Natural Dyes
Prof. Padma Vankar
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture No. # 24

So far, we have been learning so much about natural dyes and natural dyeing. And intermittently, we also learned a few things about synthetic dyes. We will now go back to synthetic dye and its use on polyester and its blends. Because, you see in the industry, the polyester fibre is so much in demand and the dyeing requires a special technique and what are these specialties is what we are going to discuss in today's lecture. So, this particular lecture will be dedicated to synthetic dyes and the use of synthetic dyes in dyeing, polyester dyes and its blends. Various types of you know cotton mix polyester or wool mix polyester; how these fibres of fabrics are to be dyed. We will take a very serious look at these techniques.

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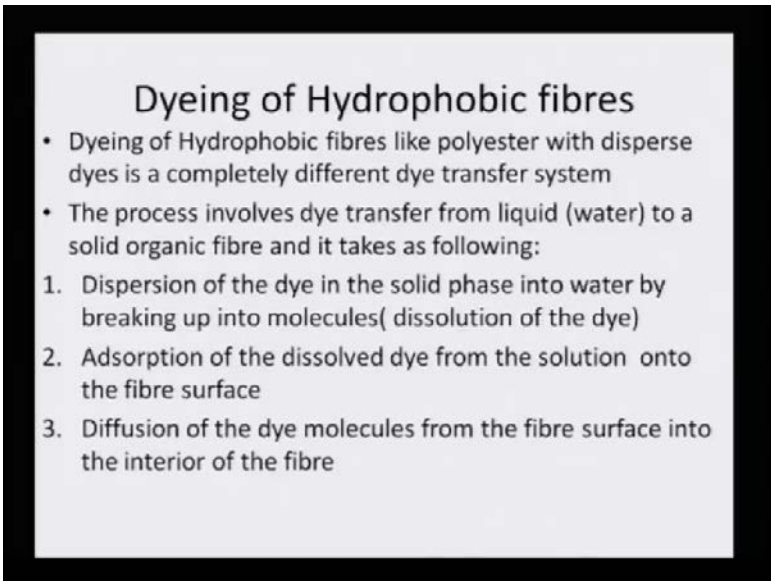

Dyeing of hydrophobic fibres: Dyeing of hydrophobic, hydrophobic means water hating, so that means, the water does not retain. Dyeing of hydrophobic fibres like polyester with disperse dye is completely different dye transfer system. So far, you have learned that the fabric which was cotton, silk or wool was hydrophilic and so it was possible to absorb water and through this absorption of water, the color or the color molecule or the colorant would get imbibed on the cloth. But that is not the situation in the case of hydrophobic fibres such as polyester.

The process involves dye transfer from liquid that is from water to a solid organic fibre and it takes as following. So, how does it take, we will just take a look at that: Dispersion of the dye in the solid phase into water by breaking up into molecules; that is the dye gets dissolved in water. But, this dissolution, you see is not very complete; it is more like you know forming a kind of a colloidal solution; adsorption of the dissolved dye from the solution onto the fibre. And diffusion of the dye molecules from the fibre surface into the interior of the fibre. So, you see three things happen when polyesters are dyed with dispersed dye.

The dye, which is first taken as a powder or a solid is dissolved in water and this dissolution is actually not a complete dissolution. There is an equilibrium, there are some undissolve and there is some dissolve. So, this dissolved dye then goes through adsorption into the surface of the fibre and then subsequently it penetrates into the interior of the fibre. So, it is a completely different kind of process.

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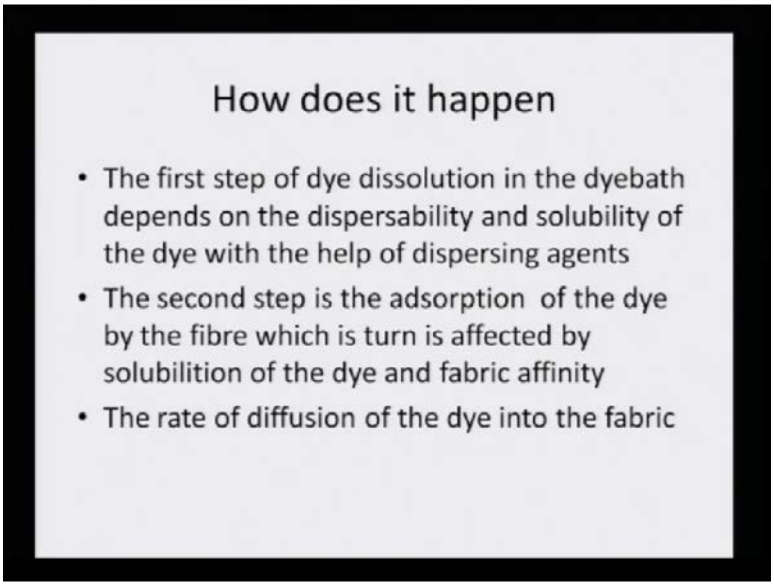

