the requirement of the end paper, fillers has to be decided. It is not like that all of them are used in all papers. No. Based on the final product requirement you have to select. Then sizing is an important ingredient often added to the slurry to reduce water of other liquid penetration into certain paper products. This also brings strength to the paper and

then usually what you do, starch or polyethylene kind of sizing components are used for this purpose.

All of them are actually mixed with the suspension after making the refined uniform suspension. What you do? You mix filter sizing and then other agents like coloring agents etc. if required, coating agents, etc. required, you mix with them.

Coloring agents are also mixed into the slurry before processing. These are generally synthetic organic dye stuffs whatever the coloring agents are there, but some inorganic water insoluble pigments are also there.

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Now see the flow chart is shown here. So, whatever the pulp is there from the stock that you take to the beater, to the beater you are supplying the makeup water as well as the white water. This white water you can take as per requirement in the beater.

The remaining one you can take it as a bleed stream. So, this beater as I mentioned here it is having rotating drum with knives or blades attached to it so that when the mixture of pulp and water comes, rigorous mixing takes place because of the high shearing action. So, then whatever the uniform fiber suspension, pulp suspension is there that you take to the conical refiner. Further refining of the suspension takes place. If sometimes you know what happens though it looks like uniform, but you know sometimes some fibers may be bigger one and others may be smaller one so that you know sizing refinement would be done in conical refiner and then after that whatever the pulp you get you know that is refined uniform pulp which will be having 99.5% water. To this pulp you can add here the fillers,

then sizing components, then if at all if you wanted to do coating, some kind of coating all of them may be added. The sizing components, etc. sometimes they may be added after making the wet paper.

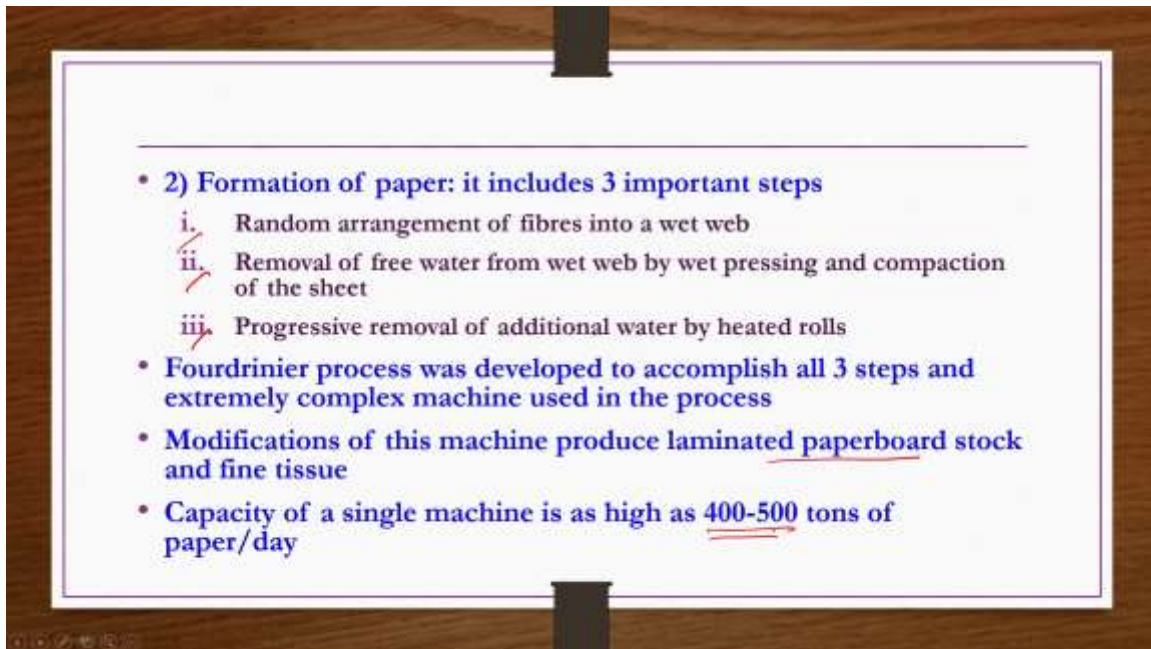
So, it can be added here also. So, this pulp with 99.5% water passes through an endless belt. So where by the gravity water is being separated, sometimes suction also applied to remove the water. So, whatever the water that you are removing here by applying a slight pressure by the pressure rolls as well as by the suction rolls and then as by the gravity whatever the water you remove from the suspension here, so that water we call is white water and that is being recirculated to the meter. So here this process is known as the wave forming process and then by the end of this process water content decreases to 80 to 82% from 99.5%. After this step it will be passed through a mild pressure roll where you know slight pressure may be applied and which we call the pressing stage. So, in this pressing stage there is a possibility of water marker rolls requirement if you are making bond paper or watermarking on the paper. So that should be done at this stage. So, this stage is known as the pressing, some slight drying also done by drying blanket.

