Module 25 - Lecture 9

Sublimation Transfer Printing : Dyes and inks

All right, so we continue from where we stopped, we were looking at transfer printing

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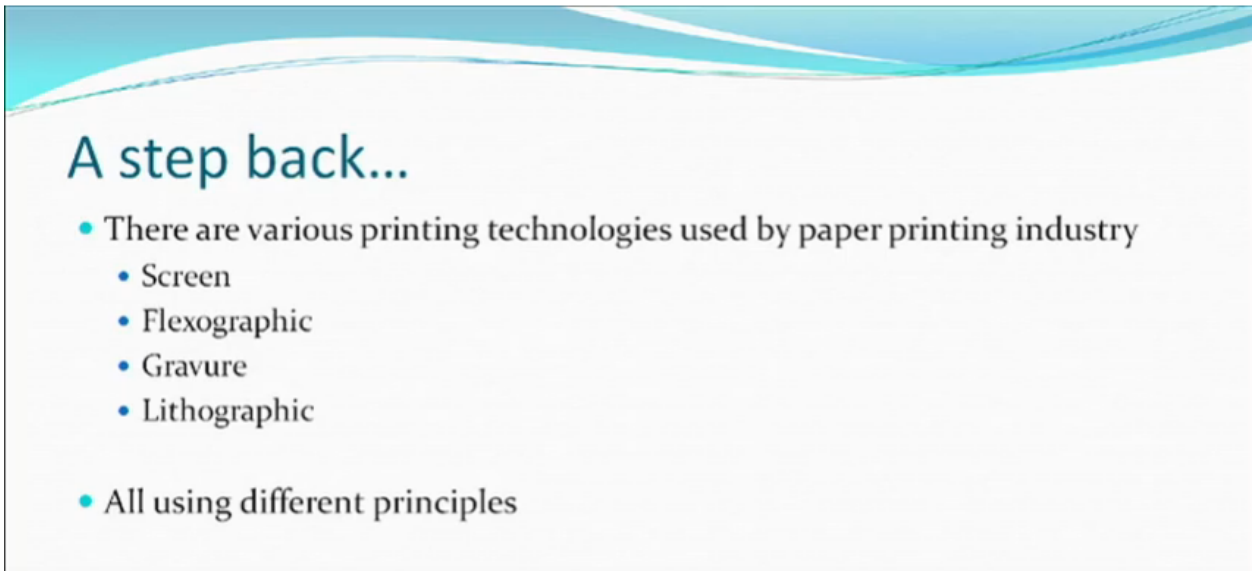

And what kind of paper, should be used for transfer printing and what are the methods, which are used for printing the paper. Screen is our own methods, of the textiles, the flexographic, Rivera and lithographic methods are, specifically designed, for paper. And now the concept, of for color printing is popular, so as the paper is concerned, all the colors can be obtained, by the four color method. And what you only have is various kinds of dots and the dots can be mixed in one proportion or the other, to get a different color and which, is what an important for the paper. And of course their principles are very different and I'm sure, you would have appreciated, the difference in the principles.

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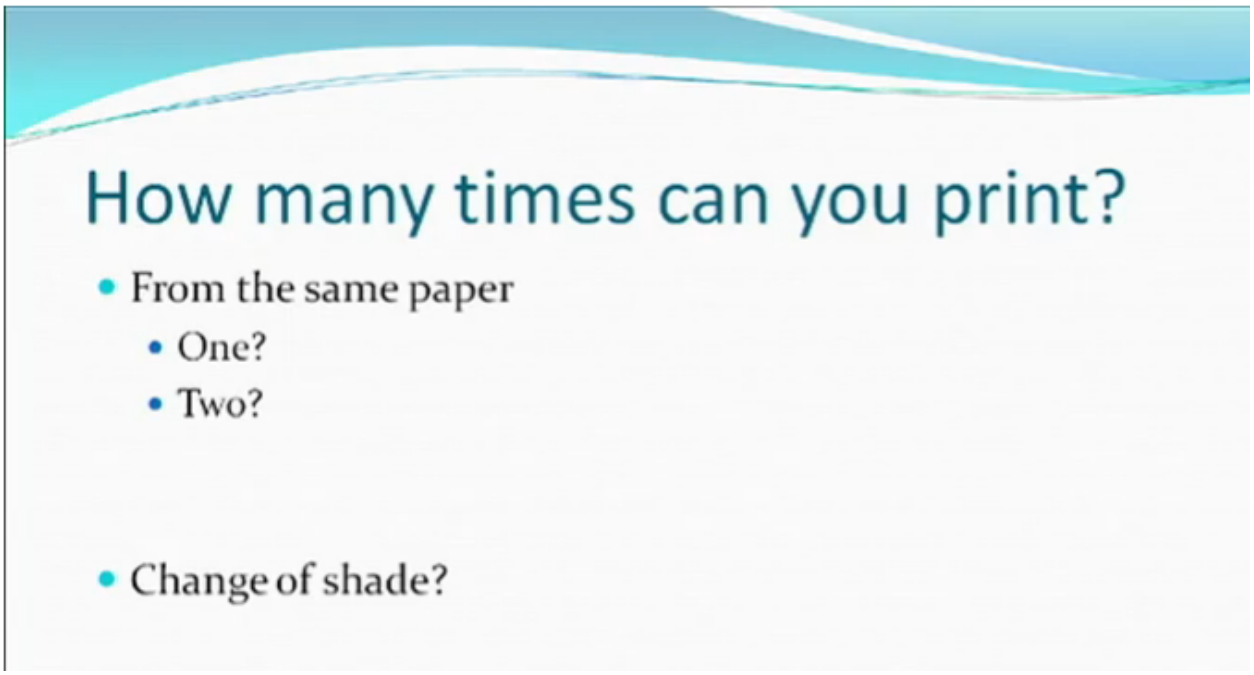

Some people can ask this question, as to if you have the paper and you've done the transfer, how many times, can you use the same paper? We said the cost of the paper is high. So, theoretically, obviously one, time you can use it. And if you do a good job, which you should a large amount of dye would get transferred. But, it is never 100percent transfer, some of the dye may actually ,remain on the paper and if you do it, second time, this dye can get transferred. But, obviously the depth, of the print will be very different. So, if you have a customer, who likes this, then you can sell it. for example, people in the upholstery, have been making combinations of light printed and a dark printed materials, which gives some kind of fashion trend, in case that becomes an issue, then you can obviously have the same print, same colors, but depths different and one can have combination of alternate, fabrics, drapes, which are light and up. So, that's another way of looking at things people do ,do these things. more than two obviously, there is no point, because you will only be having staining, there's no big transfer. So, the shade change, may happen in case the rate of transfer, of the colors that you have, are not same. let's say, you made a green and this green has been made by two different dyes and one other dye, has a higher sublimation rate, than the other, then at the end you will find in the second case, the dye is less, one type of dye is less, the other type of dye is more and the shade has already changed and so ,when you print again some chain can also occur. so that, is the thing but, if you are looking for the best fabric, then it is better only once ,if you are looking fashion statements, you can have two.

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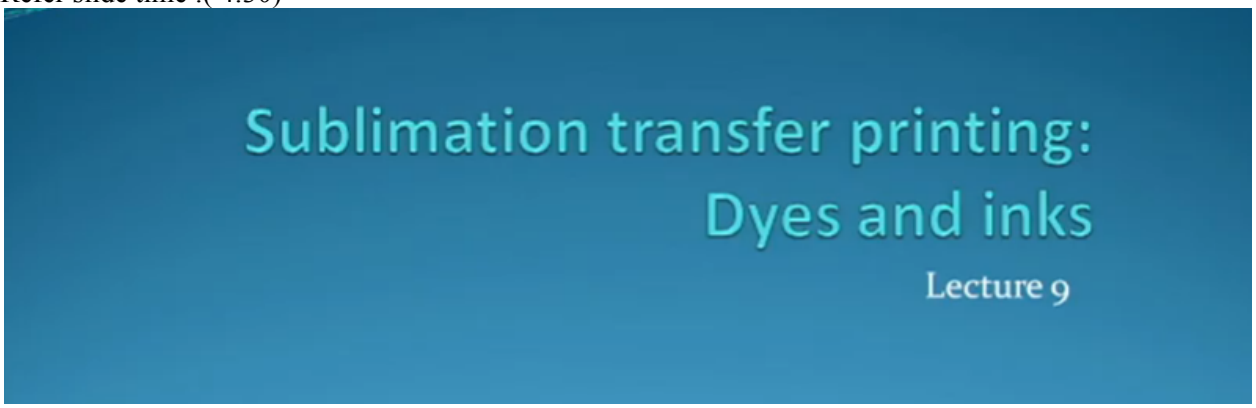

So, we will now, little bit talk about dyes and inks. So dye is the, dye that we talk about the molecule Ink is the solution, which has the dye. Right? So, Ink is like a paste, which we're having, in a printing, normal textile printing, in this case we have a low viscosity, ink. And they have the dyes, which obviously are chosen based on certain criteria, one of the criteria obviously, should be that it is sublimable. Right?