How does it happen? The first step of dye dissolution in the dyebath depends on the dispersability and solubility of the dye with the help of a dispersing agent. So, as I told you these disperse dyes are not highly soluble in water. So, they need an agent that is called the dispersing agent which creates a kind of a dissolution. If I have to explain to you, then I would say that there is undissolved dye and there is this dispersing agent, when they dispersing agent is present, it facilitates more and more of this disperse dye to get into solution state. In the absence of dispersing agent, lesser amount of disperse dye dissolves. So, you should understand from the equilibrium point of view.

The second step is the adsorption of the dye by the fibre which is which in turn is affected by the solubilition of the dye and fabric affinity. So, the second step is that this solve, dissolve dye then adsorbs simply as a, you know function of the surface area and it is affected whatever is dissolved is then adsorb. And then finally, this would depend on the nature of the dye and its affinity towards the fabric, because suppose some disperse dyes do not have much affinity for the fabric. In such a case not much dye will go into the fabric in one go. So that means, several times the polyester must be dyed again and again and again, so that the required color is obtained, because at a time, it takes only a small quanta of dye. The rate of diffusion of the dye into the fabric is very important and would depend on the nature and the fabric affinity.

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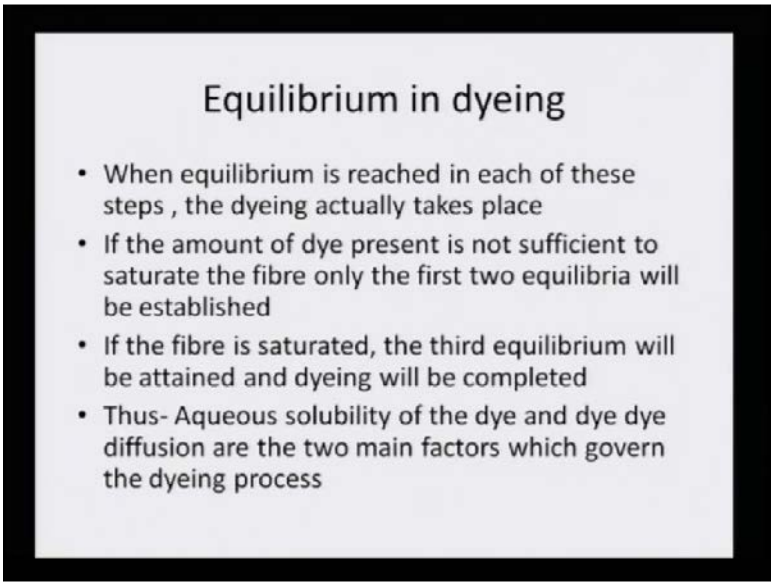

Equilibrium in dyeing: When equilibrium is reached in each of these steps, the dyeing actually takes place. So, all these steps are not moving in a forward only; they are moving forward and backward, as a result there is an equilibrium. I hope you understand, what the word equilibrium means, that means there is a rate of reaction of the forward reaction and equally there is simultaneously, there are some dissociations occurring and it is getting pushed backwards.

So, when the reaction moves both the backward and forward; it attains an equilibrium and therefore, only by parts of dye molecule will be adsorb or dissolve and subsequently each step has an equilibrium. So, you see that it is not just what we saw in natural dying, that all the dye that was present in the dye bath was slowly taken up by the fabric, because the fabric was hydrophilic. But here, because of the hydrophobicity are not loving the water content; it is not taking the water or the dissolved dye in the water so readily.

If the amount of dye present is not sufficient to saturate the fibre alone the first two equilibria will be establish. So, you see there are three equilibria, three steps and each one would be dependent. Suppose, if the dye dissolution does not take place properly, then what will happen, the dye will not… You know it will remain in the solid state and it will just be attaching on the surface. Now, this attach surface is actually not really penetrating or not able to penetrate or adsorb on the fibre.

So, there is this each equilibria affects the other equilibria and there are three such equilibria which are interrelated. So, if the dissolution is not good the adsorption will not be good, if the adsorption is not good the penetration of the dye will not be good. So, these three things are interrelated and they all are not straight forward, forward moving reaction. They go forward; they go backward. So, a part of it is only adsorb, a part of it is only dissolve and a part of the dye is only penetrated into the fibre.

And therefore, you know this whole process now seems to be quite quite different from the natural dyeing process, where we never ever mentioned that there was any kind of a backward reaction. But, once the dye is taken up; it is taken up, there is nothing like you know rejection of the dye from the fabric. If the fibre is saturated, the third equilibrium will be attained and dyeing will be complete. So, it is only when the dye dissolve dye is adsorb, the adsorb dyes starts penetrating within the core of the fibre. Thus-Aqueous solubility of the dye and the dye diffusion are two main factors which govern the dyeing process.