By the completion of the pressing stage water content decreases to 60 to 65%. After this material whatever the wet paper actually after this process whatever you get you almost get like a wet paper. That wet paper passed through series of steam heated drying rolls where drying takes place and then by the completion of the drying process water content decreases to 5 to 6%. So that means almost by the end of drying you have the complete paper but there may be some kind of non-uniformity or you may be requiring to bring more smoothness to the paper. So, then you can do this calendering rolls may be used in which smoothness of the paper may be brought in by passing these rolls. After this whatever the paper is there that you can do the winding and then get the finished paper.

So finished paper also water content is 5 to 6%. Actually, whatever the operation moisture range water percentage shown here. So, in the wave forming operation 90 to 80, 82% water reduced and the water content reduced from 90 to 80, 82%. In the pressing operation water content or moisture content reduced to from 80 to 60%. In drying operation, it is further reduced to 5 to 6% from 60 to 65%.

In the finishing there is no water reduction almost but only smoothing is done. So, whatever this process from here this pressing, etc. all this thing is there. So that we call is 4-driner machine operation. So, this is very essential part of equipment. If you have this equipment continuously working and then it can produce a higher ton of paper then you know you can depend on the pulp from the other source and then make the paper using this single machine. Of course, there is a requirement of a beater and then there is a requirement of conical refiner as well. So that to make the fiber suspension more and more uniform and refined.

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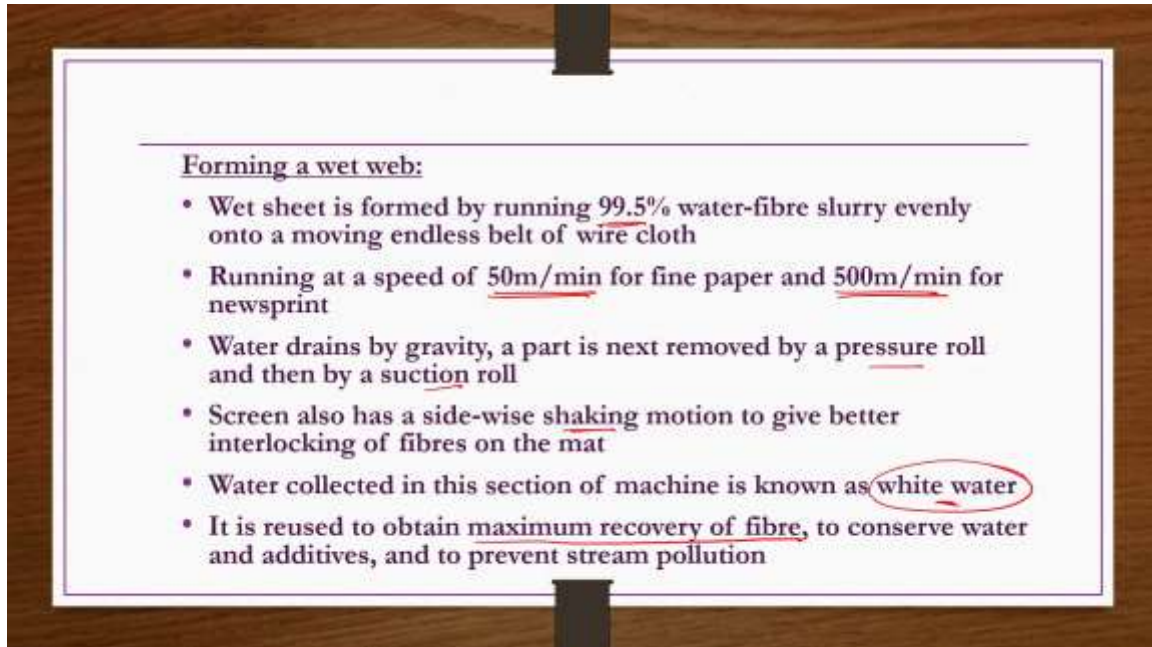


Second step of the paper formation as we have already seen in the flow chart is the formation of paper. It includes 3 important steps, random arrangement of fibers into a wet web, then removal of free water from wet web by wet pressing and compaction of the sheets, progressive removal of additional water by heated rolls. So, 4-driner process was developed to accomplish all 3 steps whatever required are shown here and extremely complex machine used in the process. The process looks simple but the machine is very complicated because you know paper thickness is very small.

So how much cap should be there between the drums? Those calculations are also very sensitive. Modification of this machine produce laminated paper board stock and fine tissues. Capacity of single machine is in general 400 to 500 tons of paper per day.



