INDIAN INSTITUTE OF TECHNOLOGY DELHI

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NPTEL PROGRAMME ON
TECHNOLOGY ENHANCED LEARNING

Video Course on
Advanced Textile Printing Technology

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Lecture # 4
Thickeners

So continuing with our journey with the printing technology, anyway remember what we are doing is we are trying to approximately you know recall what you may have learned during the undergraduate education, and maybe sometimes a few things would come up which may be of interest but it's all a recall.

So till the last time what have we done?
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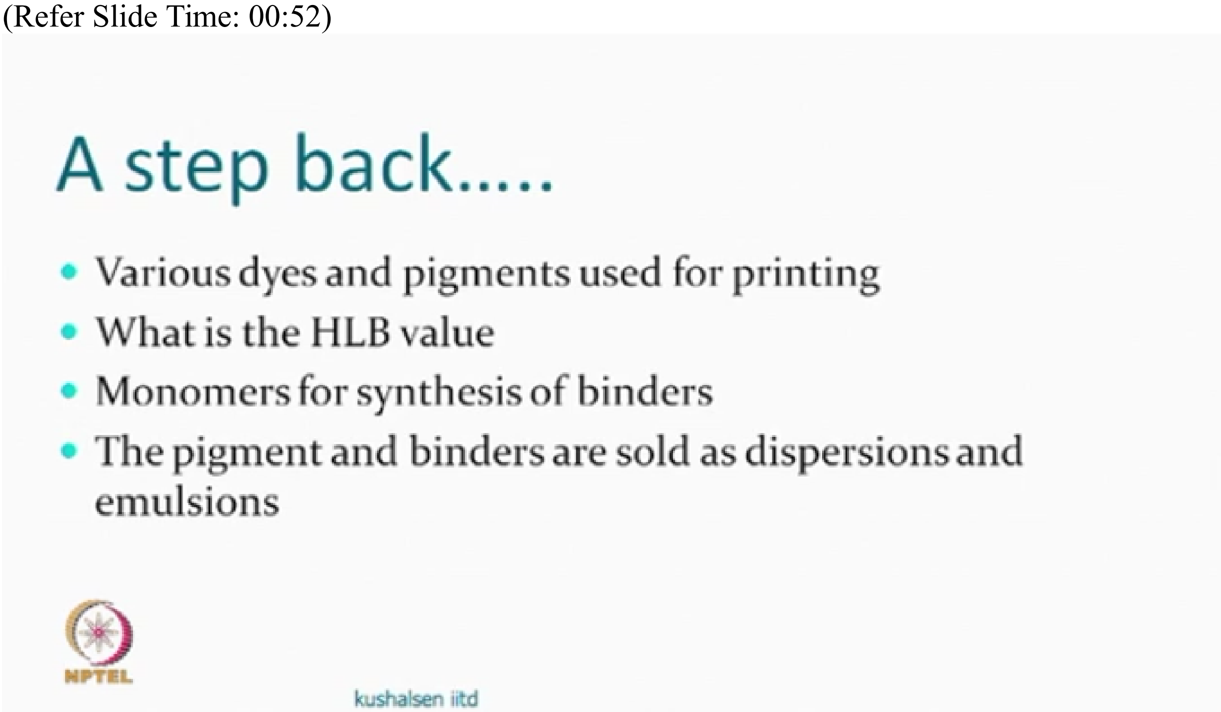

We have learned about the dyes and pigments that can be used for printing and what should be approximately difference that they, which makes the most suitable for printing, the pigments and binders are generally available in dispersion or emulsions and therefore you have to use some surface active agents and which would have what we call as HLB value, hydrophilic lipophilic balance.

And we also looked at some of the monomers which can be used as binders particularly for pigment printing, so we will spent sometime today on thickeners which you are familiar, we just revise a few things which may make it more interesting, so why thickeners?
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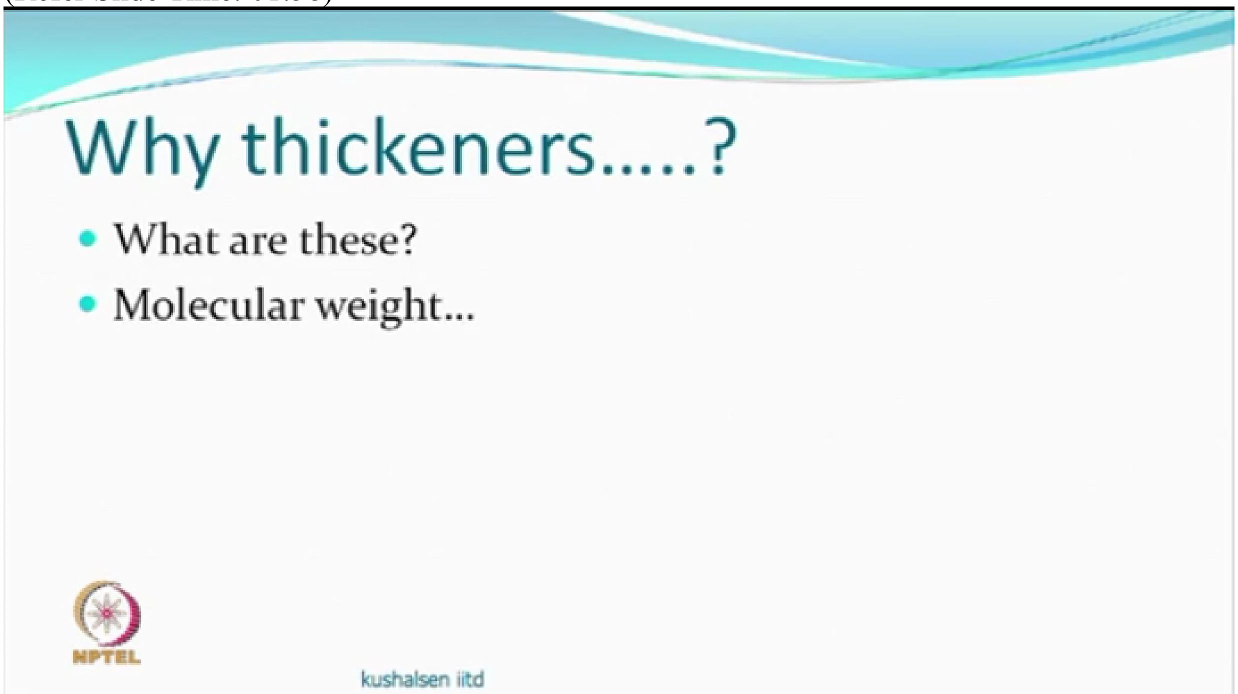

Because we believe that we are going to be working on a design and so we have a constraint, and the constraint is that the colour should not spread out of a certain area, and so we make a colour paste mixed them into some type of a thickener which is also a paste,
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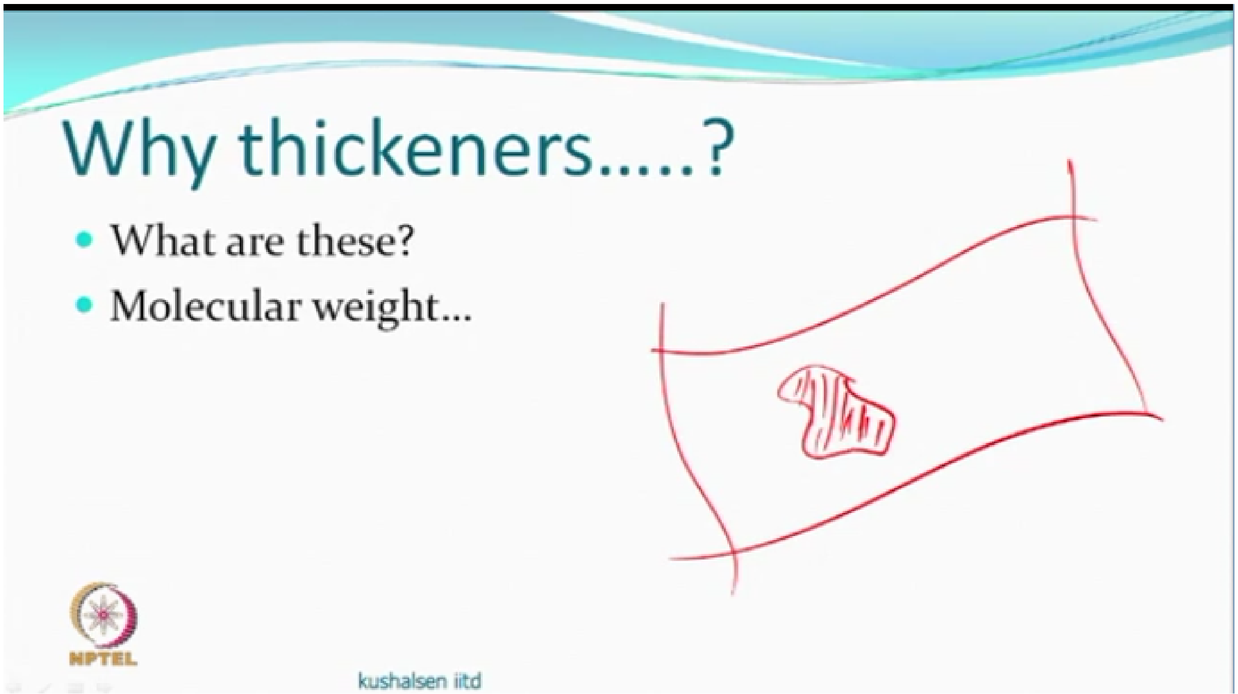

so we take a thickener, add a colorant and then make a paste and work around, because we don't want this boundary to be crossed, that is one aim, but that you can appreciate.

Finally on the fabric there will not be any thickener, and if there is no thickener then therefore you have certain expectations from a thickener that it should be behaving in a certain manner, and therefore one finds that there are too many limitations come, so what are these normally? They are polymeric compounds, so polymeric compounds so they are long chain things like the fibres also are polymeric compounds, but obviously they may not be suitable for making fibres, so they may be brands sometimes, and so they may not be suitable, but also we are expecting at the end is that they should get away from this area after my job is done which is called fixation, so after the fixation is done these type of materials and anything which has been added to them must get out, so all the things like acids and salts and deforming agent and wetting agents, they are easy to wash off, alright, but the moment polymers are added they are not easy to wash off because they are soluble, they dissolve also very with the little of hard work, and therefore they come out also with little bit of hard work, and so this selection of some of the polymers which can be used as thickeners, people have tried lot of compounds that just one.

Then we have the molecular weight, so the molecular weight is important because it can change viscosity, viscosity can be change by two ways, you have a solvent and you add something called the polymer, and keep adding the more is this percent solid, the more is likely to be viscosity, alright, what it means is these molecules are going to be wanting to be free all over the solvent, but as large number of them are available, so that is going to be some restriction in their movement and so the entanglements can happen and also therefore viscosity may change.