So, in this polyester dyeing two factors are very very important and those are the first two equilibria. And what is responsible for the first equilibria; it is the dissolution of the dye, and in the second; it is the diffusion of the dye or which was followed by the adsorption. So, unless and until the dye is adsorbed; it will not be diffusing into the core of the fibre.

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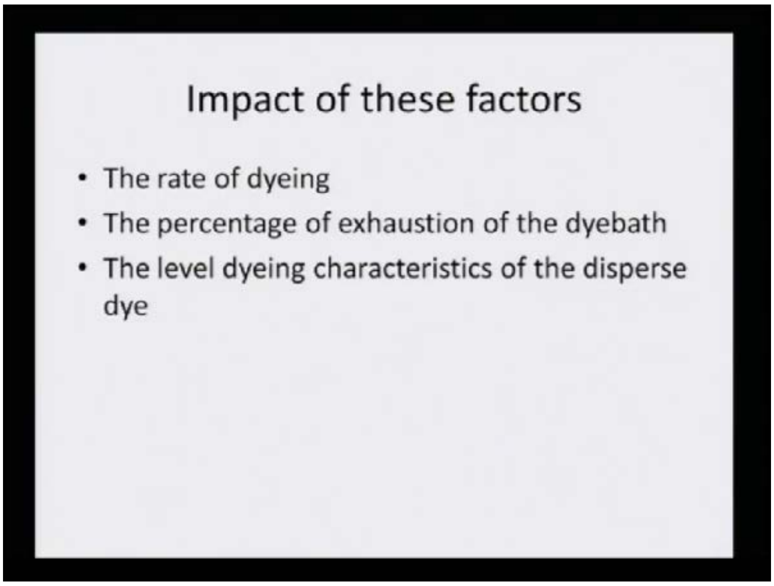

Impact of these factors: The rate of dyeing will be affected, because everything is now dependent on these three factors dissolution, adsorption and penetration. The percentage of exhaustion of the dye bath and the level dyeing characteristic of the disperse dye. So, these three factors you know are affected or they have an impact, because the rate of the dyeing will be affected. If any of these three steps is altered or slow down or it is not happening according to what it should happen.

The percentage of exhaustion, obviously if the dye substance is say 10 molecules and out of which only 2 molecules has got dissolved, and of course it is not 2 molecules; it is like moles. We talk in terms of moles or milli moles which is 6.023 into 10 to the power 23 molecules.

Now, let us talk about moles, if we are taking one molar solution of the dye. Now in that, we have this Avogadro number of molecules and out of which only say 20 percent is dissolving in that case the rate of dyeing will definitely be very very slow. And similarly, the percentage of exhaustion; that means, the dye uptake from the dye bath also will go down. And therefore, the level dyeing also characteristic will be affected, why because dye will not be taken up and they will be solid dye dispersed on the surface, which has not gone into the solution form. Although, it will be washed off in the subsequent washing step, but nevertheless the level dyeing will get affected by this kind of uneven solubility.

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For achieving good fastness, addition of small amounts of dispersing agents, leads to better exhaustion, longer dyeing period ensures better rubbing fastness, shorter dyeing time usually cause less level dyeing. So, these are… If one needs two or one aims to get good fastness time and again I have been also mentioning that no dye will be considered as a good dye. No dyeing process will be considered as a good dyeing process unless and until good fastness property is achieved, because that is the ultimate goal whether we are dyeing a polyester blend or we are dying cotton or silk or wool or anything.

The end point is that, if it is dyed by any dye, synthetic dye, natural dye, whichever dye disperse dye, this dye that dye. The final product must have good fastness property and to attain that in polyester as you would realize by now that it is tough to dye polyester, because of the hydrophobicity of the fibre and because of that dispersing agent play a very important role. And small addition of this dispersing agent can actually make a miraculous change in the dye exhaustion, because by doing that we are enhancing the solubility. If the solubility equilibria is move more towards the forward reaction; obviously, it will affect the dye adsorption equilibria also.

If dye more and more dye is going into the fabric means, the dye bath is very well exhausted. Longer dyeing period ensures better rough fastness, why because see, the rubbing fastness failure comes from the fact that undissolved dye was just attaching to the surface of the fabric. Now that undissolved dye actually comes on to the fingers, if we try to rub the fabric. If most of the dye is going in to the dissolution state or dissolving with the help of the dispersing agent. Do not you think that, it is going to create less amount of dye on the surface and that would reduce automatically the rub fastness, because you see the rubbing fastness failure comes because of the dye and dissolved dye being on the surface.