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Forming a wet web:

- Wet sheet is formed by running 99.5% water-fibre slurry evenly onto a moving endless belt of wire cloth
- Running at a speed of 50m/min for fine paper and 500m/min for newsprint
- Water drains by gravity, a part is next removed by a pressure roll and then by a suction roll
- Screen also has a side-wise shaking motion to give better interlocking of fibres on the mat
- Water collected in this section of machine is known as white water
- It is reused to obtain maximum recovery of fibre, to conserve water and additives, and to prevent stream pollution

Under the forming of wet web, wet sheet is formed by running 99.5% water fiber slurry evenly onto a moving endless belt of wire cloth running at a speed of 50 meters per minute for pine paper and then it can go to the higher speeds like you know 500 meters per minute for a newsprint as well whatever that endless belt is there.

Such high speeds it can run and then it can run as low as 50 meters per minute. Water drains by gravity; a part is removed by the pressure roll and then by suction roll and then further to make connectivity of the fiber what you do whatever the screen is there that is sideways shaking of the screen is done. Whatever collected in this section of machine is known as the wet water. Remember all these 3 steps whatever we are discussing about the forming of wet web and then drying of the paper and then finishing of the paper, etc. All that done by the one single machine, 4 drinder machine. This white water is reused to obtain maximum recovery of fiber to conserve water and additives and to prevent stream pollution.



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Pressing the wet sheet:

- Wet paper sheet containing about 80% water is fed via felt roll to the press section
- In this section, water is removed by mild pressure to reduce content to 60-65% water
- Bond or water mark, if needed, is formed on the sheet during the pressing

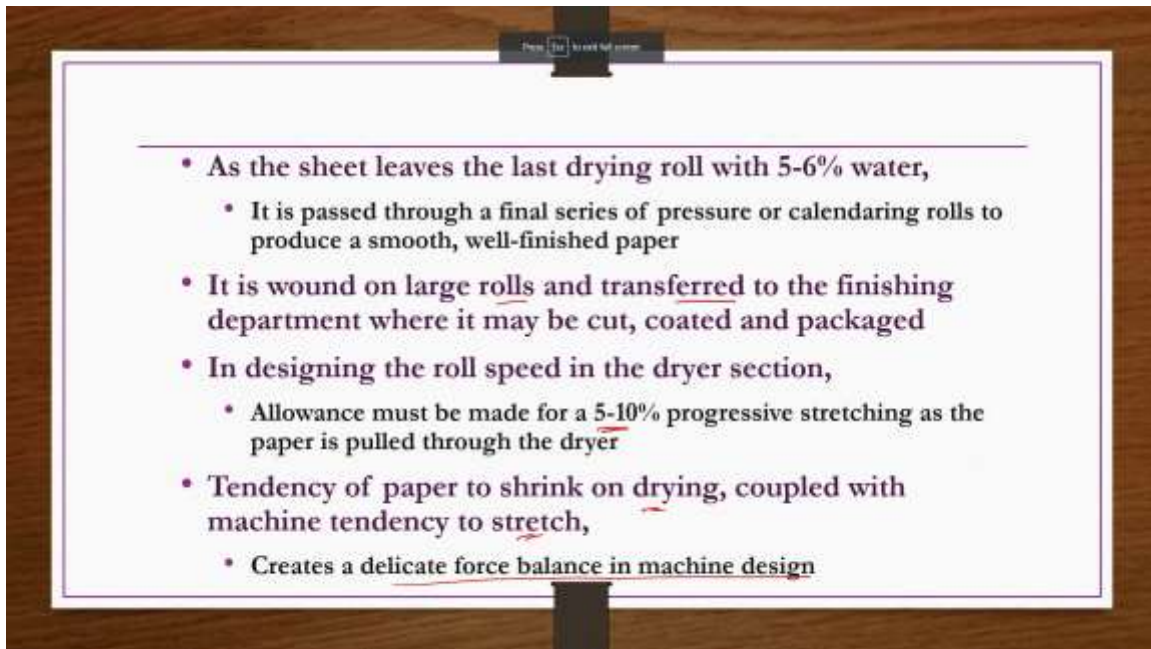
Drying the sheet:

- Sheet from press section has insufficient strength to carry its own weight
- It is passed through smoothing rolls, then a series of steam-heated metal cylinders
- In these cylinders, heat and moisture are transferred to a felting or canvas belt running on top of the paper
- Paperboard is dried directly without a felt

Pressing the wet sheet, wet paper sheet containing about 80% water is fed by a felt roll to the press section. In this section water is removed by mild pressure to reduce content to 60 to 65% water. Then bond or watermark if needed is formed on the sheet during the pressing as we have already discussed in the flow chart. Final step is the drying the sheet. Sheet from the press section has insufficient strength actually though the paper is ready but it is not having insufficient strength to carry its own weight.

So, it is required to do further drying. For that purpose, it is passed through smoothing rows then a series of steam heated metal cylinders. In these cylinders heat and moisture are transferred to a felting or canvas belt running on top of the paper. Paper board is directly dried without a felt in general. If you are making paper board so then this felting or drying by felt is not required.