And the other is at the same weight also, at the same solid percent if you increase the molecular weight, there is the length of the polymeric chain then also viscosity can increase, because now the same chain maybe entangled with other chains in different places, different points and so resistance to their motion would be felt, so the viscosity were force dependent on the concentration,

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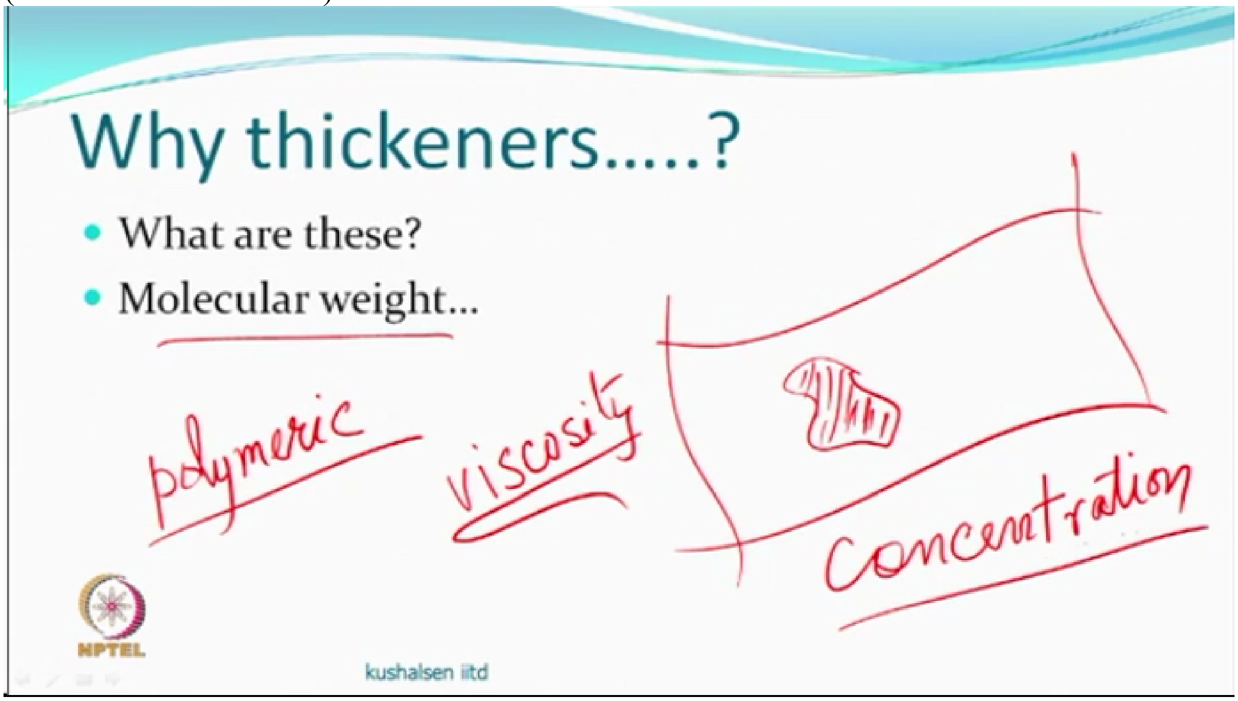

definitely and also on the molecular weight, so if you have natural products automatic difficulty comes, that how do you control the molecular weight, what you buy it today versus what you bought last month, although the chemistry is same, but the molecular weight may not be same, so what you do? So we must evaluate, if you don't evaluate and just use anything then every time whatever you add will give you different viscosities and that can mean a lot of difference.

If the viscosity of this paste which you use a coloured paste and you wanted for a particular design at particular shape goes beyond the limits that you have accepted, then the diffusion area, diffusion crossover from one design to another will also be seen, and so this is not just something which you can say well this is so easy I'll just ask so many grams and so many letters, and everything will be alright, well that's first way to look at it, but you must have some way to evaluate that whatever you have said is same, exactly same, falls in the range which you want to accept or it is different than that, alright.

If it is different than you must take an action, one of the action people will like to take is at the beginning when you buy the material and do the testing before even start printing, and if you find well it is too much of a difference then you might react to you know send back the consignment and if you find there is a difference but we can manage, in that case you must know the difference so the person who's going to make a paste must be told that this particular lot will has to be handled this way, if you have to add less because we found at the same concentration viscosity was high so you have to tell them to reduce, alright, so all that is part of process control, so it is not just that because there is a one chemical every time I'm using same chemical, and therefore everything will be same now true, so natural products obviously naturally have reasons to have different molecular weights, so either the company who sells them controls and then gives you the molecular weight, range is between this to this, because or this molecular weight can also change when you keep storing, you stored the material for a long time depending upon whether it is hydrolysis takes place or any other degradation process takes place the molecular change, so the same weight can give you different viscosity.

And at least we don't have any doubt that a viscosity is different, the print quality will change for good of a bad that's a different story, what will change? So if you say well I have been maintaining a same quality throughout my the whole day, maybe the same design is for the whole week we've been running, then it's not so easy that it appears, therefore maybe time to time you may have to advise if you are in charge that let's check before you apply with everything is alright or not.

So while we have lot of expectations when we start printing with dyes, we definitely have to be there on the fabric, also with some chemical which are not going to be there with the fabric which has been printed, so this quick drying you know, whatever it means is important,
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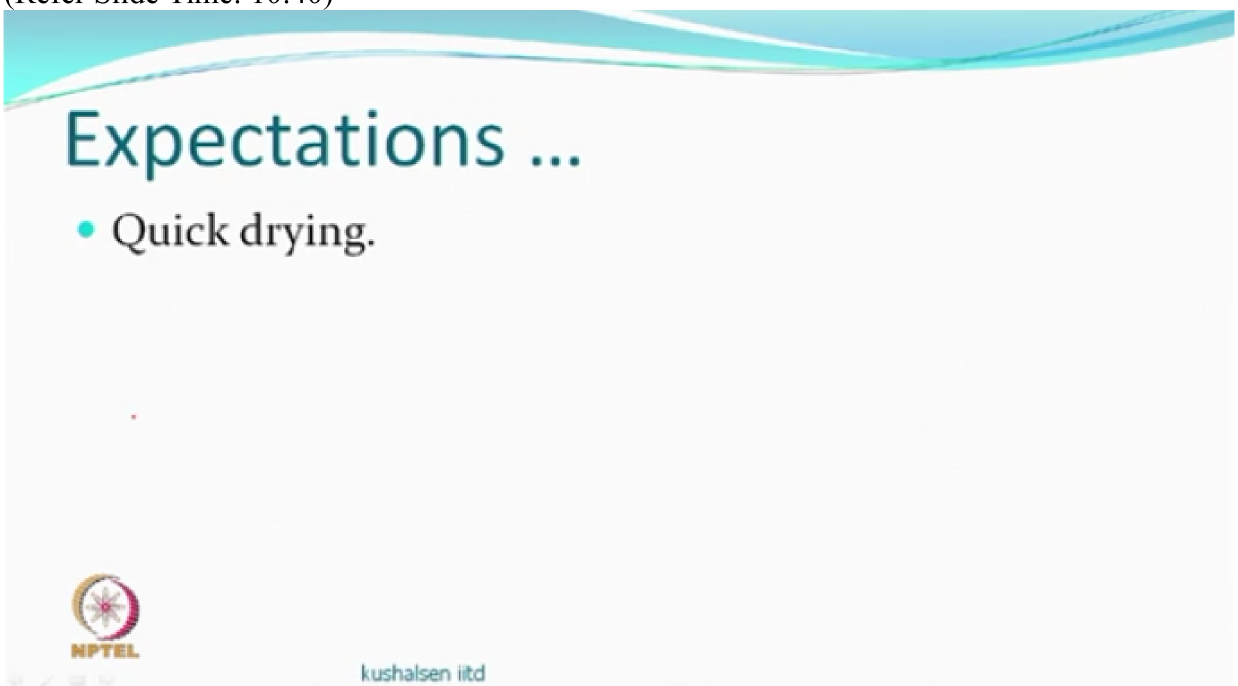

we are quite sure where you will be using aqueous based thickeners, agents which are going to give you viscosity, but invariably it is not one coloured which is printed at one time, so in a same design there are 6 colours, 7 colours and even if you look at a flatbed screen printing machine, so if it is automatic, semi-automatic machine the fabric is moving, so you have printed the yellow colour just as it moves to the next station, the red has to be printed as it moves to the next station, the blue has to be printed, so if this is the one the screen gets lifted the fabric moves the next screen comes then the fabric moves, and our during this process, this quick drying only means that when you put this screen again on a printed area, and then again you lift the already printed design must not get lifted or get stuck to the screen and then gets smudging, so bit of a drying is required, so you may help it, it's quite possible your belt on which the things are moving, the fabric is moving is also heated.

But if suppose it's very highly, it remain highly tacky because the time between the two overlaps is not very high, and so this is an expectation, there whatever you do with the paste and also the process, one design of the other there must be some drying, not fully dried that will happen later after all that colours have been printed, but you still want, it should be not too bad.

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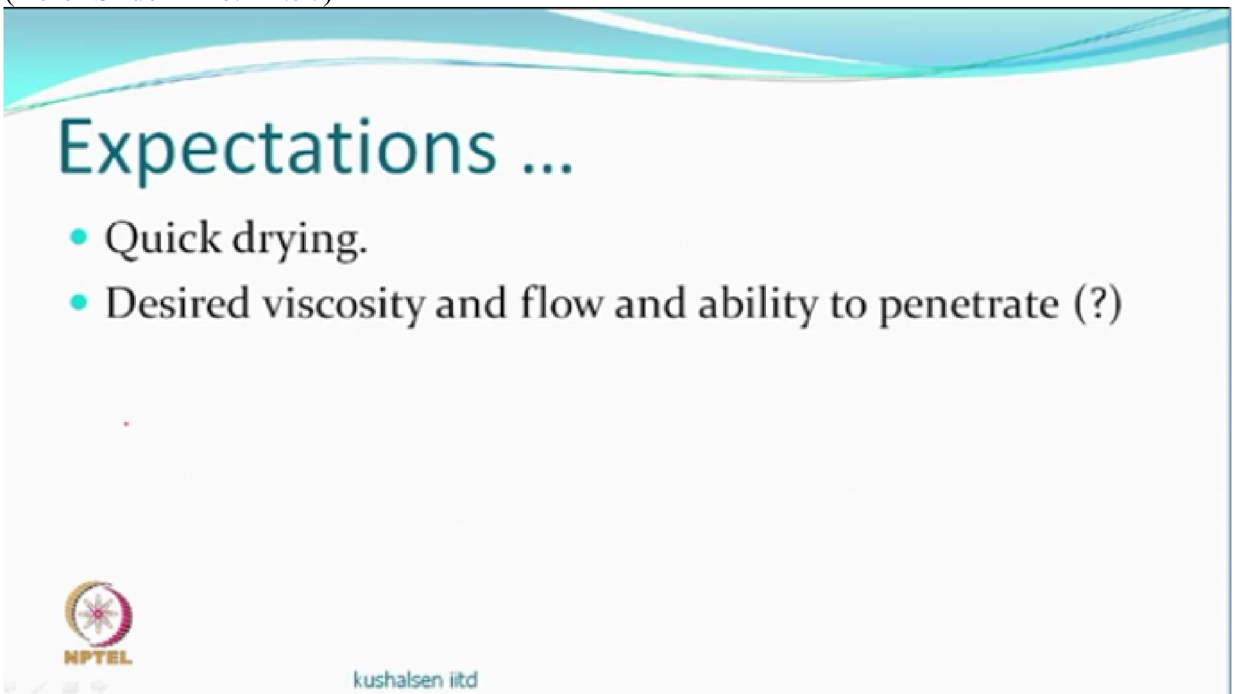

Just what we just talked about that they should have a desired viscosity which we sometime called a printable viscosity and a flow, so let's say screen has a paste and if you lift the screen, the paste doesn't come down, because if that was true then it'll keep dripping, so when does it come down? When you put a squeezy otherwise didn't come down, so there is a flow, so this flow must be maintained and so you can't say that every chemical will behave like this, let's say tomorrow I start printing with the paste of poly PET in some solvent, you might find it doesn't work, something get stuck, alright, so it's also important once the viscosity is there desired then it flows through the screen and then on the textile this should be, flow should be enough that it actually penetrates at least, if not within the fibre in the capillaries between the fibres and the yawns, and it should happen quickly, this is what is expected value of printing.