If that is reduced, obviously, the rubbing fastness will improve and shorter dyeing period usually cause less level dyeing, because you know it will be a patch work. Somewhere, the dye would have penetrated to a bigger distance; it will show darker spot. Somewhere, it would have penetrated to a lesser extend and so over all the fabric will not show too much of levelness or evenness in the… If you take a look at the morphology and even by looking at the color of the fabric, it would be very very apparent.

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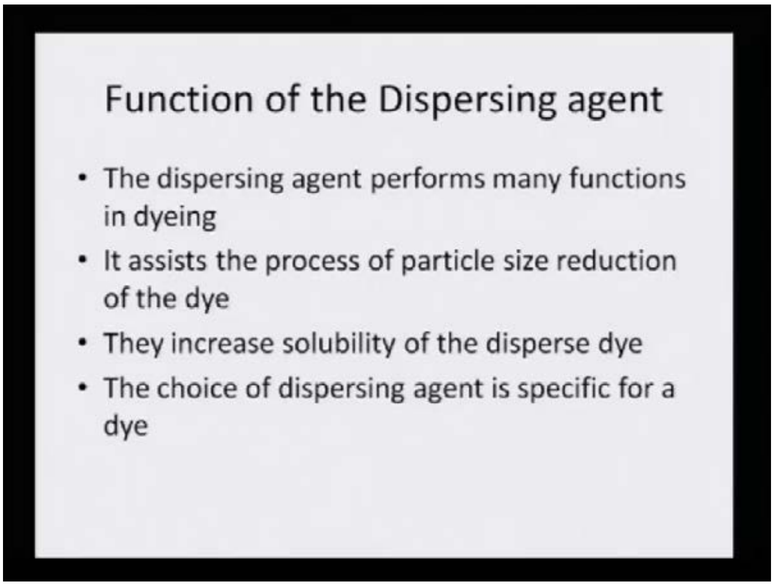

Function of a dispersing agent: The dispersing agent performs many functions in dyeing. It assists the process of particle size reduction of the dye. They increase solubility of the disperse dye. The choice of dispersing agent is specific for a dye. So, it is not that you know they are universal one dispersing agent, and that is what is added to the dispersed dye and then the dyeing carried out. Actually, the main function of the dispersing agent is to break these dye aggregates which do not dissolve. So, once it is broken down in to smaller molecules, if the dissolution is enhance. It assists the process of particle size reduction of the dyeing.

And they increase the solubility as what I suggested and they are specific dispersing dye; it dispersing agents for dispersed dye. So, it is again like you know lock and key arrangement. The other day I was telling you, how enzyme and dye have a lock and key arrangement. Similarly, the dispersing agent is also very specific with a specific dispersed dye.

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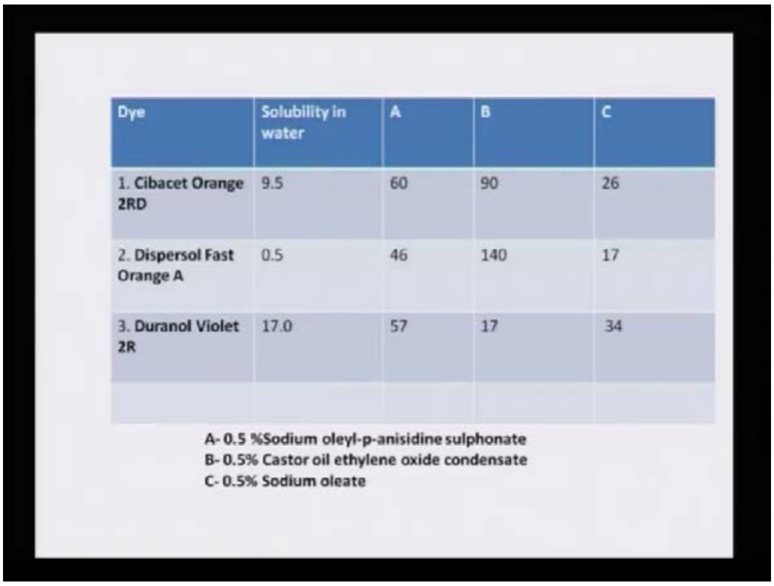

Dye	Solubility in water	A	B	C
1. Cibacet Orange 2RD	9.5	60	90	26
2. Dispersol Fast Orange A	0.5	46	140	17
3. Duranol Violet 2R	17.0	57	17	34

A- 0.5 %Sodium oleyl-p-anisidine sulphonate
B- 0.5% Castor oil ethylene oxide condensate
C- 0.5% Sodium oleate