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As the sheet leaves the last drying roll it will be having 5 to 6% water. It is passed through a final series of pressure or calendaring rolls to produce a smooth well finished paper. It is winded on a large rolls and transferred to the finishing department where it may be cut, coated and packaged. In designing the roll speed in the dryer section allowance must be made for 5 to 10% progressive stretching as the paper is pulled through the dryer because most of the drying whether it is wet paper making section or pressure compaction section or drying section the material is passing between the rotating drums or rolls. So, the how much allowance is to be given that is very essential and then up to 5 percent is minimum required.

Sometimes up to 10 percent is also required. Tendency of paper to shrink on drying and coupled with machine tendency to stretch two operations opposite are there. So, it creates a delicate force balance in the machine design. So, the design of this machine is very complicated. If we are having indigenous machine which can run continuously to produce hundreds of tons per day of the paper so then paper industry would definitely be progressing better.

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- **Recent improvements in paper making:**

- 1) **Increase in wet-strength of paper products:**

- Sizing of paper with dialdehyde starch and the use of newer types of resin and plastics such as polyethylene is
      - Responsible for the increased use of paper products under varying conditions
      - It is true particularly in Kraft-type paperboard

Recent improvements in paper making increase in wet strength of paper products actually wet paper whatever is there it is not having sufficient strength.

So, for that purpose sizing of paper with starches like dialdehyde starch and plastic such as polyethylene are used. Newer types are also using resins also. This sizing is responsible for the increased use of paper products under varying condition because it is producing the or it is making the process to produce of varying conditions. So then obviously use of such paper is increasing. It is true particularly for Kraft type paper boats only.

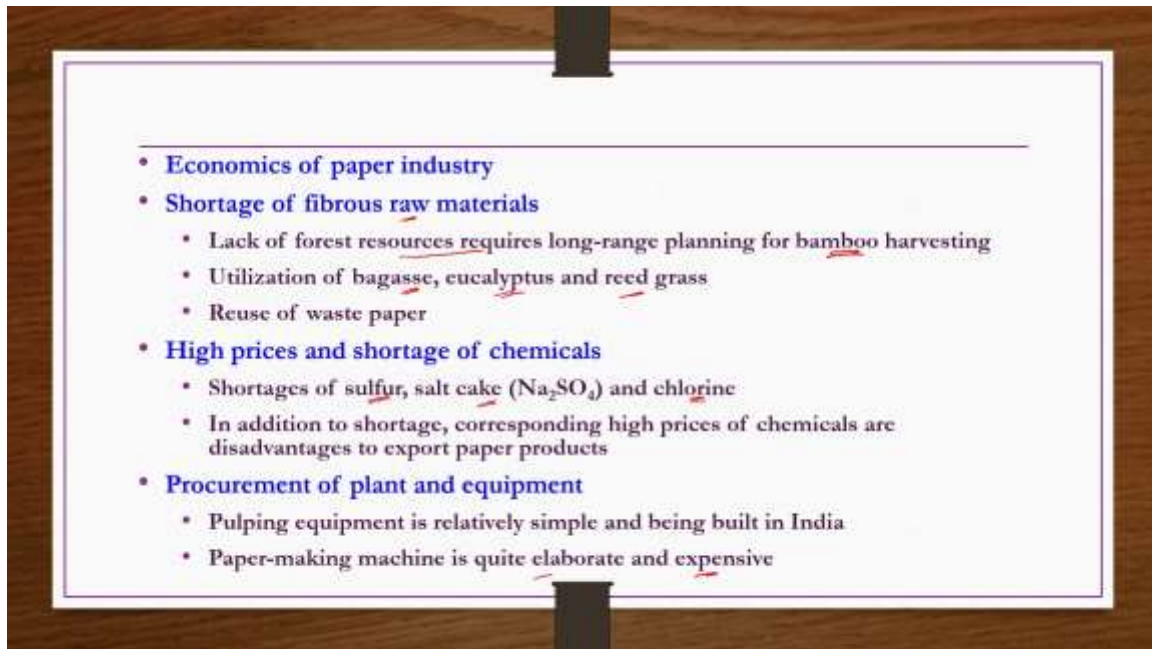
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## 2) Modification in paper machines to improve properties of paper

- Research is constantly being done to improve tensile strength of paper
- For this, a rubber belt before the pressing rolls incorporated which can be varied in degree of elongation
- By changing to a less-stretched condition at the end of the operation, the fibres on the wet web can be
  - Compressed and intertwined to give vastly improved strength on the final paper

Second one is modification in paper machine to improve properties of a paper. Research is constantly being done to improve tensile strength of paper. For this purpose, a rubber belt before the pressing rules incorporated which can be varied in degree of elongation by changing to a less stressed conditions at the end of operation the fibers on the wet web can be compressed and intertwined to give vastly improved strength on the final paper. So, such kind of improvements are going on and then more and more research anyway obviously keep continuing. So whatever discussed things are there they are basically fundamentally required information at the UG level of the course.