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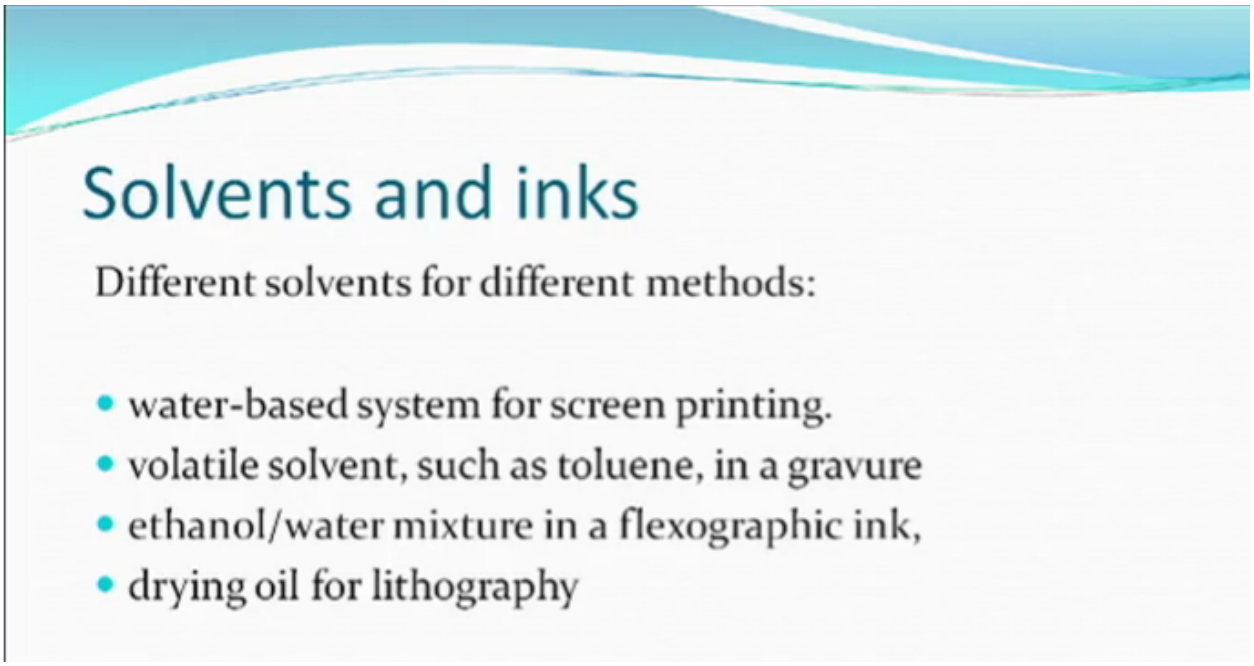

So, one can use different solvents, for different methods and maybe the viscosities may also be different. Right? so methods, the one which require quick drying, the one which do not require quick drying, have enough time, then you would be using methods and the solvents, which are different. for example, if screen printing normally people made use, water-based inks. so obviously, it's a dispersed dye, so it is water-based, that means the what - the solution, that equispaced inks, can be used for screen printing, for gravura people may prefer, volatile solvent, toluene is present here, could have been benzene also, we don't use benzene anymore, you know why, yea, hit's carcinogenic. So, benzene can only be used for research purposes, it cannot be used for any commercial product. so toluene as good, we just, the next derivative. for flex so, people use it ethanol water combinations, medium and for litho, people may use, drying oil, which can dry easily. But, Saul oil as you know you, are dealing with hydrophilic, hydrophobic, principles. in this type of renting methodology and therefore, you would like to use an oil which dries and obviously, it's only oil, because it does not like water, that's the principle of the technology.

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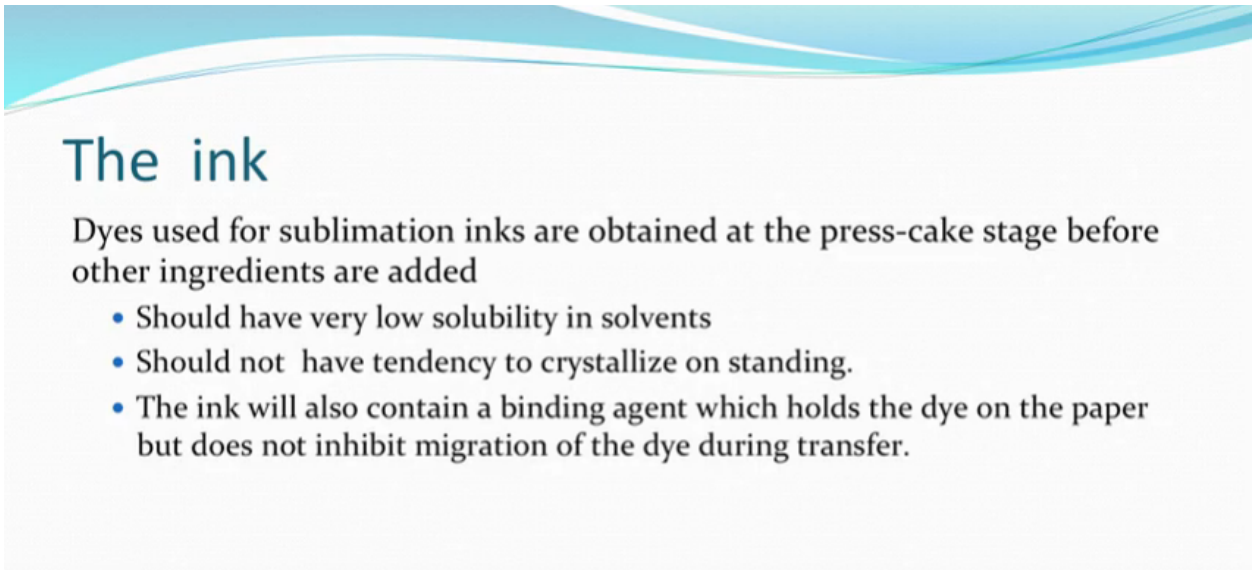

So dyes, use for this are obviously sublimation, are obtained at the press cake stage before, any other ingredients are added. So, normally if you're looking to disperse dye, you may get a paste or you may get a powder, whether it is powder or a pace invariably, they would have added some dispersing agent, in the dye powder itself. in this case, they are wanting to get precipitated dye, in a cake form and then make ink out of that, they don't want any additions, to be made by the dye manufacture, they want to pure dye, alRight. if anything has to be added, then they know what to add, rather than somebody else, because this is ink meant, for paper printing. So, they are dispersed yes and we expect also, that there should be low solubility and this is also interesting, that when as we told that the concentration of this particular thing may be very high. And when you have high concentrations, you can have precipitation, crystallization, type of things. they should remain in the solution form for a long period, ink maybe containing some binding agent, you know this binding agent, you can consider it like a binder ,which you use for a pigment printing, but obviously, this dye is in, may be in, in particulate form in some cases and being held on the to the paper, by this film. Right? so we're expecting, expected that this film is not going to inhibit migration too much, you can never say, that the migration will be not inhibited. But, then you can give little more time, so the film also should be such we does not really like, the dye so much, affinity should not be very high and the quantity of this, binder should also not be so high, because if you have more quantity, then obviously some hindrance can occur. so this is, what the people will repairing ink, so you have a dye, which obviously is the most critical part and they are the critical parts, are the binder and the solvent that you use, you can appreciate that, you will not beading anything called an acid, an oxidizing agent or things like that or alkali, because you're still using a paper, if you use paper, I sit on paper, you will have holes, so nothing is to be done, it's a simple thing, just bound and what are you saying is? that the temperature when you are going to be actually needing it, this will get evaporated and then, we'll just go from the paper to the fiber.

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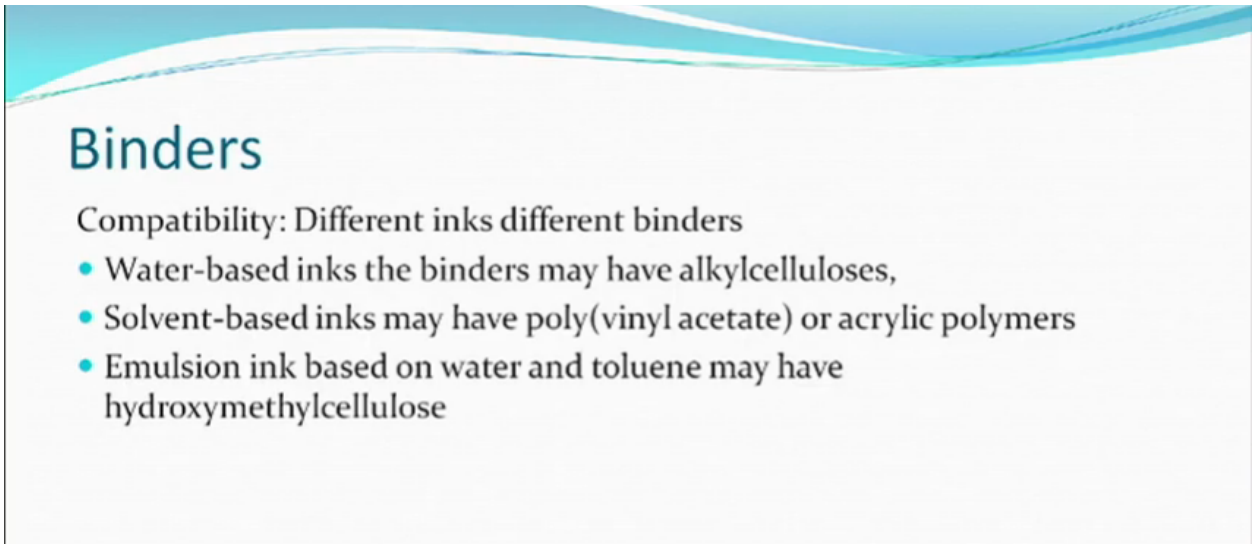

So some of the examples of the binders. so different inks, different binders, what it means, obviously a water soluble, water insoluble, all those type of things will have to be seen, so that kind of a compatibility people obviously work wrong. So, what a based inks, may have Alkyl celluloses, the solvent based inks, may have vinyl acetate waste or acrylic based, polymers, binders, the emulsion inks, with they use water solvent may have, another chemical binder like hydroxymethy lcellulose. so you have, something which is compatible with most of them, if you have incompatible then, there may be precipitation, see whenever you have in compatibilities, then you get precipitation. What you need is a nicely, dispersed free-flowing ink?