Now suppose, we I mean I took an example of a dye which is call Cibacet Orange 3 RD, if solubility in water was found to be 9.5 and with different types of dispersing agent A B C. A is 0.5 percent of sodium oleyl-p-anisidine sulphonate, B is 0.5 percent Castor oil ethylene oxide condensate, and C is 0.5 sodium oleate. These three dispersing agents were tried with the 3 disperse dyes that are mentioned here. Cibacet Orange 2RD, Dispersol fast Orange A and Duranol Violet 2R, these are the names of the dispersed dyes. And you see their initial solubility in water is fairly poor and poorest for disposal Dispersol fast Orange A; it is just 0.5. And for a Cibacet orange 2RD; it is 9.5 and for Duranol; it is still better, it is 17. But, when A was added, it became the 9.5 became 60, the 9.5 became 90 in the case of B; that means, for this particular dye, the Cibacet orange 2RD, Castor oil ethylene oxide condensate was suppose to be the best option.

So that, that is what I am trying to make you understand that with a particular type of dispersed dye; that is the dispersing agent has it is own functionality and the best one is chosen for the dyeing process, because the one which is most comfortable is the one which should be chosen. So, in the case of Cibacet Orange 2RD, B was the best one in the case of Dispersol fast Orange A. Again B was better; however, for Durenol Violet 2R; it was not one of the best, but A was better as compared to B, and C was also like medium dye. So, A and C could be the choice of dispersing agent in the case of the third dye. But, in the case of the first and the second dye; it is always the B is the best choice of dispersing agent.

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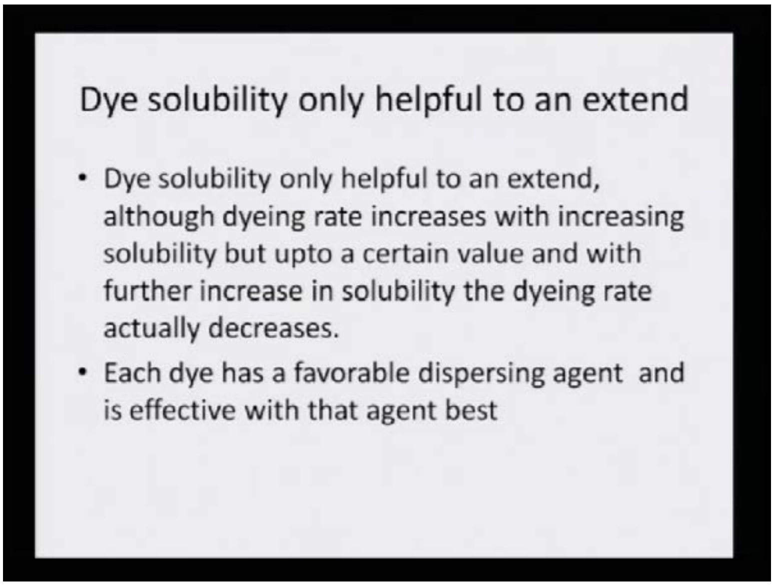

Now, dye solubility only helpful to an extend: The dye solubility only helpful to an extend, although dyeing rate increases with increasing solubility but upto a certain value and with further increase insolubility the dyeing rate actually decreases. See what happens, as I told you this is an equilibrium reaction, the rate of forward reaction and rate of backward reaction. So, they both are actually forming a kind of an equilibrium after a point. Initially, there the reaction moves forward but after some time, because there is so much of dye in the solution the start the dye starts dissociating and coming out as insoluble dye. So, this insoluble to soluble and soluble to insoluble forms a equilibrium.

So, when it is moving forward that time the rate the increase in dye solubility helps in the rate of dyeing. But after a point, it starts dissociating and that is the time when it decreases the dyeing rate. So, you have to imagine this as an equilibrium function rather than you know just a single step reaction, because both the processes are moving simultaneously. And the reason for this movement is that to begin with the fibre is hydrophobic and the dye is also of the insoluble or partly soluble nature. Each dye has a favorable dye dispersing agent and is effective with that particular agent best. We just saw in the last slide, how we made a comparative data of the three disperse dyes and three different dispersing agents. And we saw which one was good for which the particular dye.