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Economics of the paper industry can be affected by 3 important sources or 3 important factors. First one is the shortage of fibrous raw materials. Second one is high prices and shortages of chemicals. Third one is procurement of plant and equipment. Raw materials as we have already seen the lack of forest resources requires long range planning for bamboo harvesting because it is better and it is mostly used for paper making. However, alternatives like you know use of bagasse, eucalyptus and then reed grass also as raw materials is essential and most importantly as mentioned previous lecture as well as now reuse of the waste paper because nowadays so much of paper is being used.

So, at the same rate if you are producing paper by cutting the plants, trees, etc., you know we are going to have the disastrous situation especially environmentally. So, we have to reuse and then make approximately 60 percent of the paper demand by reusing the waste paper. So, we have to meet approximately 60 percent of today's paper requirement by reusing the waste paper for the production of such new papers. Chemicals also like you know we do not have indigenous sulphur.

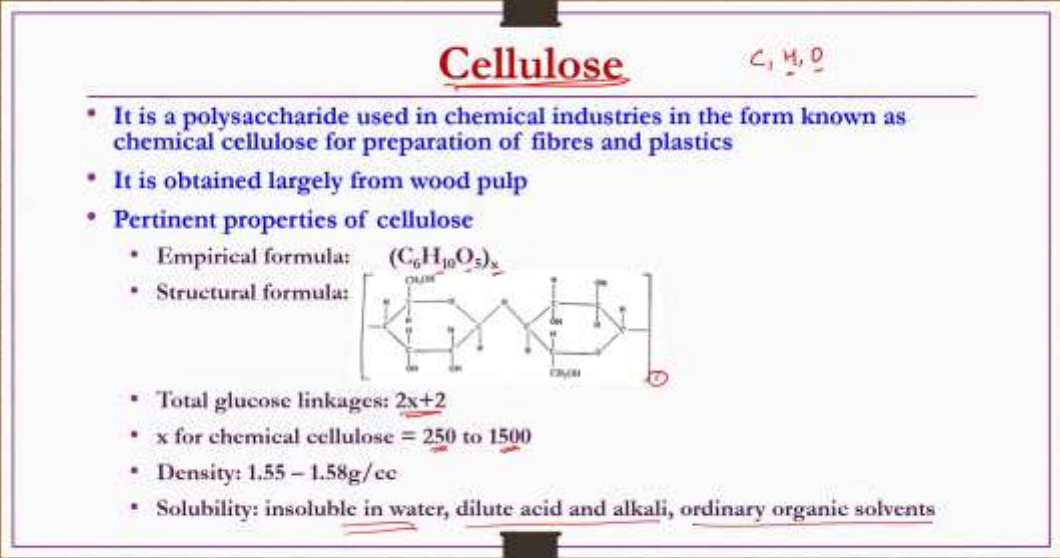
So, shortages of sulphur and then other salt, cake like  $\text{Na}_2\text{SO}_4$  and chlorine you know there is a shortages. So also, if you are let us say sulphur, etc., you are importing. You convert that one into the Indian rupee. So then corresponding high prices of chemicals you can realize.

So, these are very disadvantages because of that one we are not able to export much and much paper to the other countries. Procurement of plant and equipment. Pulping equipment is relatively simple and it is being built in India but paper making machine, fortrane

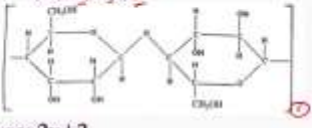


machine, etc., is quite elaborate and expensive as already discussed. So, if we can make such kind of machines ourselves and then run the process continuously then there would not be setback for the paper industry.

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**Cellulose**  $C_6H_{10}O_5$

- It is a polysaccharide used in chemical industries in the form known as chemical cellulose for preparation of fibres and plastics
- It is obtained largely from wood pulp
- Pertinent properties of cellulose
  - Empirical formula:  $(C_6H_{10}O_5)_x$
  - Structural formula: 
  - Total glucose linkages:  $2x+2$
  - x for chemical cellulose = 250 to 1500
  - Density: 1.55 – 1.58g/cc
  - Solubility: insoluble in water, dilute acid and alkali, ordinary organic solvents

Last part of the lecture is the cellulose because cellulose whatever is there that is nothing but the commercial pulp or the pulp is nothing but commercial cellulose, okay? It is polysaccharide used in chemical industries in the form known as chemical cellulose for preparation of different types of fibers and plastics.

It is obtained largely from wood pulp. Actually, when we are discussing about sugar and starch industry, we understood that cellulose is a carbohydrate. It is having only C, H and O and then H and O also in such a ratio that the number of H atoms are there. They are twice the number of O atoms like pertinent properties of cellulose, empirical formula like  $C_6H_{10}O_5$ .