Actual dye penetration will be during fixation, but it should not happen that it only remains on surface, whole of the textile is just not touched by capillary pressures, capillary forces, the printing paste also should be able to go inside as much as possible, you know, so that between the fibres is moved in, the capillary forces a strong enough, and so the viscosity the flow, this is interesting, and happens quickly, you can understand you just putting a stroke, taking it up and within that time the paste has gone out, is gone on to the fabric and with that stroke it's gone a bit inside as well, and so it may appear as a commonsense, but if it does not happen then you have a problem.

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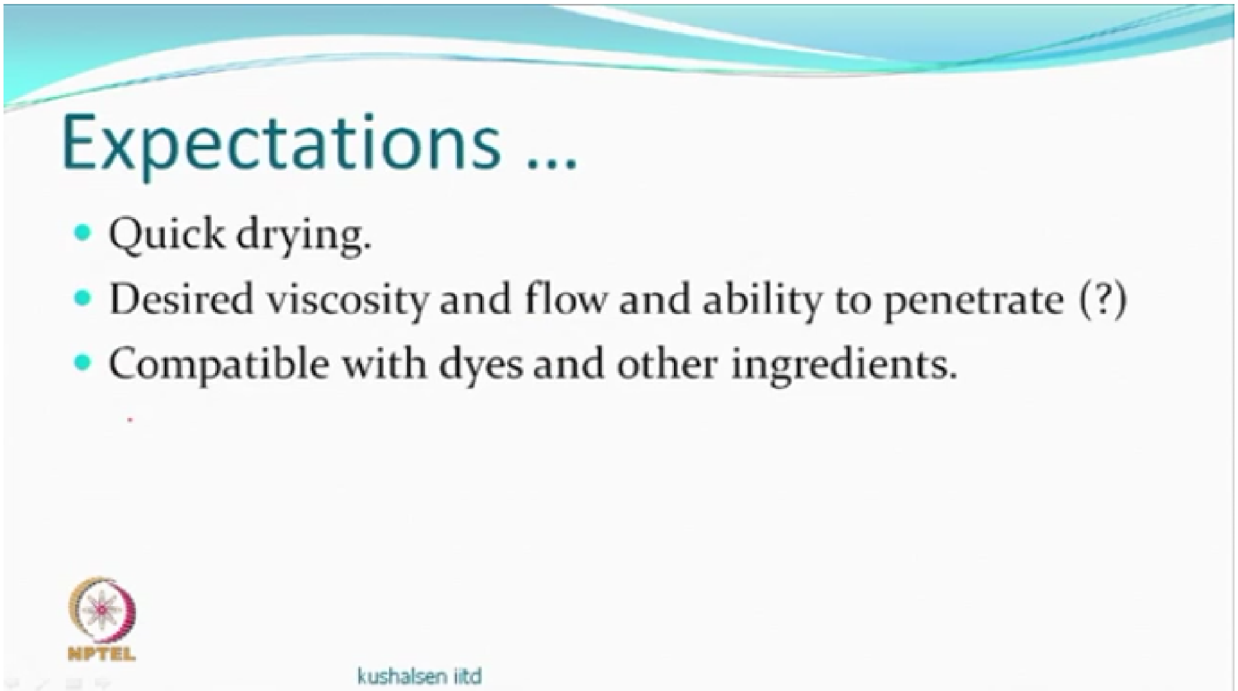

Compatibility, now for various reasons your dyes as a cationic there are soluble, non-soluble, there anionic, so you have ingredients which are also could be ionic or non-ionic, so adding so many things and if suppose they interact with this polymer which is called the polymer for generating viscosity of thickening agent, then you have problems again, because we thought this particular material is inert which may not happen, so it may not form the bonds that you are looking with the fibre, but it may have enough reasons to have Van Der Waal forces, hydrogen bonding or sometimes even covalent bonding also, so those kind of compatibility that thing you have to choose what kind of a thing it is there, so you expect that it would not do anything with any other ingredients, so if you have any system viscous or otherwise if you add salt and check the viscosity it may be different, if you add little another solvent the viscosity changes, so every time something happens these things will change, but at least it should not happen that there is some anionic thing here and you put some cationic thing there and then they precipitate together and everything is over, it will become ticker lump, so that selection process would be there and you will say if, if he can find an ideal thickening agent which you would just so inert, you add whatever you want to add, nothing will happen, beautiful, this is just a dream. Of course is the same thing,

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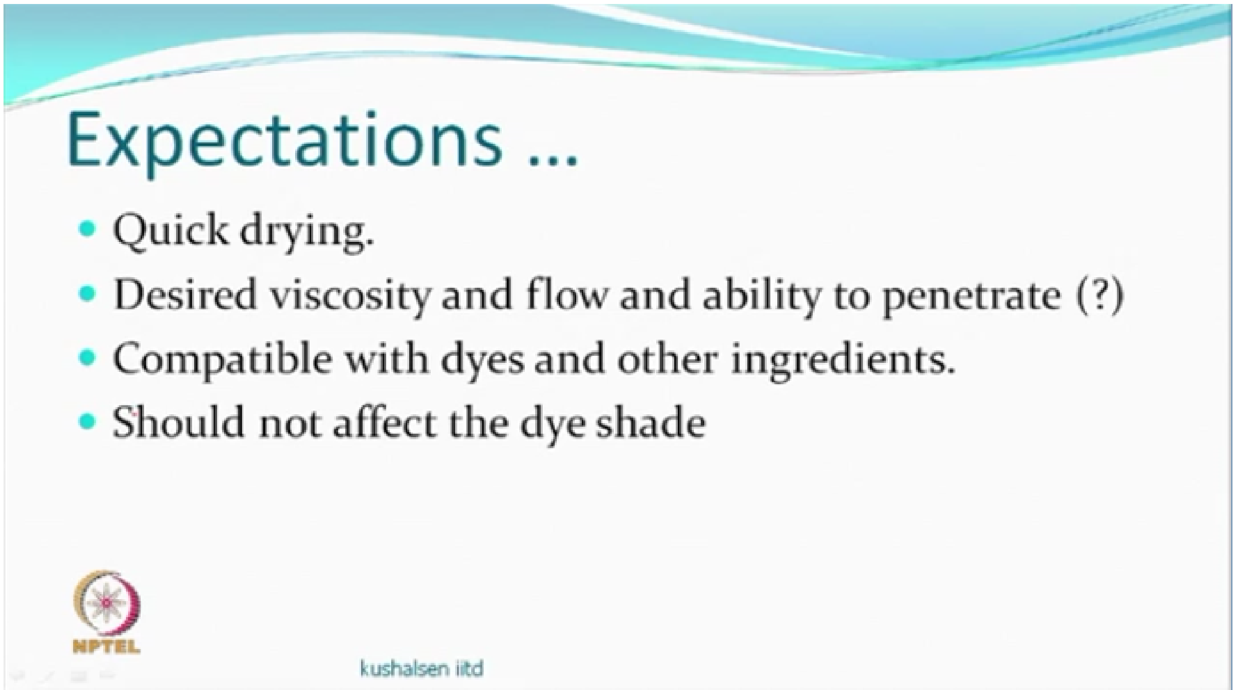

should not affect the dye shade means that it is not reacted with the dye in any manner and part of it is changed.

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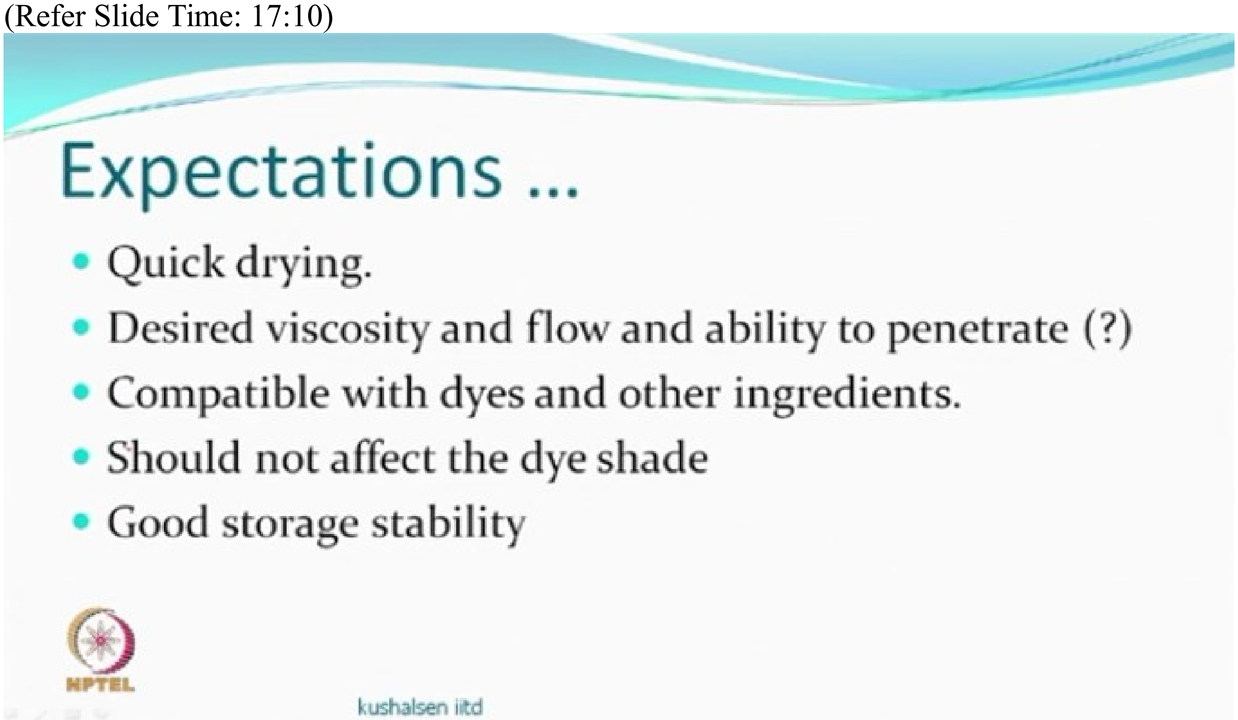

Storage stability, now this storage stability means that one is the storage when you have this material in a solid form, so that storage is fine you have powder particles stored somewhere, the other storage is that you actually have made a paste, once you make a paste, now it is in a molecular form, so the particles have been now separated out and they are in the molecular form and they are generating viscosity, so now they are also more vulnerable to any thing which you add to that like you add acid, so if the so called printing paste has to stay for 24 hours, sometimes 48 hours what happens to this when you have added something else? The storage stability is there which has to be seen, if you find that it gets hydrolyze soon so you have, you should know how much time it should give, before you completely use this, you must know it, you may desire the storage stability for one month it may not happen, but you should know what is this stability, in terms the how much time can you give so that you can use it, nobody will have any problem or it will be the, problem will be within the acceptable limits, you can't say there is no change, change will take place.