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So after this, we can look at some of the characteristics, of the dyes. We call them dyes, because they are dyes and you can appreciate that, paper is only being used as a medium of transfer. So this dye, is not actually for printing a paper, it's only printing, a paper, for transfers. So, dye is exactly the dye that, we are interested in, in the textile.

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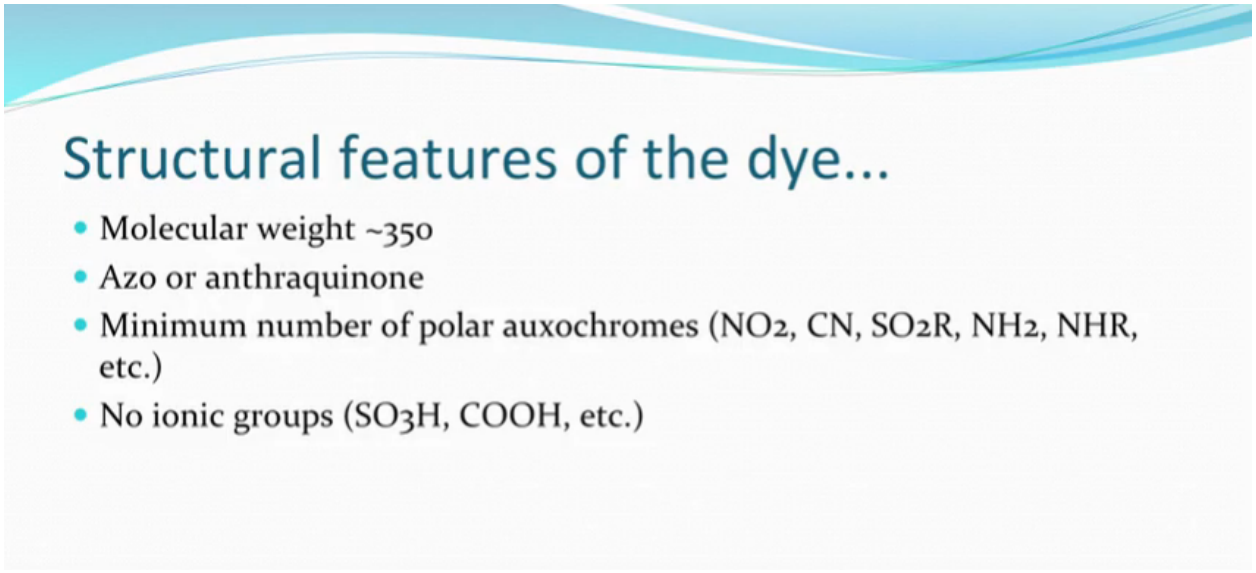

And we are looking at the dry heat transfer, which dyes is the question? Which may try to appreciate obviously it has to be a dispersed dye, the transfer rate should be same for the mixture ? This one has to work carefully, by in consultation with the dye manufacturer. So, dye manufacture will give you charts, which has all the experiments done on the dyes and when you try to mix them up, you should know, which dye to mix, because you'll be using, mixtures of dive to get different shades. The temperature, where reasonable amount of sublimation takes place, may be different for, different dyes. That also must be checked, so one is transfer rate, the other is that the temperature, at which the maximum rate is obtained, should be also approximately same because, you invariably would not be varying the temperature during the transfer. You will use one particular temperature, could be hundred eighty degrees or 280 degrees centigrade, therefore the dyes, must be compatible in that manner. fabric structure, theoretically one can say well, why should there be any difference is the chemistry of the fiber, which is an important thing, but not necessarily true ,suppose use a non woven, polyester mat versus a tightly woven, polyester fabric, versus a knitted fabric, there are openings, there'll be enough space and so the dye, can go through the spaces also, on the other side, may get deposited, may not get deposited and transferred. Right? so the shades, that you will obtain will be dependent on the fabric that you obtain. So, this is true, theoretically this is true, with other printing also, Mr. Moore you want to print carpet, so everything there is a pile and you will not really get, the same effect, as you get enough tightly woven fabric. But, that's nothing to do with the transfer printing process. But, one thing is interesting, that you are pressing, the paper, the fabric are being pressed and heated, some of the fabrics, structure may collapse under the pressure. so then, you don't know, where you are going to printing, on the side of the fiber or on the fiber which is you know, so there is a loop for example, so you wanted loop normally supposed, to be vertically thing, so you want the colors and print on the surface, if all of them collapse, because of the pressure, then the side will be printed ,which will not be seen and so, one should know exactly, how much pressure to put? If you put less pressure, obviously you can appreciate and I will go somewhere else also. and so, that part remains, this difficulty is almost, with every type of printing, that you want to use, even a roller printing as a pressure.

So, if you use, compressible material, then you can get different results. So, the dyes are known as, the disperse dyes, have been categorized into various categories A,B,C,D, which is based on their, sublimation fastness you know .so, if the sublimation fastness is poor, you say well, it is a type of dye, if it's very high, then it is d, also they are sometimes classified as low energy, medium energy, in high energy. Low energy means, you require less temperature, for sublimation. And medium energy is the same, in high energy means, you require more energy for sublimation. So, advantage, disadvantage, will all absolutely be understood, in the normal dyeing processes and printing processes, the wash fastness, may not be affected ,but the sublimation fastness, may be affected by this. So, they had decided to classify them, based on what you want to use. in the requirement of a Dyer or the printer otherwise, they would have loved to go for always D. right? But, in the case of transfer, we really want transfers, we want sublimation take place. So, there are opposing, needs that we have, from the fastness you like, high energy dyes. But, then they will not probably vaporize the way you want it and so transfer may be, efficiency may be very poor. so maybe, somewhere, somebody will say well, somewhere the medium energy, type of dyes are good for transfer printing, all right. So, some other things which obviously based on, the experiment that people done. If the molecular weight is very high, then it is also a high energy. If it is very low, in the range of 200, 250 s then, again it is low.

So, somewhere in the moderate range of 350, around 350 is not exactly a number, around this thing, people may like to have a molecule of this size, they could be a azo or anthraquinones, which the disperse dyes obviously, are made, one important thing which as an Auxochromes requirement is, they should have minimum number of polar, so polarity has to be less, non polarity is better. Okay? So, minimum number of polar, Auxochromes, some are required because you have to give some shade. Right? And no ionic group, fortunately dispersed I do not have any group, you know, the ionic groups if they are there, they these molecules do not sublime. So for, sublimation what is important is? The inter, molecular, bonding forces. So, when you say, high energy, that means, that the inter molecular binding forces, bonding forces are stronger. If they are stronger, you require more energy to separate them ,vaporize means, you have to separate each molecule. and therefore, you are interested that as less bonding that takes place, will be good, so that you give the increase the temperature, kinetic energy will increase, any little less small bonding that they have, will break, molecules will free, to move to the vapor and then go to the fiber surface and then go into the fabric. ionic groups are obviously stronger than hydrogen bonds or Vander Waal forces, if you have only Vander Waal forces, it'll be nice, they will evaporate faster, if you were smaller molecular weight and sublime faster, so this is what how you people will be, looking at some of the dyes and their features, definitely no ionic.