If 5 O's are there, 10 H atoms are there. So, it is a carbohydrate and then there are only C, H and O only. No other elements are there. So, it is a carbohydrate but it is a polymerized. So, several units are there. Structural formula if you see, this is the structural formula and then it is being repeated, next time repeated.

Total glucose linkage is  $2x$  plus 2 in general. x for chemical cellulose is in general 250 to 1500. Density is 1.55 to 1.58 gram per cc in general. Solubility it is insoluble in water, dilute acid and alkali, ordinary organic solvents. It is insoluble in all of them actually.



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- **Preparation of chemical cellulose:**
- **Process choice is either sulphite process or sulphate process as summarized earlier in the tabular column**
- **However, following modifications are required**
  - Sulphite process with longer digestion times (9 – 10hrs.)
  - Sulphate process modified by subjecting the chips to a prehydrolysis using acidic high temperature conditions
- **Principal requirement is pulp with**
  - Better bleachability and less ash, lignin and pentosans than paper grade pulp

Now we discuss about preparation of chemical cellulose. Process choice is either sulphite process or sulphate process as we already discussed for the pulp making. Either of the process we can make but there may be slight modification. What are those we discussed now. Let us say in the sulphite process you know you need to go for the longer digestion times 9 to 10 hours, etc. If you have sulphate process, then you have to modify what kind of modification by subjecting the chips to pre-hydrolysis using acidic high temperature conditions.

You have to use acid and then high temperature conditions for the pre-hydrolysis. Once you do the pre-hydrolysis, then you do digestion, so then you get the better chemical cellulose. Principle requirement is pulp with better bleachability and less ash, lignin and pentosans than paper grade pulp. In the paper pulp allowed level of ash, lignin, pentosans, etc. are there compared to that one much less should be present in the case of a chemical cellulose.

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- Chemical pulp is bleached with chlorine as with paper pulp
- However, caustic bleaching is done at  $95^{\circ}\text{C}$  to increase the insoluble  $\alpha$ -cellulose content to 92-95%
- This is major purification step since a very high  $\alpha$ -cellulose content is mandatory in chemical cellulose products
- Bleaching with hypochlorite, then  $\text{ClO}_2$  followed by drying is carried out as in the paper pulp operations

Chemical pulp is bleached with chlorine as with paper pulp as we have discussed already. However caustic bleaching is done at 95 degrees centigrade to increase the insoluble alpha cellulose content to 92 to 95%. This is major purification step since very high alpha cellulose content is mandatory in chemical cellulose products because of that one this purification is very much essential. Bleaching with hypochlorite, then chlorine dioxide followed by drying is carried out as in the paper pulp operations more similar to that one. In fact, whatever the paper pulp processes, sulphate or sulphite processes are there, same processes you can use with little modification as mentioned. In the sulphite process, you have to do digestion for little longer time whereas in the sulphate process you have to do pre-hydrolysis using the acid and then high temperature conditions.

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- End uses: primarily as cellulose fibres and for cellulose derivatives as described below:
- Cellulose fibres: Rayon
  - Chemical cellulose can be prepared in the form of fibres called rayon
  - Principle involved is to solubilize the cellulose using cuprous ammonia or CS<sub>2</sub>-NaOH
  - Then precipitate the cellulose in acid solutions while spinning a filament of regenerated cellulose

End uses primarily chemical cellulose is used as cellulose fibers and for cellulose derivatives, different derivatives are there. Most of derivatives are either esters or ethers, we are going to discuss them. Let us see first cellulose fibers in which we start with rayon. Chemical cellulose can be prepared in the form of fibers called rayon. Principle involved is to solubilize the cellulose using cuprous ammonia or CS<sub>2</sub>NaOH, carbon disulphide, NaOH mixture or cuprous ammonia you can take, solubilize the cellulose, then precipitate the cellulose in acid solutions while spinning a filament of regenerated cellulose. Simple process, first you have to take the chemical cellulose, solubilize it with cuprous ammonia or a mixture of carbon disulphide and NaOH, then whatever material is there that you have to precipitate using acid solutions and then whatever the slurry that you will get that you have to do this spinning into filament of regenerated cellulose. That spin regenerated cellulose whatever is there that is nothing but the rayon.

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- Cellulose derivatives:
- All commercial derivatives of cellulose are compounds in which cellulose has reacted as an alcohol, giving rise to ester and ether linkages
- Thus primarily cellulose derivatives are either cellulose esters or cellulose ethers as detailed below
- Cellulose esters: can be inorganic or organic
  - Inorganic: nitrate (nitrocellulose): replacement of some of the hydroxyl groups by  $-\text{ONO}_2$
  - Low  $\%N$  nitrocellulose (10.7 – 11.2%N) is used for lacquers
  - Intermediate (11.2 – 12.5%N) for films, particularly movie-type film
  - High (12.5 – 13.5%N) for smokeless powder

Coming to the cellulose derivatives, all commercial derivatives of cellulose are compounds in which cellulose has reacted as either an alcohol giving rise to either twisters or ether linkages, those things we see. Thus, primarily cellulose derivatives are either cellulose esters or cellulose ethers. First, we see cellulose esters, they can be inorganic or they can be organic as well. In the inorganic category of cellulose esters nitrate or nitrocellulose are there where replacement of some of the hydroxyl groups of chemical cellulose taken place by this functional group  $\text{ONO}_2$ , so that you get the nitrocellulose. In this nitrocellulose low percentage of N is used for the lacquers that is if you have the low percentage of N in the nitrocellulose low in the sense less than 10 to 12 percent of N, then that can be used for the lacquers.