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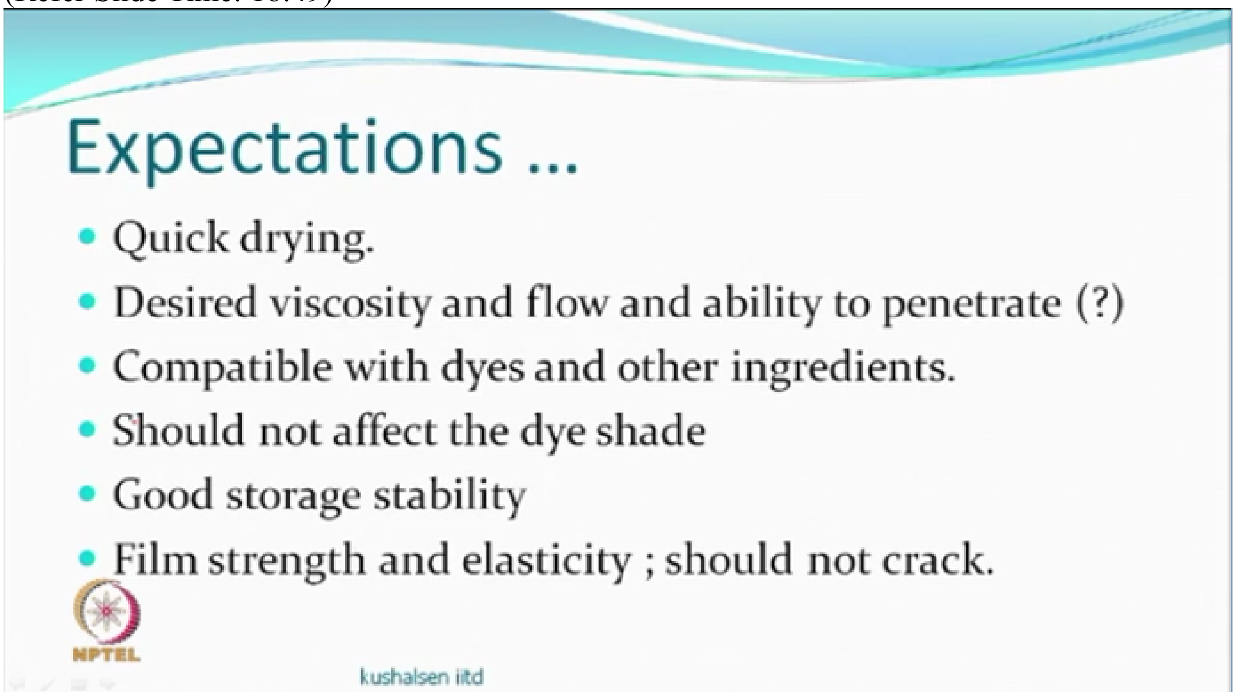

Then after so called printing and drying, the film should not crack if the glass transition temperature of this polymer is high, then it becomes more rigid and then during the folding processes, before you have fixed, it can develop cracks, and if the cracks develop then the penetration, diffusion etcetera are those portions will be affected and you may see some change, and if it so happen that actually the whole film goes down packs, the dye holes will come out with it, so there should be elasticity in the film in the sense that during the temperatures when we are working it should remain flexible enough so it doesn't fall off, this I think we talked earlier also,

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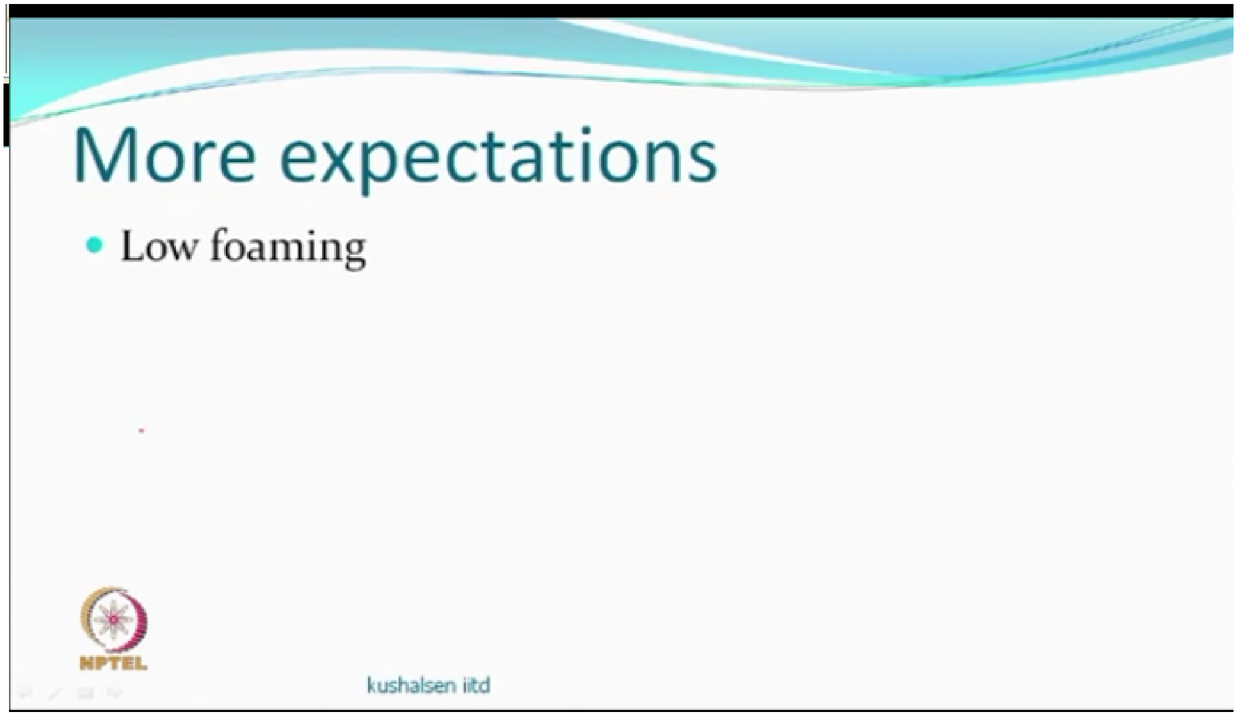

the whole paste should be low foaming because the word low has been used instead of no, because you're adding a wetting agent there while doing so, all the surface active agent when they're agitated can form foams, this is normal conventional printing there was a time when people were promoting foam printing, not printing of a foam but printing by a foam because foam also is a state of matter which also gives viscosity, you see you can have a nice kind of foam which actually almost looks like a solid, alright.

And why they want to do is, because if you can printed very nicely with the foam, then when you dry most of the foam which has air goes off, and so energy requirements are low, then washing requirement would be different and so on and so forth, but that technology hasn't really picked up so much because the stability of the so called foam is always a question, the bubbles can keep rising up and then suddenly find if the bubbles initially where spread out across the whole bulk versus some of them have now come up the viscosity at two different place are different, so this has become much more difficult to handle then the normal polymeric compound which gives you viscosity, so generally we believe low foaming is a better one, so that it's just a paste which can be applied very easily, so sometimes you have to add some agents.

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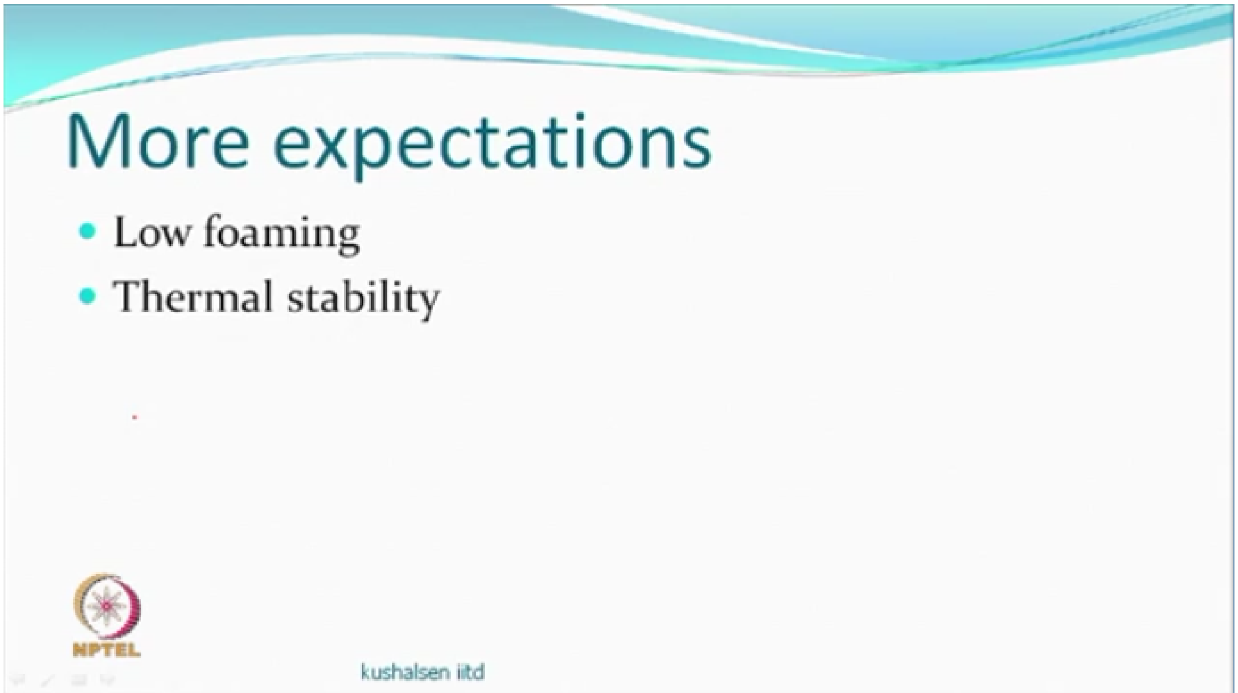

Well thermal stability is only till the time or the under the constraints of fixation, so we are not really so much concerned about this that it the printed material is going to be stored at very high temperatures, but it will be fixed at different temperatures and that could be depending upon which is the fabric, if it is polyester then you are actually looking at superheated steam, maybe dry heat 175, yes it can do thermal soling for example that kind of a method could be used, thermal fixation or normal pad dry cure or steam, so that must stability should be there that should actually fortunately that's not too much of a problem.

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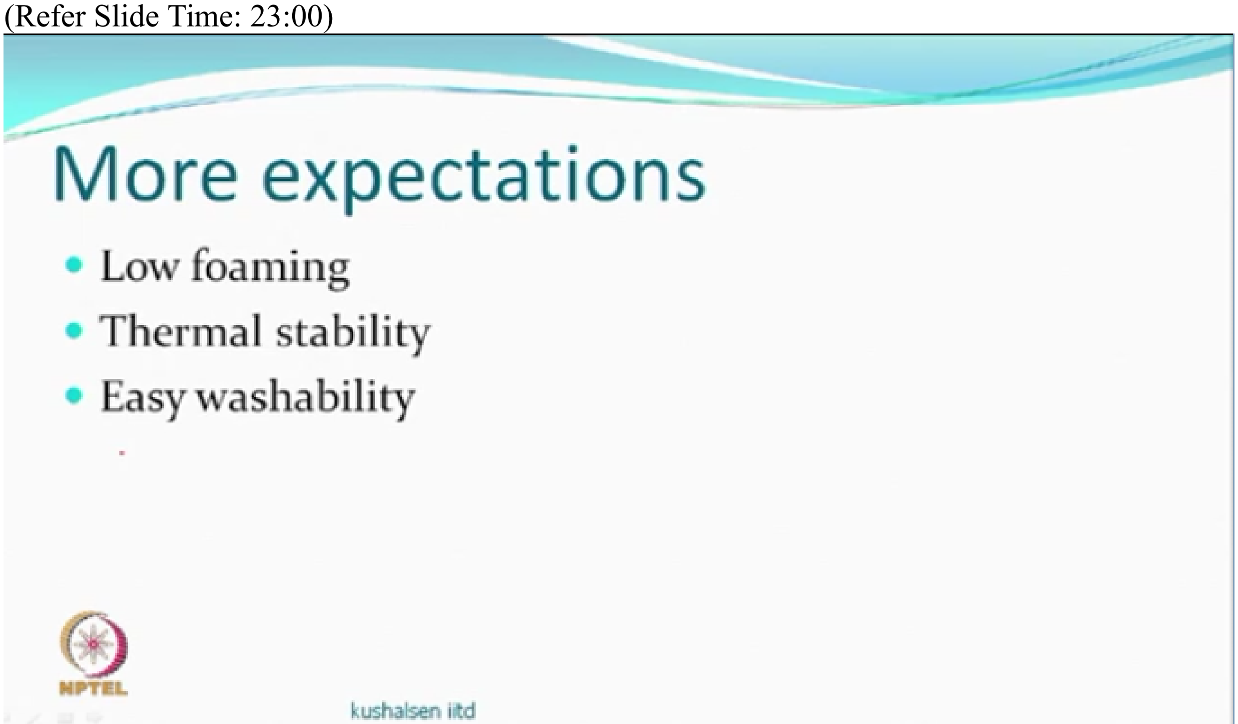

And this of course after you've done your job, you wanted it to stay there on the fabric till the time the fixation, after that it must be able to wash. Washing anyway we said is a problem, one colour flowing over the other, and if this also becomes a more problem then this will flow with the colour, and get stuck also the colour can diffuse also, and wherever you have printed and if the thickener has not been washed off it is tough, so you want the original handle of the fabric to be restored so this must be washable.