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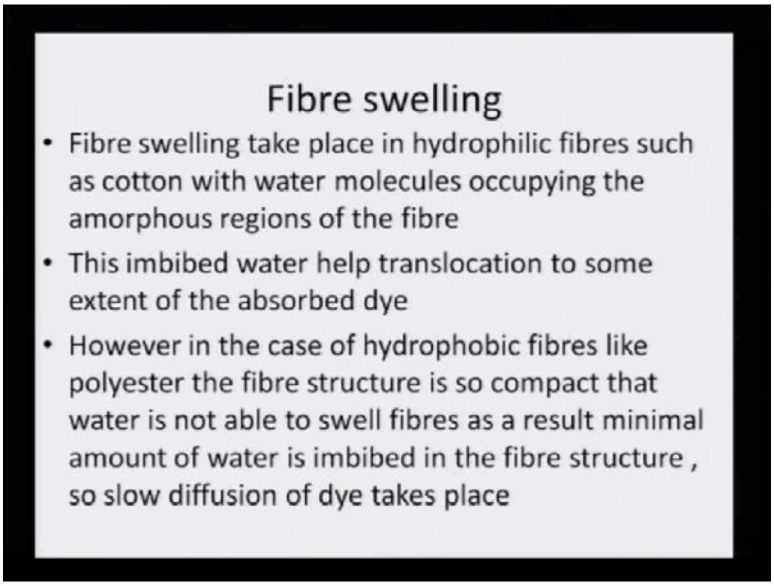

Fibre swelling: Fibre swelling takes place in hydrophilic fibres such as cotton with water molecules occupying the amorphous region of the fibre. This imbibed water help translocation to some extent of the absorbed dye. However in the case of hydrophobic fibres like polyester the fibre structure is so compact that water is not able to swell fibres as a result minimal amount of water is imbibed in the fibre structure, so slow diffusion of the dye takes place. Now, another drawback with this particular fibre is that it is not only hydrophobic; it also is very compact, and because it is so compact there are no pores.

Remember, I told you that in cotton dyeing or silk dyeing or wool dyeing; the warp and the weft these are the two you know ways the yarn is interwoven. Now, the warp and the weft have enough pores and these ports help in taking up the dye through the capillary action and moving the dye upward into the fabric core. But that cannot happen in the case of polyester, because it is interwoven in a very compact manner know. Because, there is no space and plus the fibre is hydrophobic; it does not help the fibre to swell. Whereas, in the case of cotton, because of hydrophilicity the fibre was swelling and water was entering. And this water was helping the dye to translocate was helping the capillary movement of the dye, but that cannot happen in the case of polyester blends and the polyester. So, there are many many dissimilarities and therefore the same process of natural dyeing or the same process of direct dyeing cannot be applied to disperse dyes with polyester blends.

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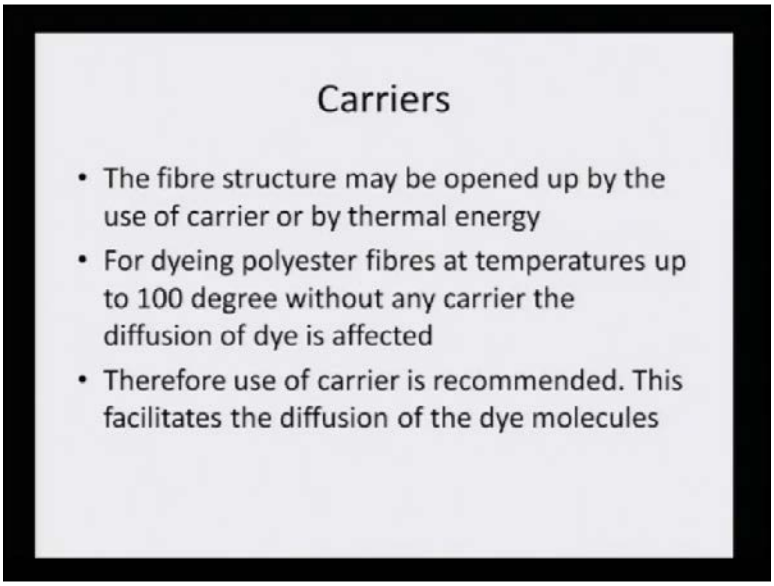

Carriers: The fibre structure may be opened up by the use of carrier or by thermal energy. So, to in order to come, overcome this problem there are carriers as the name suggests they carry, so or the use of carrier or with the help of thermal energy this can be facilitated. For dyeing polyester fibres at temperatures up to 100 degree without any carrier the diffusion of the dye is affected. Now, because polyester dyeing have to be carried out at a higher temperature, because of these problems of in solubility of the dye and then the hydrophobicity and the rate of absorption being poor and then the penetration for the being still more poor.

It cannot be carried out at room temperature or at 45 degrees or at 80 degrees. It has to be carried out above 100 degrees and sometimes at 130 degrees will see one of the process at which the dyeing is done at 130 degrees. So, when such a situation arises there has to be some facilitated which can help in doing the dyeing process in a more facile manner and careers are one of them. Therefore use of career is recommended. This facilitates the diffusion of the dye molecule, because the main problem in polyester is the diffusion of the dye. Dissolution can be facilitated with the dispersing agent, but how to make this solubilize dye get into this compact structure of the fibre; that is the main adsorption and diffusion rate are the main problematic steps in the polyester dye.