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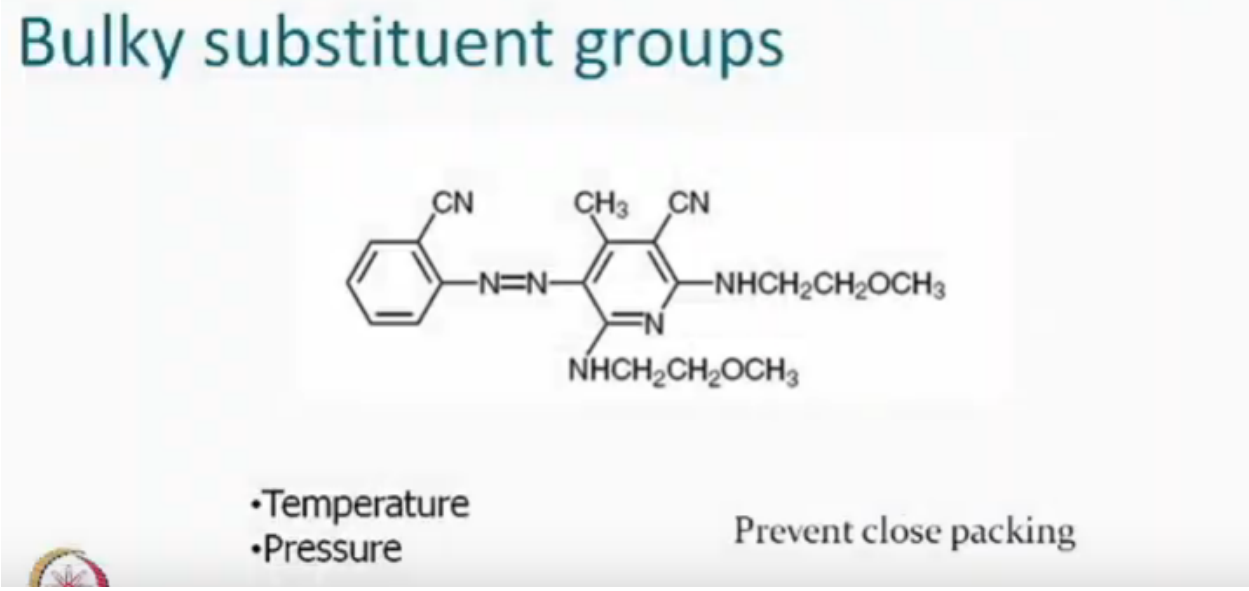

If you have, dyes with bulky substituents, the satiric, hindrances would ensure that the close packing of these molecules does not take place. So even if some, dye and there are some groups which may like to make certain kind of bonds, but you have to come closer, you remember, bonding is like a contract. So, two molecules come together, because by coming together, they get to a lower energy state, otherwise they will not come together. if anything is a solid here, it's because the molecule like each other and therefore they want to come very close and stay there, so if you have bulky substituent groups. The temperature required to you know, facilitate, vaporization ,could be low. The pressure, when you say pressure, what it means is? That when you touch a paper end, of fabric, we say we have touched and we are pressing, but it does not mean that, the there is no gap and gap which we are talking about is let's say air gap, two sheets of thing, there is an air gap. This is good enough, a gap for a molecule, molecule is very small. And therefore, this gap is important. What is important? if the gap is more obviously the molecule can go anywhere and so, the pressures will be also interesting. But, bulky substituent groups are be, let's say, it's a molecule which you would like to prefer.

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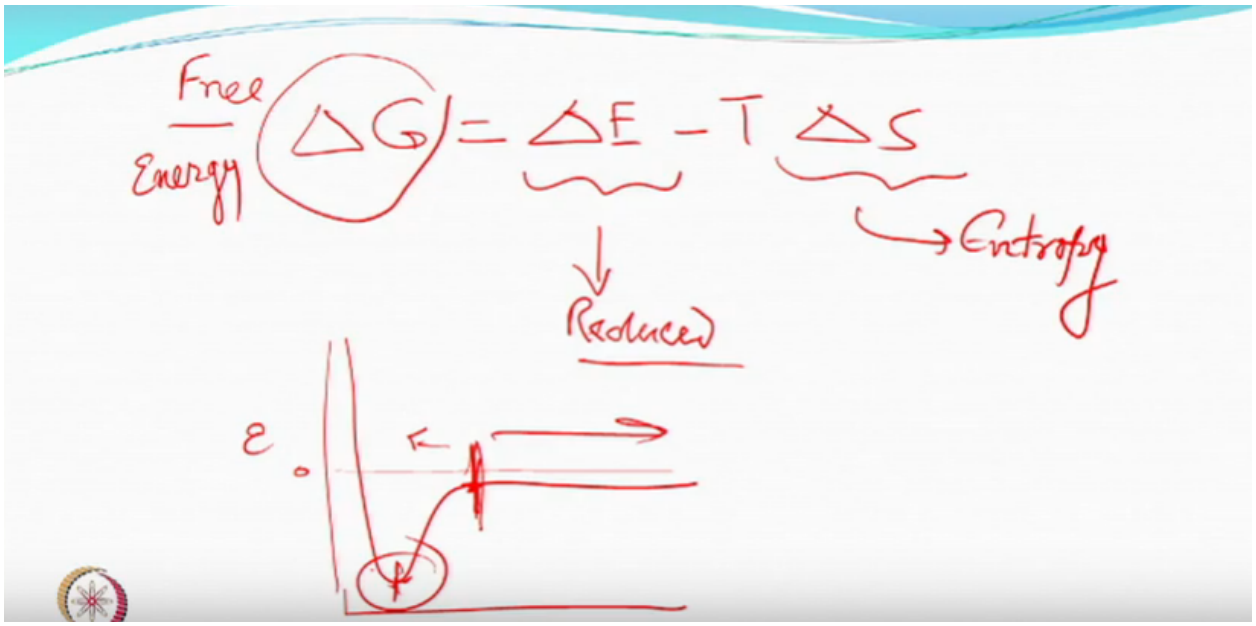

So this is what I was talking about? free energy, which is known as the, G or change in the free energy, this Delta G should be negative ,for anything to become stable, all right. And how can it become negative? If Delta e is negative? That is the internal energy of the systems are negative? Or the entropy is high, entropy is a disordered structure in universe, without your liking, everyone wants to be free and move around everywhere, that freedom is basically the entropy. So, when the molecules come together and when they will not come together, depends on the distance between the molecules, if the distance is large, then they may not come together, they may like to remain at their liquid form or a vapor form. Right? And because there is a kinetic energy available or whatever, so they are far off, so they can't make whatever you call the bundle? For formation of a bond the distance must be, less than a certain value. if this is less than let's say ,in this case this, then automatically these will reduce the distance and come closer, if this is the distance between the molecules or Adam's. Right? So this is general principle, which will happen, same molecule would love, to remain in random form and this is thermodynamically, acceptable, structure, condition. But, they do come together, when they come together, that means, a situation has been created, where the distance between the two, has been brought down to a level, after which they will come automatically to this point .why? because, all the masses attract each other, they attract each, so they come closer, so coming close is a good idea, but they cannot go beyond a certain value, because if you come closer than that, then you have everywhere electrons, so they start repelling, if you come together, so the energy goes up tremendously. And therefore, whichever type of a structure is possible, a hydroxyl group coming very near, another amino group and they can make iron bonds, they can only make the iron bonds, when they come to a certain distance, similarly to make a vandal for so you have to come, to another distance. Right? so or a covalent bond for that matter also, understand you come so close, that you are able to share your electrons from one to another. And so, you will make different kinds of bonds, so when we talk about high energy? That means, there were some groups we could ,we could allow the molecules to come close together and therefore, to separate them, you will have to supply more energy. Right? And that is how we have particles coming together, because they like and when they come together mean, they are making some bond, may be physical bond. But, they are making bond.

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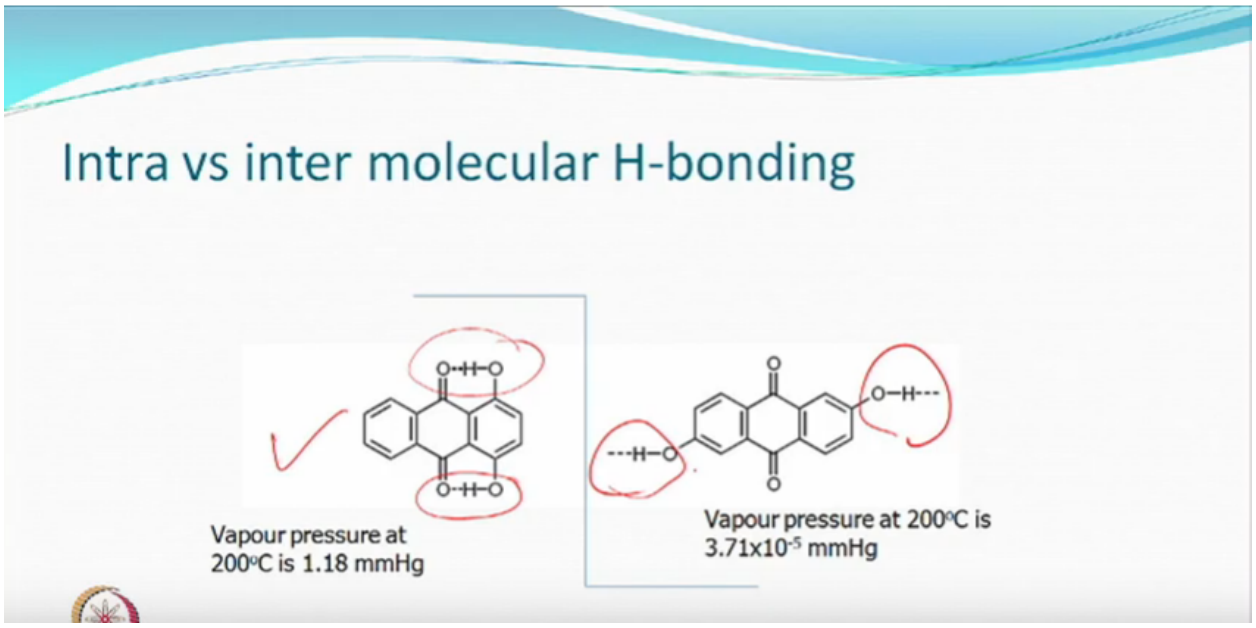