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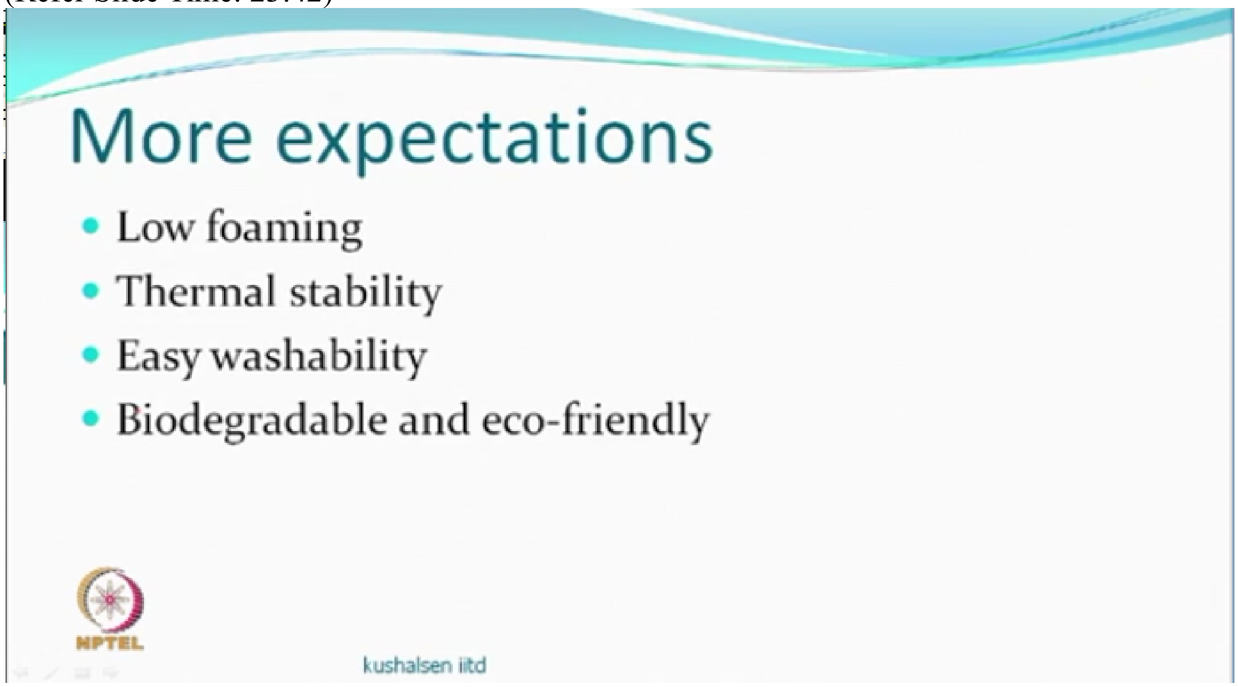

And of course these days we must talk about this that part of it is going to go into the wash liquor and into wherever it is going, if it is not biodegradable then you can be in trouble. In fact when you have polymeric material and you do the ETF you know effluent treatment, it's not easy, there is a difficulty with salts, there is a difficulty with acids, chemicals, dyes, but if also polymeric material which have to be removed, it becomes more and more difficult, but that's it, you still have to worry about it,

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and of course one would want it to be as cheap as possible, sometimes there is too much of an expectation.

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Stock thickening the term that means like you have stock solutions, have you heard of stock solution? Right, so in dyeing also we make a solution first and then keep adding little bit from there to make a dye bath, so similarly you have stock thickening, why do we have a stock thickening is the printing paste preparation is a TDS process,

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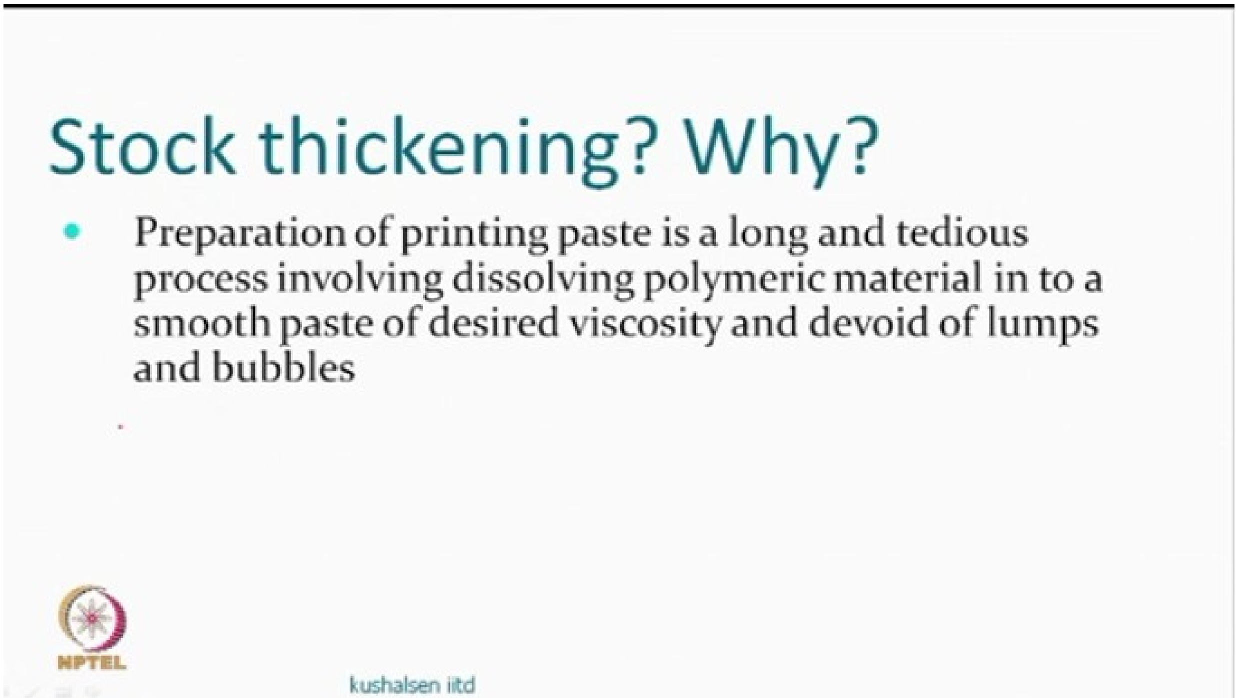

it’s not easy dissolution so you have to dissolve it much in advance, because it should not have lump, it should not have bubble, it should have desired viscosity, low molecular weight compound are easy to dissolve, high molecular weight compounds are difficult to dissolve, so you have to work for hours to make a smooth nice paste, and so you say well we’ll do this work before and so nice paste is available, and this is what we call as a stock thickening, and this thickening is also contains various ingredients also,

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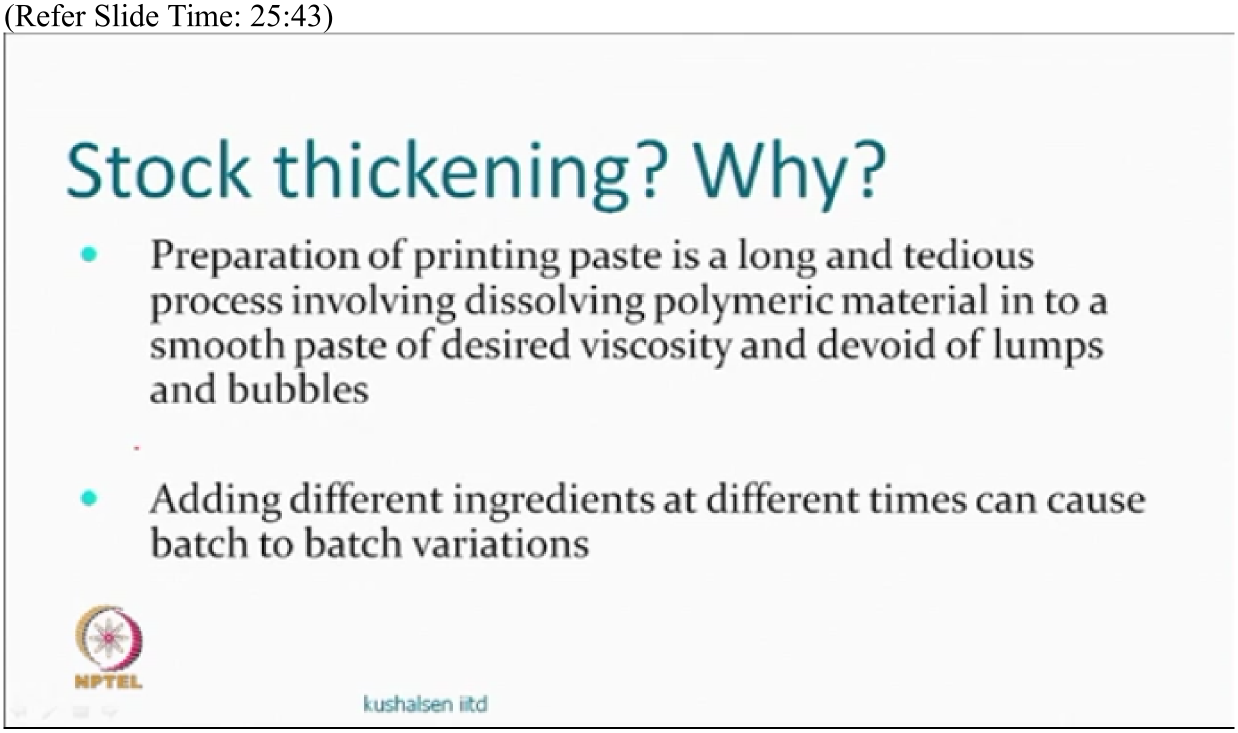

suppose you have, supposed to print with their reactive dye, then some of the ingredients are put in the stock thickening itself, and so if you keep adding and making the thickening paste at every time that you need then you will cause lot of batch to batch variations.

And as we said the material itself is based on its own molecular weight, maybe having different molecular weights so you have batch to batch variation, that we say at least one lot we make and finish and work on the stock,
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so the colour is added later and because of that this also may have to have let’s say you are doing the red, blue, green kind of a design, so red, blue, green itself may have to be stable for let’s say at least one shift is possible, therefore the stock thickening is supposed to be maybe lasting 3 days, 4 days or even more.

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So what do we envisage in case we have to store? So one of the thing which you can think of or all the additives that you have added, will they have any effect? Do they have any effect on the hydrolysis and therefore the viscosity, and so these complications can be there and one must know what things can be added, what cannot be added that’s one part, and then also check if the viscosity has changed in any manner which is not conducive to your printing, so those kind of things we may have to work on.