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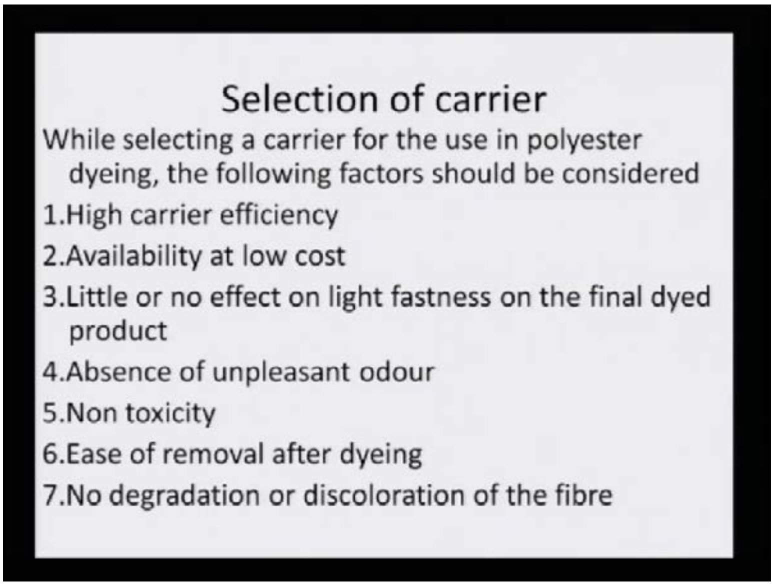

Selection of carrier: While selecting a carrier for the use in polyester dyeing, the following factors should be considered, high carrier efficiency, availability at low cost, little or no effect on light fastness of the final dyed product, absence of unpleasant odour, non toxicity, ease of removal of dyeing, no degradation or discoloration of the fibre. So you see, if we have to choose a carrier, a carrier must not have any kind of its own color or odour. First thing is that; it should not add on to any you know unwanted property on the dyeing fabric; it should have a good efficiency. It should be available at low cost and it should not have any effect on the light fastness of the finally dyed product and it should not be toxic, because, these are certain things which an industry has to keep in mind.

We cannot use a chemical which is very costly, because otherwise the entire process will become very costly. So just the way, you know the choice of dispersing agent is done looking at the compatibility with the dispersed dye. Similarly, the choice of carrier has to be done with the help of what is doable. And in the doable category these factors should be kept in mind that it should have good efficiency; it should be available; it should have little or no effect on light the fastness; it should not have any unpleasant odour; it should be non toxic and it should be able to be removed after dyeing.

You see, because otherwise it will have its own role to play on the fabric and that is not desired, because its role is only at the time of dyeing. After that, it should be able to be removed very easily and no degradation or discoloration of the fibre should take place when it is being removed. It should not be that you know the dye is also running off, because of the bleaching of this chemical. So, that is where all these things have to be kept in mind when such a selection of the carrier is done.

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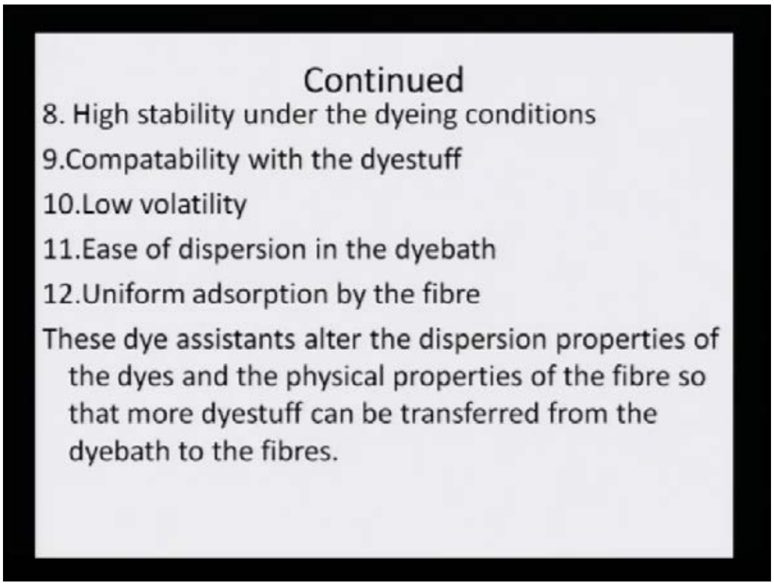

High stability under dyeing conditions, compatibility with the dyestuff, low volatility, ease of dispersion in the dyebath, uniform adsorption by the fibre. These dye assistants alter the dispersion properties of the dyes and the physical properties of the fibre so that more dyestuff can be transferred from the dyebath to the fibres. So, there only role is to hold. First thing is that they should dissolve the dye to the maximum amount and they should alter the physical property of the fibres. So that, more and more dye can get into it; that is all the role, but they should not hamper in any way that dyeing process.