So any situation, that you create other than, it being a dispersed dye. Both are disperse dyes here. And both have, same molecular weight, so molecular weight is one part, size of a molecule is one. The chemistry is also important and here, it is not van ionic, in that sense. Right? But, what you see, one of the molecule which is this one, can make intra molecular hydrogen bonds. They can make, within the molecule itself, so satisfied, if there is a possibility of making a bond, within the molecule itself, they are satisfied. you don't have to go anywhere else, in the other case, when you have one hydroxyl group here, the other hydroxyl group on the other side, you see ,that within the molecule they cannot, make any hydrogen bond, they will make heightened bond with another molecule, that will be called the, Inter Molecular H- Bonding. So, intermolecular hiding will be possible in this, but not intra, but see the interesting part, at a given temperature let us say 200 degree centigrade here, in one case the vapor pressure is 1.18 millimeter of mercury, all right. In the other case, it is three point seven one and 10 raise to minus 5, you see what the difference we are talking about, which order are we talking about, a small little change, can actually make such a big change, in the vaporization sublime ability. Because, the molecules can make intermolecular bonds or separating them, they'll require more energy, in the other case, they are not making any such bond because, they are satisfied with each other. So, between the molecules they will be on Vander Waal forces. Right? Well that's interesting.

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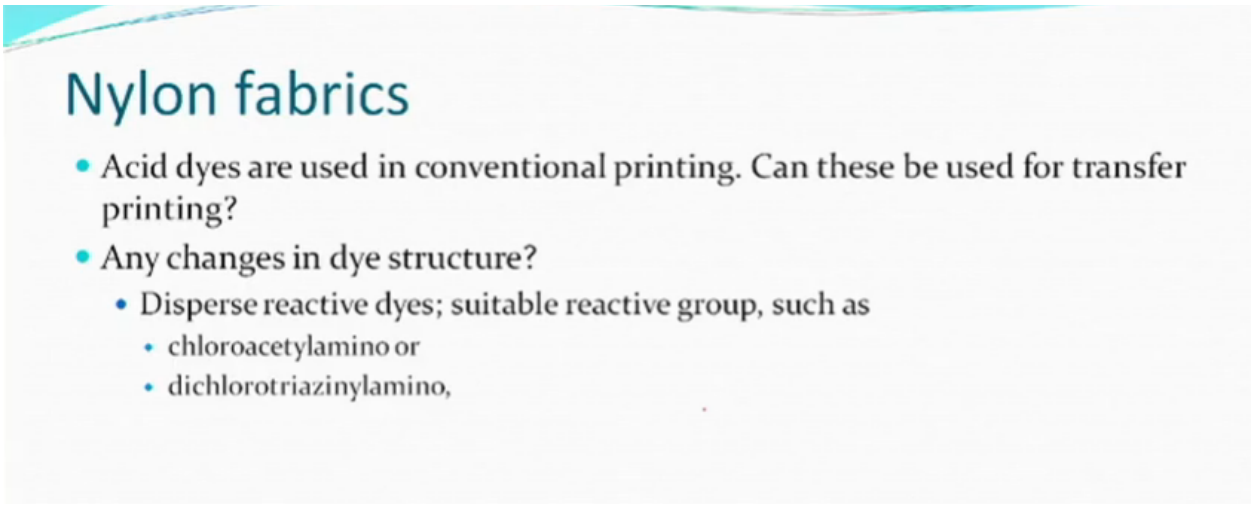

So that was the polyester. So you can, obviously use polyester and disperse, as I said is a good combination. So, can we do the transfer printing, a nylon, yes. We can do. Right? So, in a conventional printing you like to use, ACID dyes. Right? Can these be used for transfer printing, at the moment we are talking about, sublimation transfer. Can they be used, they cannot be used, because they are ionic, we said this is something which should not be there, there is no sublimation that will take place. One interesting thing, is that disperse dyes, obviously dyed in nylon, disperse dyes obviously will print the nylon and disperse dye will also have the transfer also. one of the interesting thing, which has been seen in nylon which has not been seen in polyester, is the wash fastness of the dispersed dyed nylon fabrics, will be low, compared to the same dye on polyester .if the same dye has been dyed or printed on to polyester, the wash fastness is higher, compared to the same dye, in nylon. And one of the reason, why it is there is? Because, the glass transition temperature of nylon, tremendously goes down in moist conditions, that means, at a very low temperature, which is room temperature, there is enough mobility ,of the molecules available, so during washing also, it can come out. Right?

So, if you do all the hard work, with the dispersed dye and you find the washed pants is not so good, we're not talking about sublimation fastness, the document wash fastness ,then it doesn't make much sense, but they can acid either good, they give good colors, whatever they give of course you have complemented complex, they'll give you fastness also, but they cannot be used for thermal transfer. So there is a loss of dye, which is being generated, called, 'Disperse Reactive', I mean, you did not obviously can understand you, you did not want this type of a dye, for polyester. What do you do with this? Right? So I mean, what will you do with the dispersed dye, on polyester is anyway nice, so you don't require a disperse reactive dye so polyester. So these dyes are the such, which behave like disperse dye at one stage and after that, you can get them reacted also. So, in that case, what fastness issue will be taken care of and good for nylon actually, theoretically you can always think, well if you keep changing certain groups, in a manner, where they can react with any other group, like hydroxyl group, then you can do and sorry Lowe's also, nice thing would be that the same dye, could be used for an polyester or nylon ,cotton blend or something. Only thing is, how many people make nylon, cotton blend. Right? Or you can say polyester, cotton blend, where the reactive component can go to the polyester, reactive can go to the polyester. But. It was the best for the nylon. if you use such dyes, then you can do thermal transfer printing as well, that goes by its sublime when it is just behave like a dad, disperse dying and then, when it reaches there you can always

create conditions, which will then they can react, you can appreciate like, we already know that, the activity in neutral conditions of the amino groups is quite high and so, one can react in acidic medium, so you can have a fixation in a different way, so you may require ,another fixation, either it happens in the same time. But, if doesn't then you can change conditions and then fix them up.

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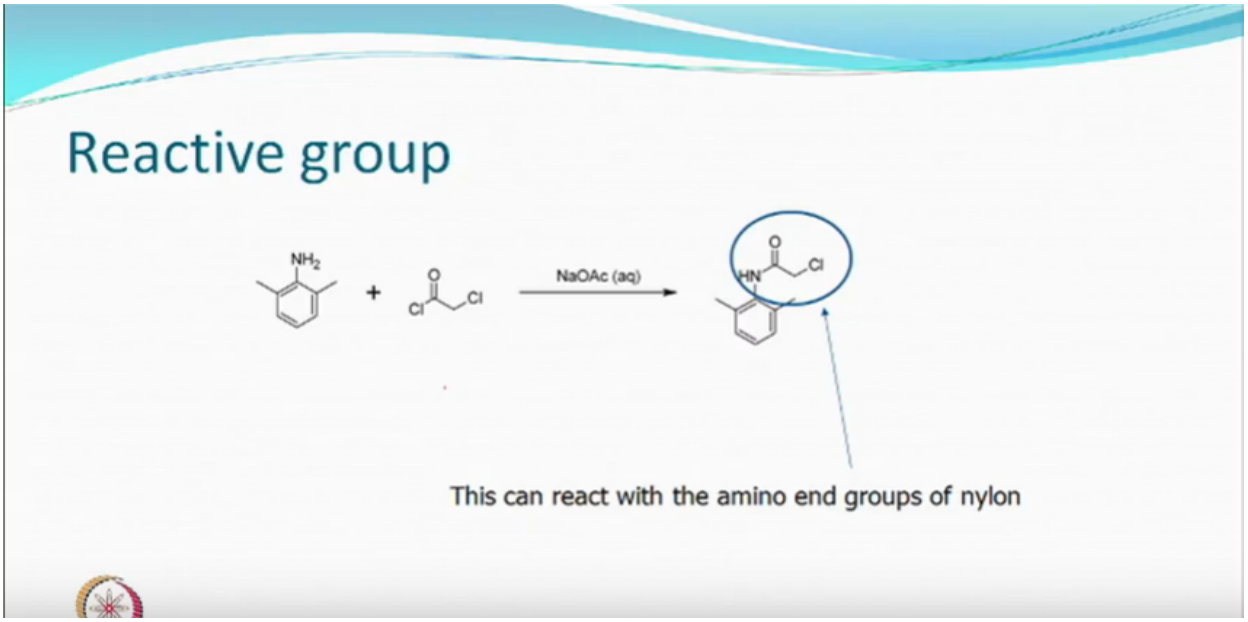

For example, if this kind of a group is available, this group can react with the amino and groups of nylon and if that happens after, it has sublimed into or transferred diffused ,then you get the good fastness also. So what is also important is ? That whenever there is a problem, you do not give up, but try to find another way, another solution, to reach to some same goal. Right? This is the way, the organic chemists, would be working, making a different kind of molecule, which should do the same job.