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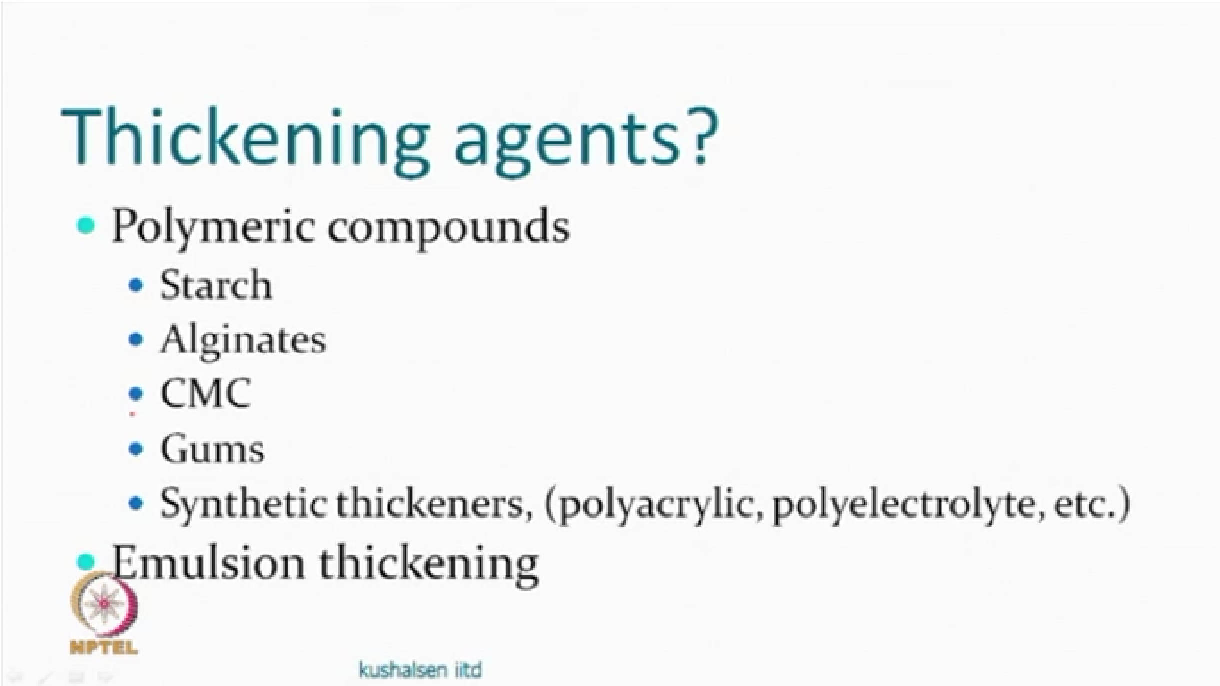

So various thickening agents, so as we said they are polymeric compounds, starch flow is one of the early agent which was tried for printing paste, different molecular weights of starch were used, some were pre-hydrolyzed and you had to use lot of solids, almost as much as 50%, okay, but a normal starch would be good at 10% but you hydrolyzed it to such an extent that the molecular weight has reduce, so you had to use more solid content.

And why does they want more role so is that it was believe that it is easy to wash smaller molecular weight it will come out easily, the viscosity will be the same, so starch first right. If somebody ask a question, can the starch form fibers because this is quite similar to the cellulose, can it form fibres? Why not? Is because the branch structure, so you can appreciate that if you have lot of branches and large branches, then fibres will not be formed but you can still form films, so these polymeric compounds can form films, the kind of films that we require.

The most important change that people were looking at some different times was when the reactive dyes came into play, the moment reactive dyes were there for printing they found starch cannot be used, why can't we use starch? Yes, right, starch also has hydroxyl groups, yes, so at a particular condition when hydroxyl groups react with the reactive dyes starch also gets, so you will have lot of wastage almost more on starch less on fibre. So this is something which people were not very happy about, you can always go back and see the structure of starch and the cellulose how they are different.

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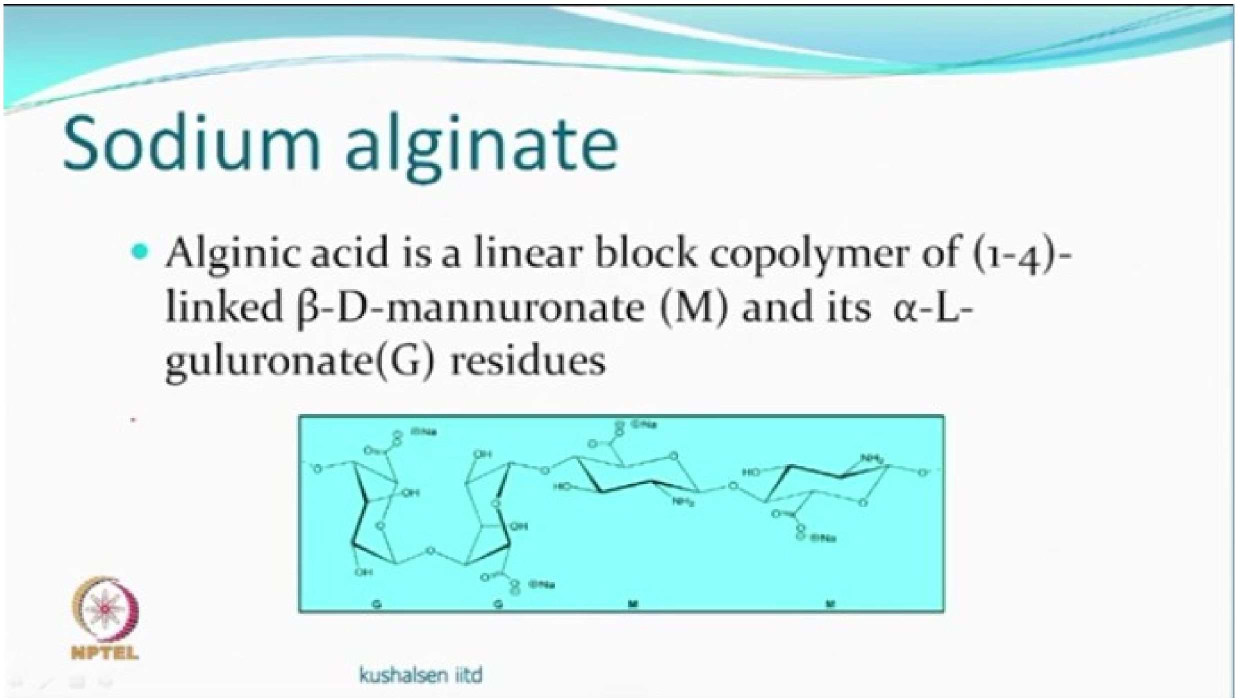

One important compound it came to rescue is called the alginate, the major change that you should be worried about or interested in, other than these names you understand one for linkage right, this area, so the alginic acid was an acid, so it was sodium salt,

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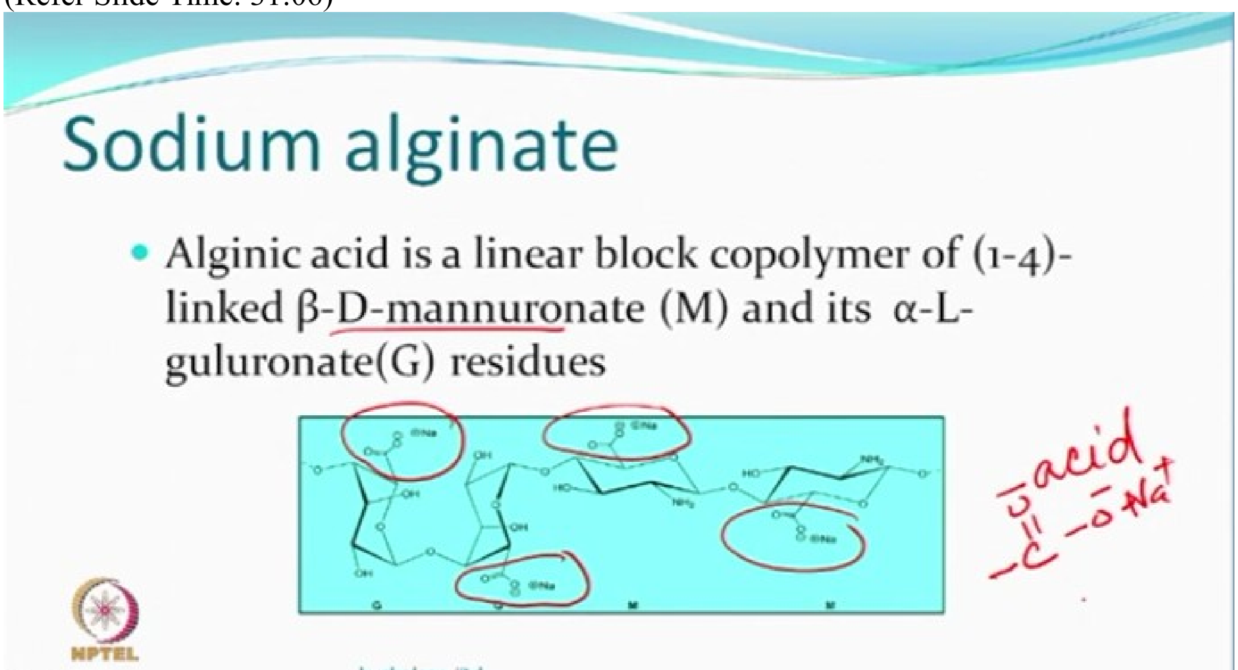

so now particularly the CH2 OH which used to be one of the hydroxyl groups the primary that has been replaced by an acid group, so you can always say that well the other hydroxyl have not been replaced, then how does it help? The most important point to note is the most reactive group is the one which is the primary and that primary has been changed in this particular alginic acid.

And so because of this the reactive dye doesn't go, doesn't like it so much because that also is negatively charged, and so this was one of the reasons why alginate became very successful, of course later on people talked about other acids also, you can think of once you know the principle that now reactive dye will not be able to react because it is acid, it doesn't like, both are negative also they want to go away, so that's true both are negative if, but can you use basic dyes with alginate? You will not be able to use it, because is this non-compatibility, whether reactive dyes are anionic compound as such and you want preferential reaction with these hydroxyl group of cellulose, and in this starch, in the starch you had the primary hydroxyl group there as well, CH2 OH and the cellulose also you had CH2 OH and they were reacting now in the so called paste in this alginic acid compound you have, this compound has acid and the primary side and therefore it's not easy for dye to come here, so the affinity questions and then goes somewhere else, so very successful compound, but again it was a natural compound like starch.