If it is in the intermediate level like 11.2 to 12.5 percent, then this is used for the films particularly movie type films, etc. If it is high 12.5 to 13.5 percent N in the nitrocellulose, then it is used for this smokeless powder. Actually, these percentages are about N content, nitrogen content in the overall cellulose.

Cellulose you know structure it is having you know  $2x$  plus  $2x$  is equals to 250 to 1500 times would be there. So, now, each molecule of the nitrocellulose you are having one N so like that in the chain how many N molecules are there all that percentage if you count it should not be more than you know 12 to 13 percent if it is up to 12 to 13 percent it is considered as high nitrogen cellulose.

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- Organic:
- (1) Acetate: soluble in cheap solvents such as acetone and methyl acetate, has good film and fibre forming properties
- Produced by acetylation of cellulose with a 50 – 50 mixture of acetic acid – acetic anhydride using H<sub>2</sub>SO<sub>4</sub> catalyst
- Reaction conditions are room temperature for 5 – 8hrs
- Cellulose acetate is precipitated by dilution with water, then centrifuged and dried
- Solution in acetone and spinning in moist, warm air forms cellulose acetate fibre or acetate rayons
- Acetate rayon forms 35% of rayon market Term

Coming to the organic cellulosic esters acetate or cellulose esters are the mostly used one. These are soluble in cheap solvents such as acetone and methyl acetate has good film and fiber forming properties. We are not going into the production process of all these things because that is out of the scope of the so we are taking them and then we are trying to understand their end uses.

These are produced by acetylation of cellulose with 50-50 mixture of acetic acid, acetic anhydride using sulfuric acid catalyst. Reaction conditions are room temperature and then reaction is taking place for 5 to 8 hours then you can get this cellulose acetate. Cellulose acetate is then precipitated by dilution with water then centrifuged and dried. Reactions are simple steps are there so we are not going by flowchart. Solution in acetone and spinning in moist warm air forms cellulose acetate fiber or acetate rayons.

Acetate rayon forms 35% of rayon market that much market is there for the acetate rayon it 35% of rayon market that means very high. So, these particularly important from the textile industry point of view, but we are not going to the details of their manufacturing process.



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- (2) propionate
- (3) butyrate
- (4) combination of acetate (1) and propionate (2); or acetate (1) and butyrate (3)
- These are prepared by mixtures of corresponding acids or anhydrides
- Have better film forming properties
- However, these are somewhat more costly than the acetate alone

Other organic cellulosic esters are propionates, butyrates are the combinations of acetate and propionate or the combination of acetate and butyrate. These are prepared by mixture of corresponding acids or anhydrides as we have discussed in preparation of cellulose acetates.

They have better film forming properties. However, these are somewhat more costly than the acetate alone. So, acetate rayon that is the reason it is having more market because it is making up for that acetate rayons is commercially more viable and profitable.