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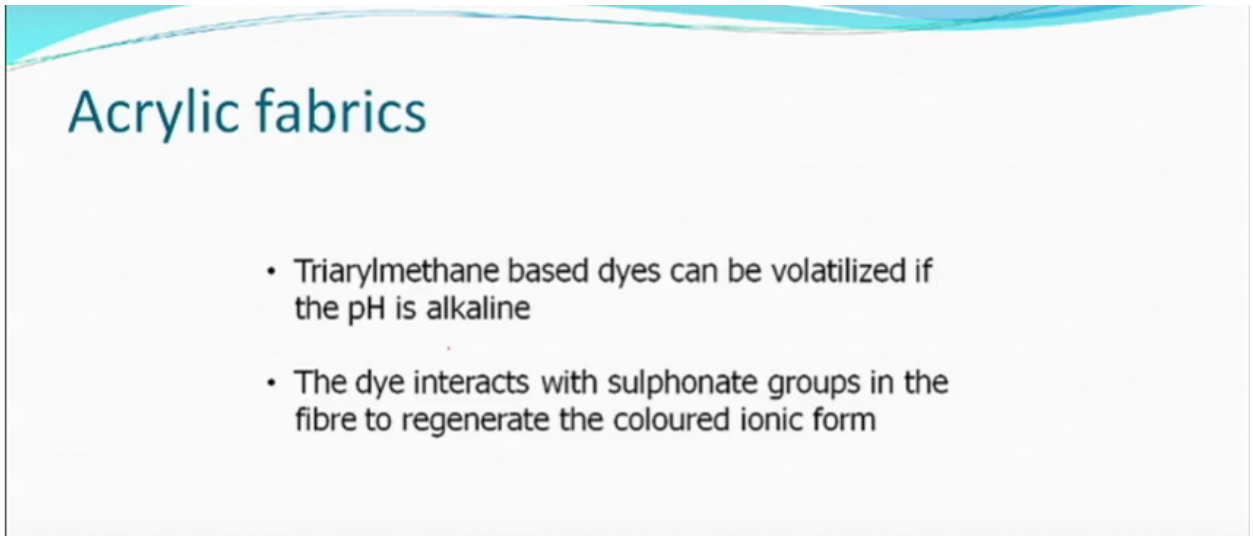

Acrylic fabrics, you know that they like cationic dyes, which are also ionic and therefore, they were not sublime. But, they are very good, from The Ting to riel value and fortunately Acrylic fibers are much more hydrophobic, compared to nylon. And therefore, whatever goes in doesn't come out very easily, All right. But, you have to ensure that they go in first, so dyeing or printing of acrylic is anyway, more difficult in some sense, but once you do it ,then they remain. So, some of the dyes which are in Acrylic they, you see that, rhyme rile methane-based eyes in the acidic medium or ionic. Right ?but in alkaline medium, they are not ionic and they can volatilize, whether you will like, printing ink to be alkaline is a story because you have to store. Right? Some effects can be there, but this is what.

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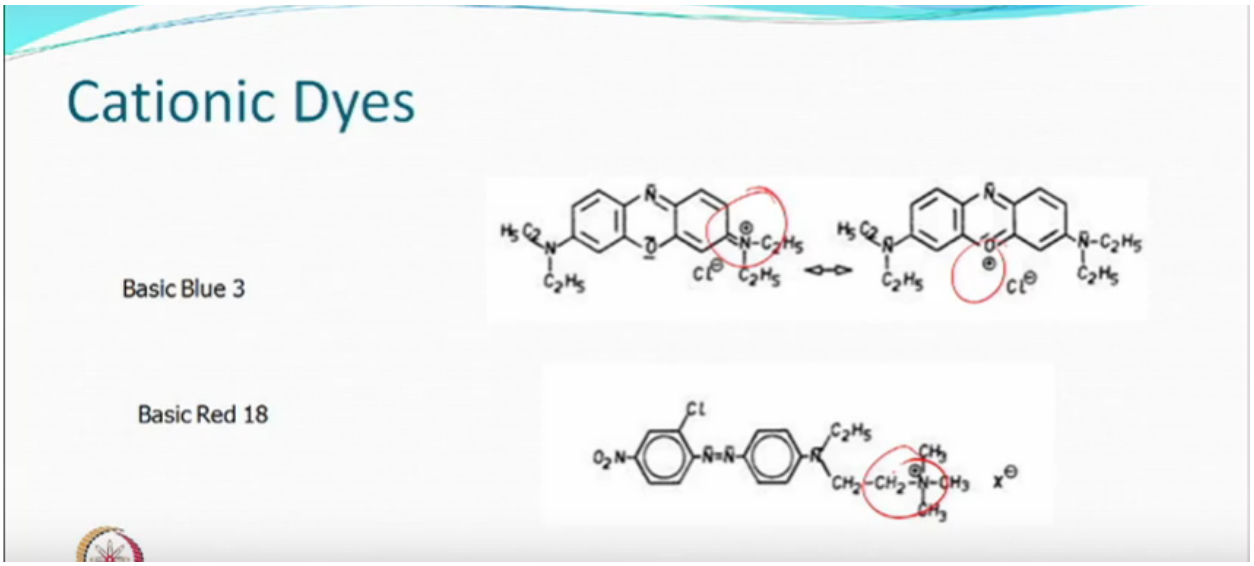

So, the normal dyes which are there, nice beautiful ones. There is an ion everywhere, it is not going to work. So you have, some iron here, some iron here, these are the resonant forms. If you do have ions,

then you have a problem. Okay? So there is an ion here, on the nitrogen. So, there is a common cationic dyes, which are good for the acrylic printing, but not for sublimation transfer printing.

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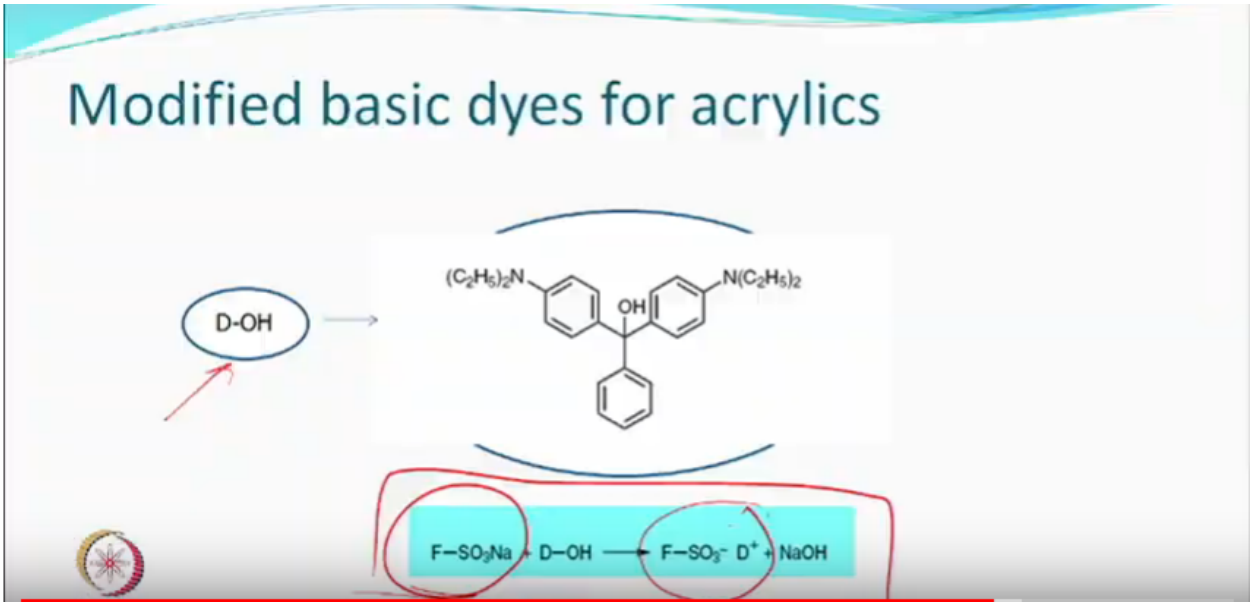

But if you have a dye like this, we should call the, 'Dye', you represent the dye as, dye which has got a hydroxyl group and all other is dye phenyl methane type of a group. and because, of this H being there, it is possible not to have that means, not to have, any iron there. if that is not there, then this can sublime, another disperse dye any sublime, that disperse dye can also go like it can go, to the nylon. But, normal basic dyes, cationic dyes, of hiding total value, which everybody likes. So if you want that, then you have to modify the dye in a manner, that it is not ionic. but once, it vaporizes which is from the paper, to the fabric it goes, there it can do this reaction which you know, this type of groups are available on acrylic fiber, from where do they come, these groups, anybody else, in groups in acrylics we can't use cyanide group eyes of folding, instead of that sulfites and by a sulfites groups. Right? So, the initiator, the initiator, which is used in the polymerization, obviously doesn't go anywhere, it stays at the end. And we call this stays at the end which is ionic, so that ions are there. So this dye, can react with those at suitable conditions and this type of a bonding may form, with your ionic bond ,which is good enough, once it is ion, then its iron anyway it goes out, you can do some washing later, all right. So, this one of the ways, in which you can have a relatively better looking dye on acrylic, like. All the normal dispersed dye, we are going to polyester can also go there, but then they don't give that, kind of editorial shape.