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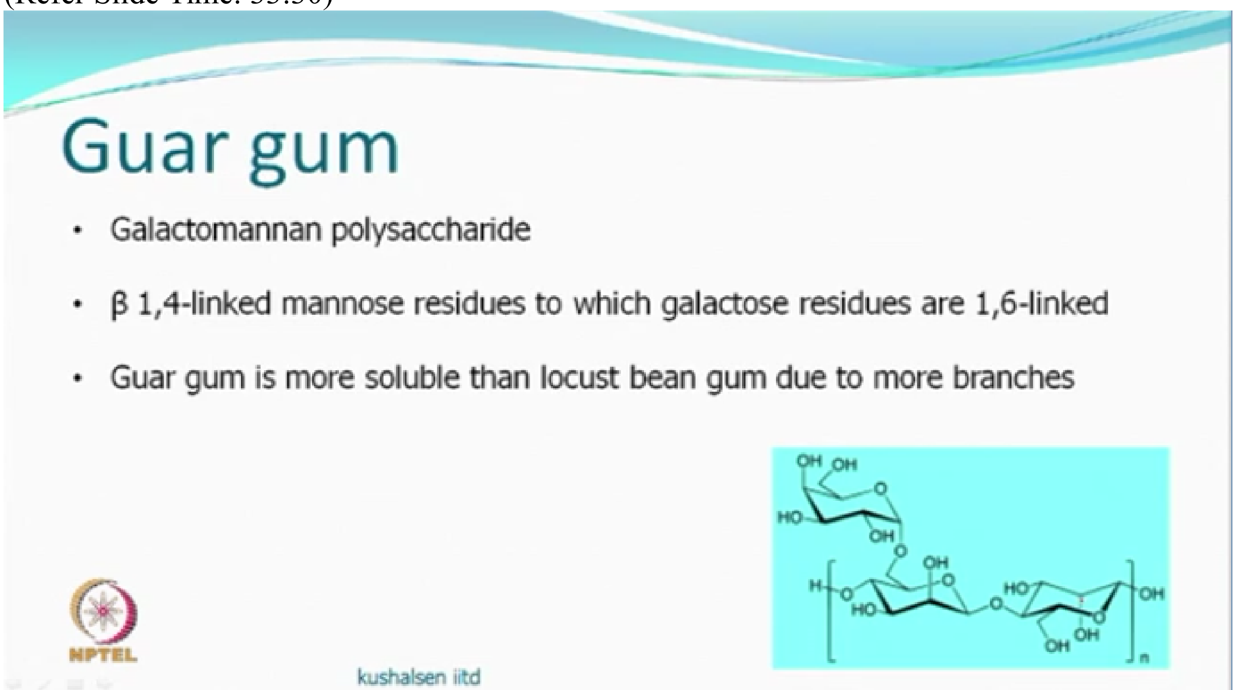

Here is an another interesting compound which is not good for reactive dyes, but important thing is that it has very high molecular weight and because of the high molecular weight and we got small branching also, very regular branches and because the regular branching so the structure is not very compact, and the things are not compact then water molecule go inside and then washing can become easy, alright, it was a very compact structure let's say, very compact structure can be even crystalline structures, nothing can penetrate, dye cannot go into crystalline region, the water cannot go in crystallization but this type of compound will be more amorphous, so washing etcetera are easy.

And the molecular weights are very high, at very low concentrations like if the starch, normal starch required 7 to 8% for printable viscosity you can obtain printable viscosity with 1% or less of this compound, so you'll be very happy about this, and of course all these compounds can be modified you know by grafting or other reactions, so that some of these hydroxyl groups can change, so that's the modified you know gums would be available, and they sometimes will be much better than the, so those principles will have to be used again.

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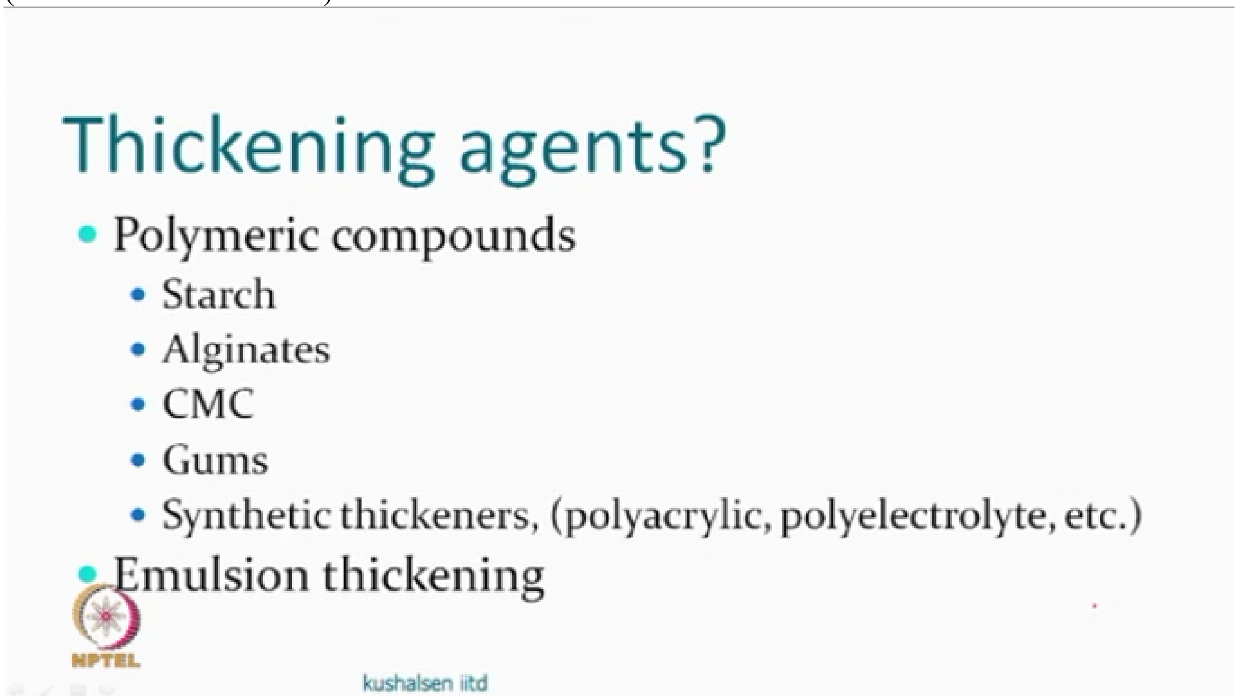

I did not talk about let's say CMC, I think you can learn about it, I've just gone below the synthetic thickness will talk about little bit and emulsion thickening, okay.

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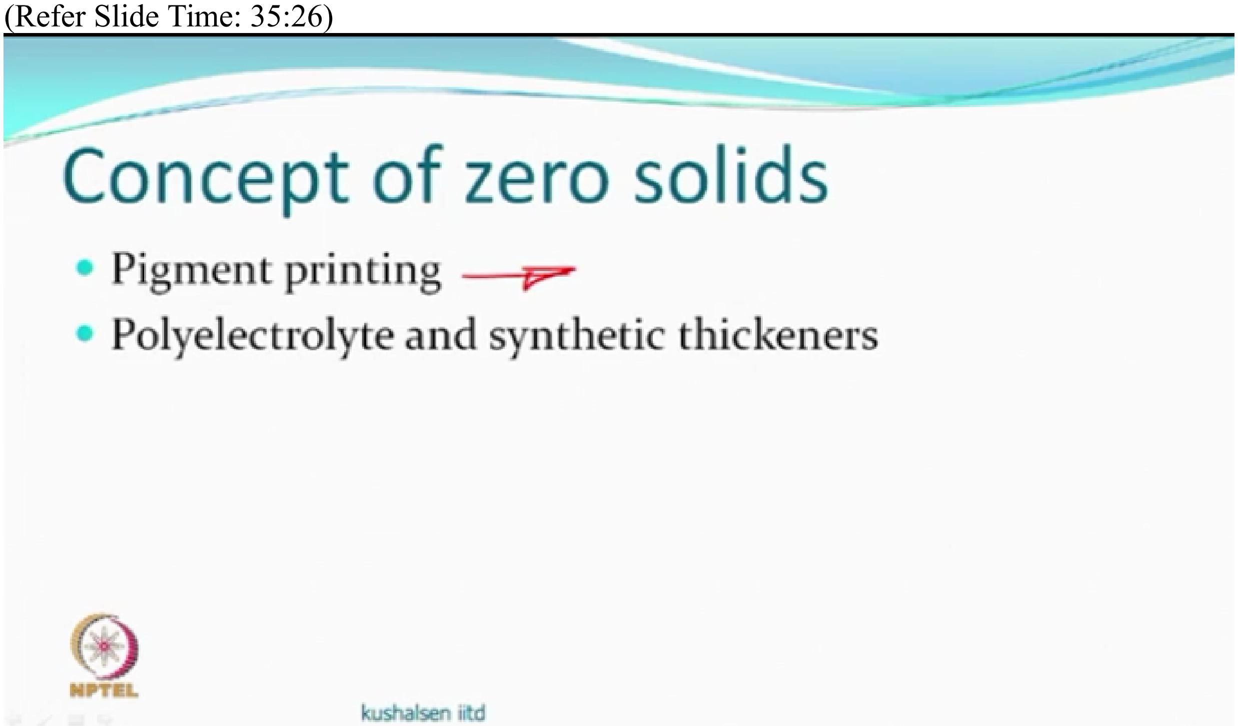

So emulsion thickening is for printing of pigments, and one of the reason is that the emulsion thickening has zero solid content, that I say how do you get the viscosity with zero solid content, how do you get the viscosity with a zero solid content, so what was being done if you remember that you were not using any other polymeric printing thickening agents, we're not using starch, we're not using any other agent, what you were using was? Oil emulsion, oil water emulsions, and oil water generally was a kerosene, so oil water emulsion,

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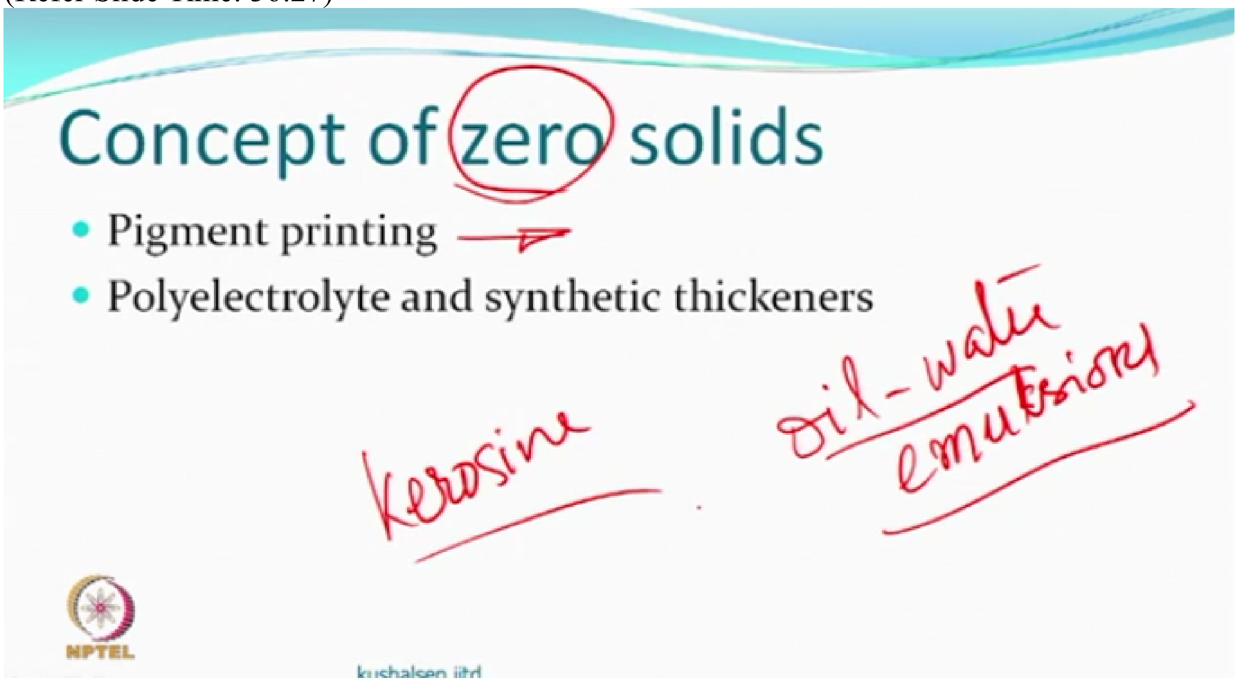

why was calling? We were had to add some oil, water anyway was there in every thickening so oil who could be, and was evaporated during the curing process.