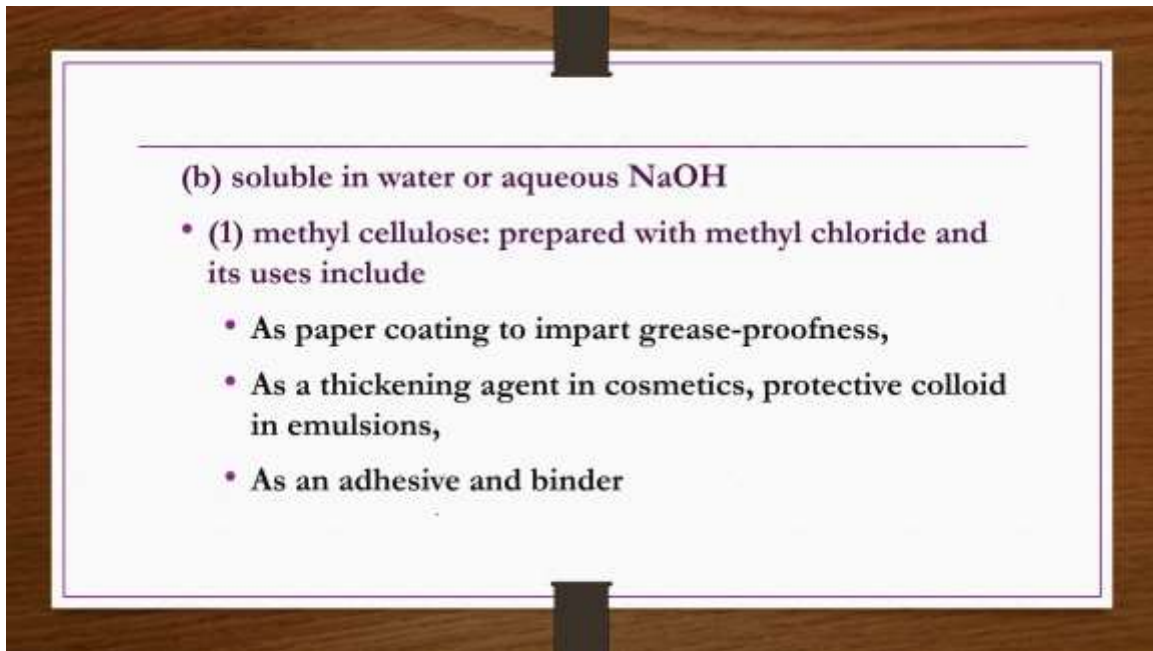
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- **Cellulose ethers:** can be two types; soluble in organic solvents or soluble in water or aqueous NaOH
  - (a) soluble in organic solvents:
    - (1) ethyl cellulose: prepared with ethyl chloride
    - $R \cdot OH(\text{cellulose}) + NaOH \rightarrow R \cdot ONa + H_2O$
    - $R \cdot ONa + C_2H_5Cl \rightarrow R \cdot OC_2H_5(\text{ethyl cellulose}) + NaCl$
    - Ethyl cellulose is used in plastic and lacquer compositions
      - Because of its compatibility with plasticizers and resins, strength, flexibility and ultraviolet stability
    - (2) benzyl cellulose

Next one is the cellulose ethers category or the other type of cellulose derivative is the ether type that is cellulose ethers. They can be 2 types soluble in organic solvents or soluble in inorganic aqueous NaOH or water. Soluble in organic solvents we have ethyl cellulose prepared with ethyl chloride where the reaction is this one.

Cellulose react with sodium hydroxide to give the sodium salt RNa or the ester cellulosic ester sodium acetate. This RNa is nothing but the sodium ester of the cellulose. This will further react with the ethylene chloride to get ethyl cellulose which is soluble in organic solvents. Ethyl cellulose is used in plastic and then lacquer compositions because of its compatibility with plasticizers and resins strength flexibility and then stability etc. Other type of cellulose ether is benzyl cellulose which is also soluble in organic solvents.

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(b) soluble in water or aqueous NaOH

- (1) methyl cellulose: prepared with methyl chloride and its uses include
  - As paper coating to impart grease-proofness,
  - As a thickening agent in cosmetics, protective colloid in emulsions,
  - As an adhesive and binder

Coming to the cellulose ethers which are soluble in water or aqueous NaOH or methyl cellulose prepared with a methyl chloride and its uses include as paper coating to impart grease proofing etc. as thickening agent in cosmetics protective colloid in emulsions as an adhesive and binder.

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- (2) sodium carboxymethyl cellulose
- $R \cdot OH(\text{cellulose}) + NaOH \rightarrow R \cdot ONa + H_2O$
- $R \cdot ONa + ClCH_2COO \cdot Na \rightarrow R \cdot OCH_2COO \cdot Na$  (sodium chloroacetate) +  $NaCl$
- Properties: high viscosity in dilute solutions, good film-forming, non-toxic, compatible with direct and acid dyes
- Used as thickener in foods, emulsion stabilizer, adhesive

Other one is the sodium carboxymethyl cellulose which is also soluble in inorganics like NaOH solution or water. Reaction is that whatever the cellulose ester that reacts with NaOH to give R<sub>ONa</sub> which further react with ClCH<sub>2</sub>COONa to give sodium chloroacetate which is nothing but sodium carboxymethyl cellulose. Properties, high viscosity in dilute solutions, good film forming, non-toxic, compatible with direct and acid dyes, compatible with acids directly as well as with the acid dyes. Used as thickener in foods, emulsion stabilizers, adhesives, etc.

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- (3) hydroxyethyl cellulose



- Used as textile finish by acid precipitation from alkaline solution
- Other uses same as sodium carboxymethyl cellulose

Hydroxyethyl cellulose is the other one, the reaction is the cellulose react with the ethyl oxide to give the hydroxy ethyl cellulose used as textile finish by acid precipitation from alkaline solution.

Other uses same as sodium carboxymethyl cellulose as we discussed in the previous slide. This is all about the cellulose and then derivatives and then with this we complete the chapter on pulp and paper industries.

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The references for the today's lecture as well as the previous 2 lectures on pulp and paper industries are provided here. However, primarily most of the lecture notes is prepared from these 2 reference books. Thank you.