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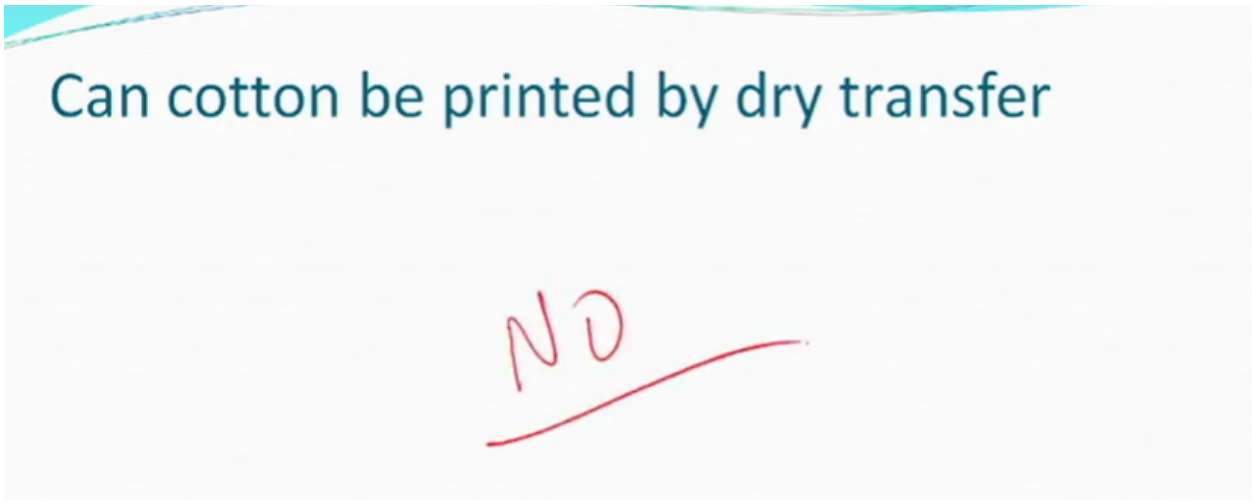

Can't cotton be printed by dry transfer. The dry transfer means, you have this first day. Right? So, normally you will say, it cannot be. Right? So, you can say well normally, no unless ,you do something.

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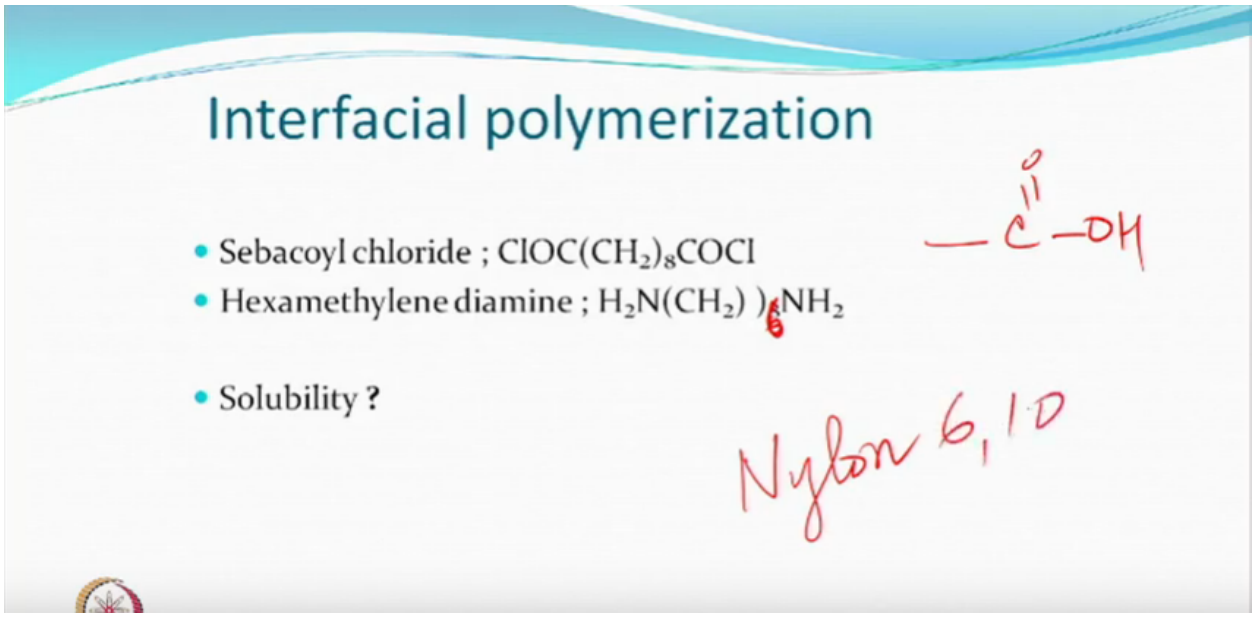

Have you heard of interfacial polymerization. Interfacial polymerization is the polymerization, which takes place at the interface, at the interface. And if you have, highly reactive compound monomers, in this case for example, a civic oil chloride, which has got c10 and it's a chloride, not an acid, if it doesn't acid, simple coil chloride if it is subarctic acid. Right? Instead of COCL, if you have COOH, this is not reactive, not that reactive. If you take a dichloride of this acid, which is super coiled chloride, it's very reactive, at room temperature reaction can take place with let's say, an amine, Hexamethylene diamine; so this is 6, Hexamethylene diamine. So have, Hexamethylene diamine which is the same amine, which is used for nylon 6,6 manufactures. But, super coiled chloride is a different monomer and this, can react at

the interface, the moment they touch, each other they react, so you have to keep them separate, so what you do? One of them is soluble in water, other is soluble in organic solvent. and water and organic solvent don't mix, but if you create a situation, that you are pouring something very slowly, immediately at the interface you will have a polymerization, in fact you can keep drawing the polymer from the interface continuously and the continuously polymerization can take place, this is called, 'Interfacial Polymerization', at room temperature. You can use isocyanides, you remember isocyanides it's a very, very reactive just touch the water and then react. Similarly this is one of the interesting part, what kind of a nylon can form? It can form 6,10. So this particular impound, you can make any of the nylon also, change the monomer.

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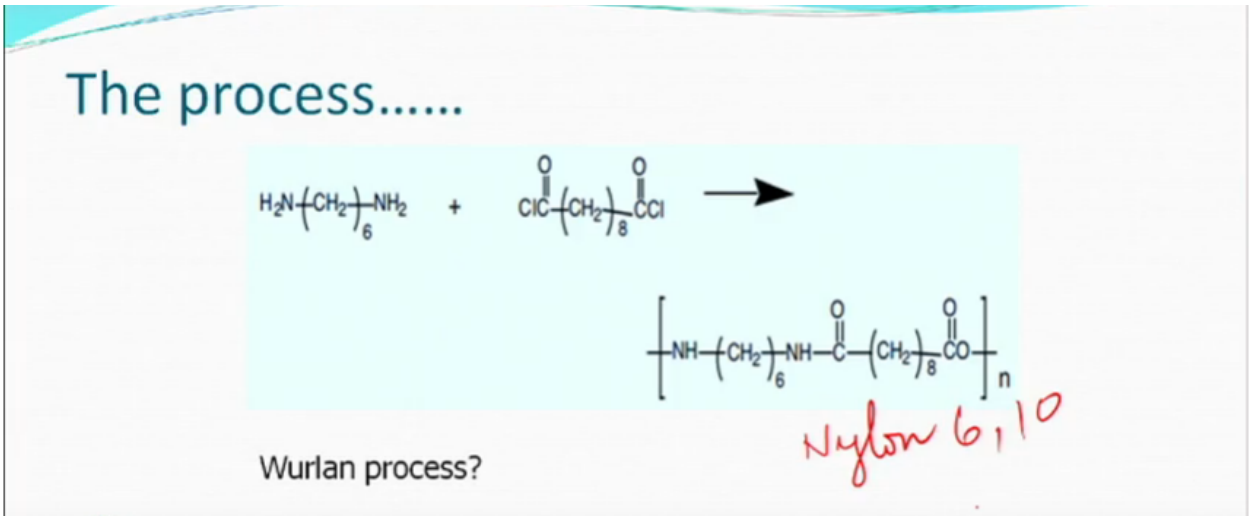

So, you have one monomer, which is the HN ethylene diamine and the other is super coiled chloride and they will make a polymer, which is this 6,10 have you heard of a process called, 'Wurlan process', no Wurlan process is the process which used this, polymerization technique to onto the wool, so that the scales on the wool could be masked. Because, you have felting, the properties of the wool and if you don't want felting to take place, if you want to make shrink crew wool, where they say, so one of the processes that you coat the surface, with a polymer. so there the scales get masked, so this was a commercial process for wool, you could do tops, that you could do fabric, nylon 6 10 the, coating of nylon 6 10. Using interfacial polymerization, so what you do? pass the wool from one solution and then pass into the other, so one of them is absorbed first, then you squeege and after squeezing take it to the other solution, in a continuous manner and suddenly find, as it goes in and comes out the polymerization is complete on the hips. Right?