So everything which is called the thickening, which was giving viscosity, we just go away, so you don't have to wash it, that's one, but why did we need that? Why did we need this kind of thing for pigment printing? What was the need? If you remember all the pigment printing people were using emulsion thickenings, the one of the reason is because pigments have no affinity, and therefore affinity for the fibre, and therefore you are using a binder, it is the binder film when it get fixed then you talk about the fastness of the print, but it is the fastness of the film which is responsible for the fastness of the colour or design, and how does it happening is because this film is able to interact the pigment particles and keep them in the position.

If you use thickening agents which have certain solid content, those agents also will be trapped and you will not be able to wash them off, so within the binder file you will not only have pigments but also you will have some polymeric compound other than the film also trapped, you need a viscosity without that you can't print and so people found that if you use oil water emulsions using a suitable surface active agent, then it is possible to print you can get desired viscosity and during the process when the film is getting cured, this oil water emulsion evaporates, water evaporates anyway, this oil also evaporates and you have a clear transparent film of the binder, so you can see nice colours otherwise they would all be dulled, okay.

At a latest date people found that they are dangers of two types, one in this tender when there is a too much of a oil concentration you can have fire that was one, so if it exceeds the critical concentration and you can get fire, temperature is anyway very high, but if you could look at and look after this problem also then people will worried about the oil going into environment, and so that also was the environment problems as also the problems related to the fire hazard also were taken into consideration then thought about synthetic thickeners and polyelectrolyte structure, you see the best part of one of this polyelectrolyte is that at a given concentration when you dissolve them the viscosity is very low, it just flows like water, but you change the PH and suddenly you have very high viscosity.

For example, if you have this polymeric molecule and you generate negative charge because of change of PH, so you have large number of let's say negatively charge sites, and then there are so many molecule like this and all of them have negative charges, alright, if you can create that, so lot of negative charges all around, so what will happen?
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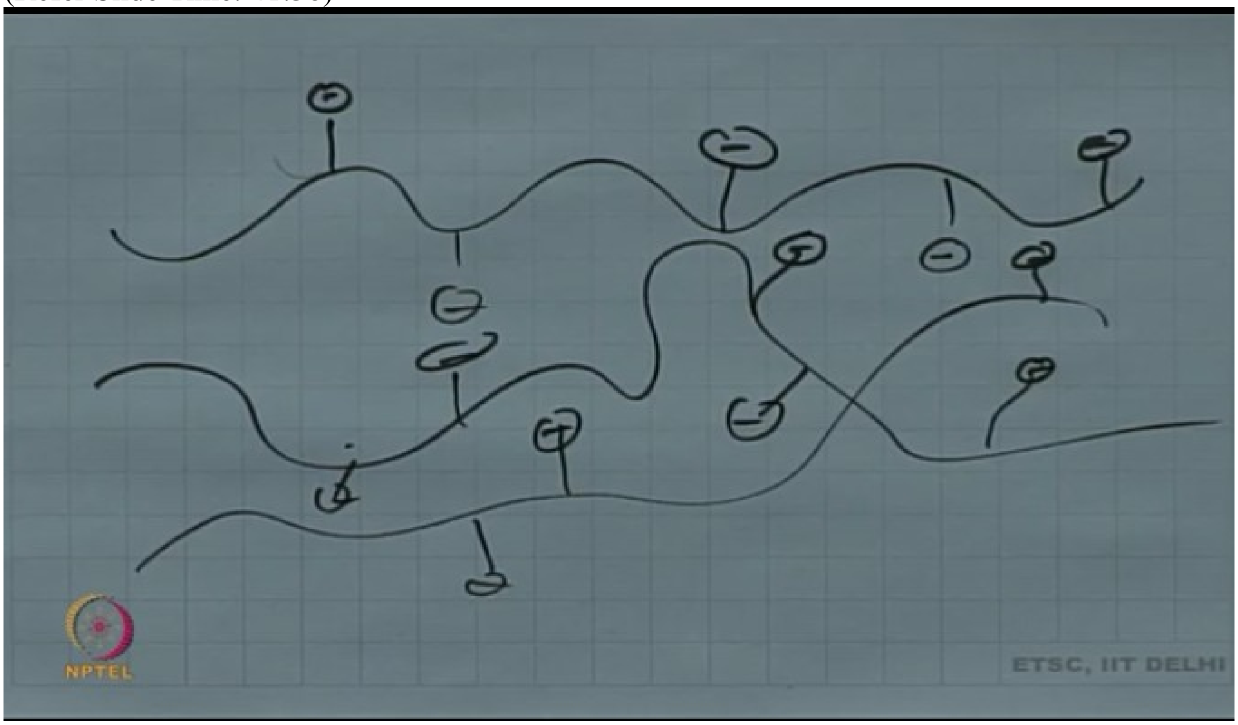

They repel, and they repel to such an extent that the friction between the two becomes very high, and immediately viscosity gets generated, so these are called polyelectrolytes, so one of the popular type of a synthetic thickener could be let's say poly acrylic acid based, so poly acrylic acid obviously will have CO OH type of groups all over, isn't it? Can you see the structures? So the acrylic compounds and so there will be large number of CO OH groups, but the CO OH group by itself is not ionic, not so much ionic, so when does it become ionic? When you let us say add an alkali, if you add let's say ammonia or ammonium hydroxide or sodium hydroxide, then they will get ionic, so they become ionic, so once they become ionic then we get lots of viscosity,
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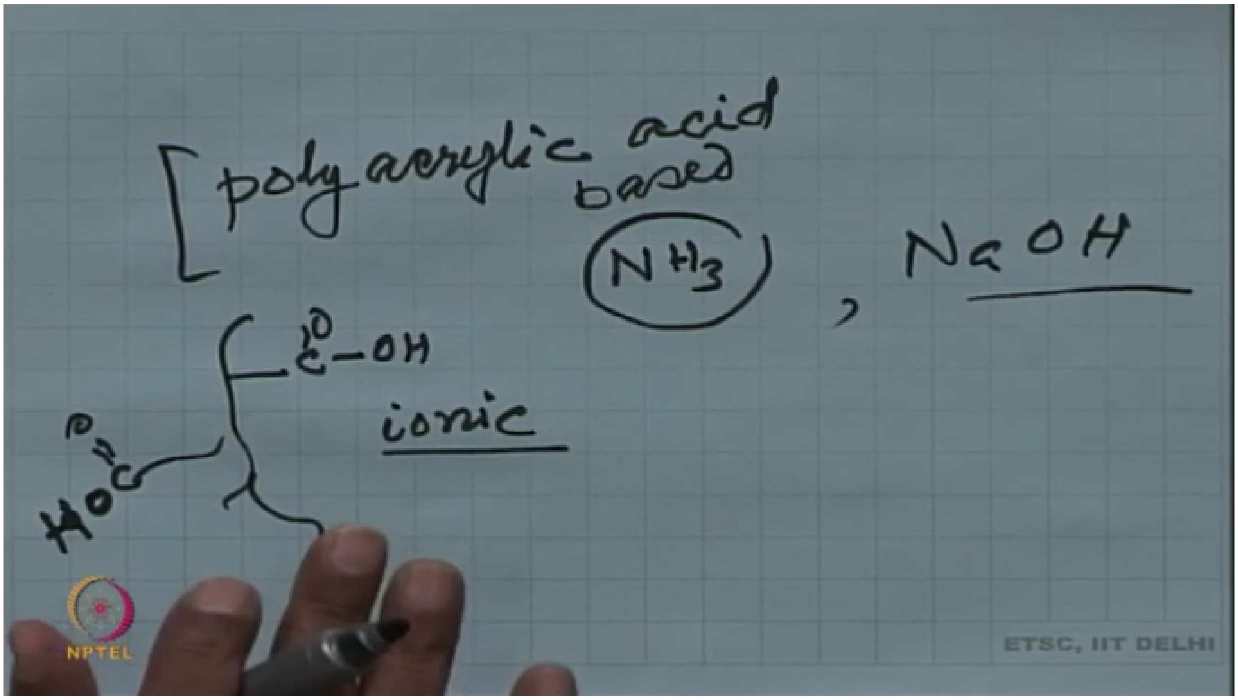

you change the PH there is no viscosity, so this is a very interesting compounds, so it's very interesting as well as very delicate.

But then how did it come to zero solid? The zero solid concept meant that no solids, but if you use polyelectrolyte cannot be zero in true sense, but very, very very low concentration,
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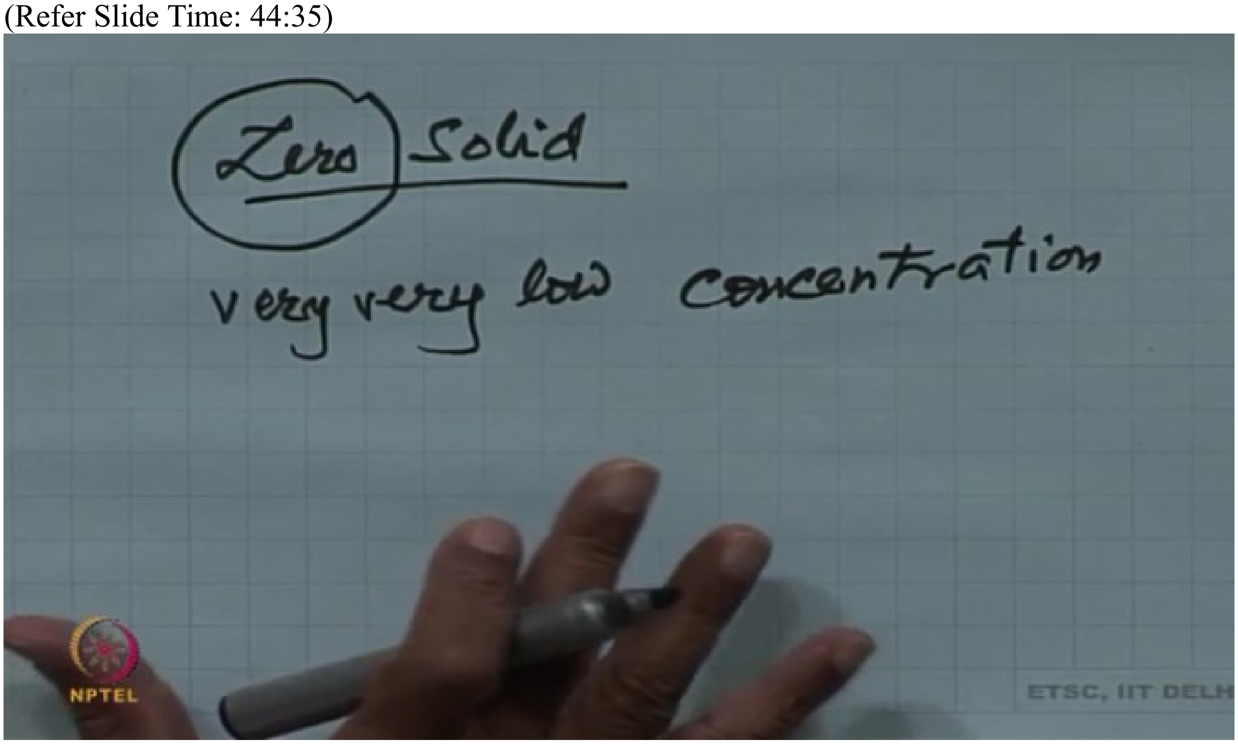

so you have very low concentration, low viscosity and suddenly you add alkali very high viscosity and then when you wash alkali is gone, viscosity is low, and even if it is trapped in the binder film it would not change the tone and the brightness of the print, okay, this is an important part of the concept of a zero solid, so very very low means you can actually be thinking of 0.2%, 0.1% type of things which also can give very high viscosity, so the concentration will adjust based on what you want, but no oil, so no fire hazards and no environmental problems.

So today we shall stop here, and pick up a few more interesting topics in the conventional printing next time.

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