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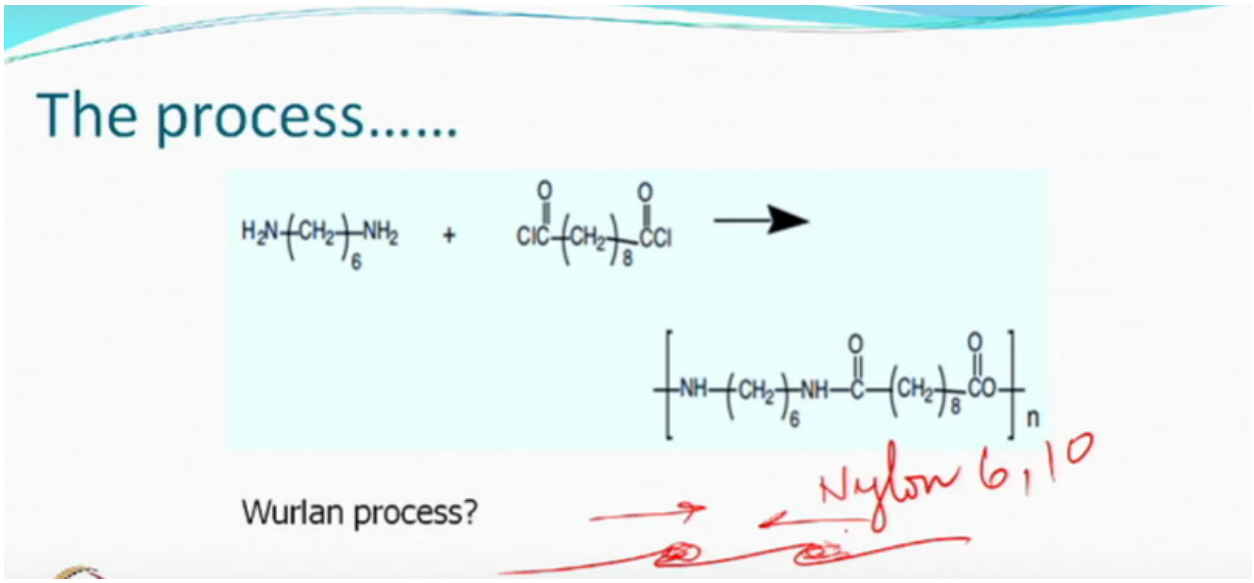

If you do, the same thing on a cotton fabric, you will get nylon 6 10, if you do isocyanides and Hexamethylene diamine, you will get, poly iconic, polyurethane both of them are hydrophobic. And theoretically, the dispersed dye can go and sit there, after transfer. Can they do what? I said, dying during dyeing and printing of the wool coated with nylon 6 10, why of course it, would but then if you come to the wood finishing, they will say well do not, you know, make a complete layer like, sheath core where the fiber is absolutely, inside the polymer. When there then it will not be whole, it'll be in the polymer property. So, they apply very less ,very less, only thing they do, in the case of wool is that you have the scales, so you say well the polymer will be here and here they'll be very less polymer, so because of surface tension and other kind of things, the first liquid has to go, somewhere there don't absorb too much ,your aim is that something if goes here, then the friction in this direction, in the friction in this direction would be, more or less similar, so that directional frictional effect, which is responsible, for the movement and the felting will be taken care of to some extent. They are the polymers also, available so polymer coating is one of the ways in which you make, shrink resistant rule.

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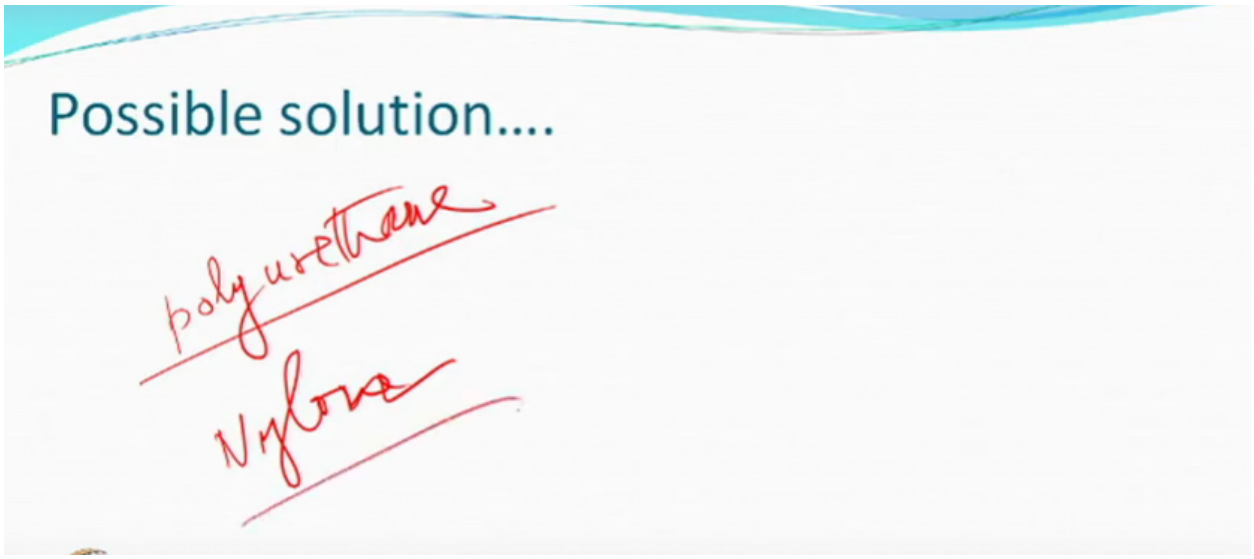

So that's the possible solution. So you can, either do polyurethane, with isocyanides or nylon, nylon with super coil or any other is it right. You can get by the interfacial polymerization a layer, of polymer you can absorb, it will never be as good as you say, you know, like a polyester. But, it will still do and certainly be very interesting prints ,of course you'll have to worry about, what will happen to the abrasion resistance, what will happen to all those kind of things, they will definitely be something which, one should bother.

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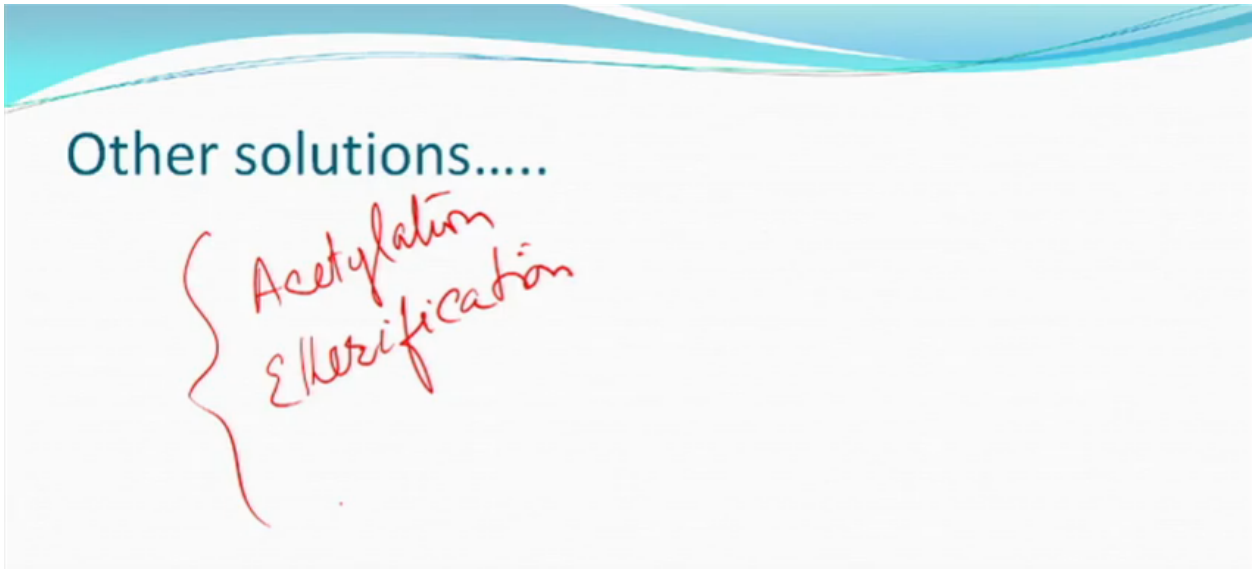

Other solutions, could also be will you talk about cotton. Etherification, etherification, they also make material hydrophobic, like triacetate is fully hydro phobic. Right? So this is where, we can stop, that these are the methods, which can be used to do dry transfer printing, on polyester definitely, which is the best

substrate. And hopefully you can use, for other substrates as well, by some modification of a dye or some modification of the surface, of the polymer. So, can be used for cotton and theoretically, can be used for any other fabric, if you can make a code, there we go. Thank you.