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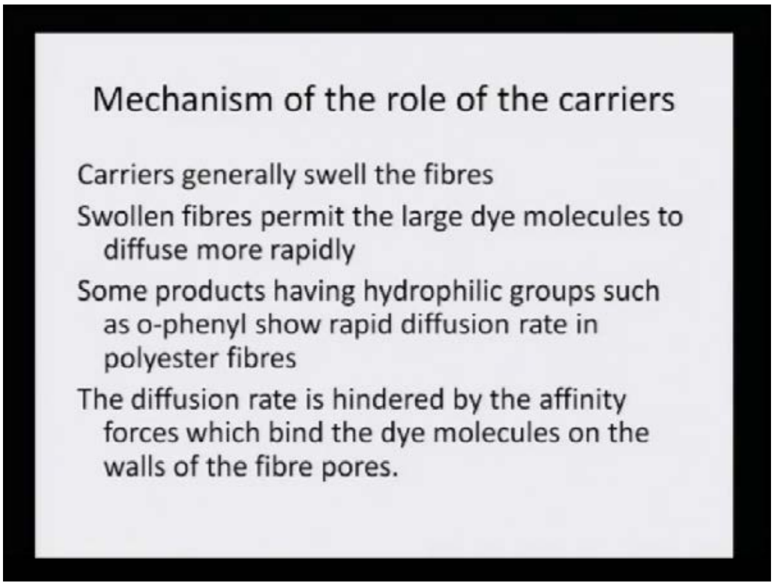

Mechanism of the role of the carrier: Carriers generally swells the fibres swollen fibres, because you see when I was telling you about the cotton dyeing and the hydrophilicity of the cotton, the main functioning that was happening for the fibre swelling.So, here the role of the carriers is the same that in such a compact fibre stage. They are creating swelling within the fibres and swollen fibres permit large dye molecules to diffuse more rapidly. Some products having hydrophilic groups such as o-phenyl show rapid diffusion rate in the polyester fibres. The diffusion rate is hindered by the affinity forces which bind the dye molecules on the walls of the fibre pores.

So, you see that they have such a immense role to play, because the compactness the hydrophibicity or the polyester is actually the main hinders. And these carriers are then happily helping the process of swelling and ones the fibre swells, then the facility of dye diffusion is enhanced. And many hydrophilic groups on these carrier molecules actually help to facilitate this diffusion process, otherwise the dye keeps taking to the fibre walls. So, it is there, but it is not diffusing. It is just adsorbed on the surface, but unless and until it penetrates into the fibre, the dyeing is not complete and dyeing is not even. It is not leveled and it is bad dyeing. So, in order to achieve good dyeing with polyester fibres using disperse dye one has to use dispersing agents and these carriers.

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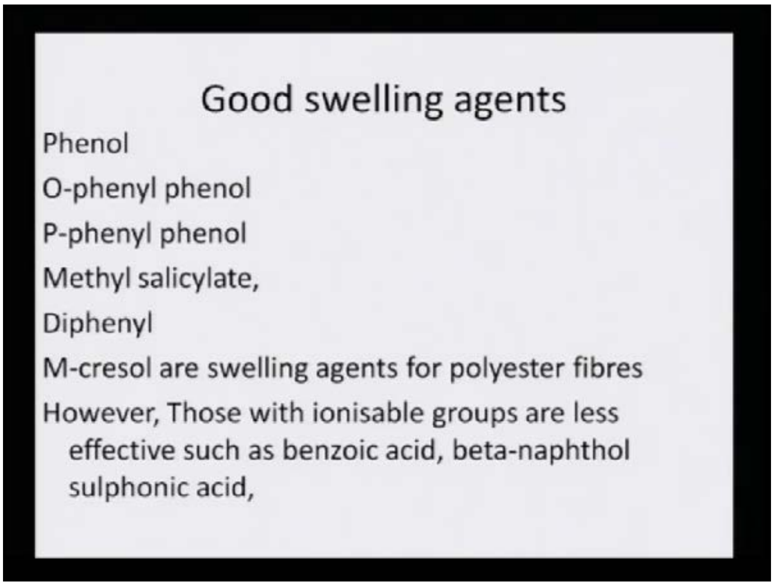

Good swelling agent: the list of good swelling agents includes Phenol, ortho phenyl phenol, Para phenyl phenol, methyl saliciate salicylate, Diphenyl, Meta-cresol are some of the swelling agents for polyester fibres. However, those with ionisable groups are less effective such as benzoic acid, beta-naphthol, sulphonic acid and so on and so far, but nevertheless these carriers as I told you help in swelling action of the fibre and swelling action enhances the rate of diffusion.

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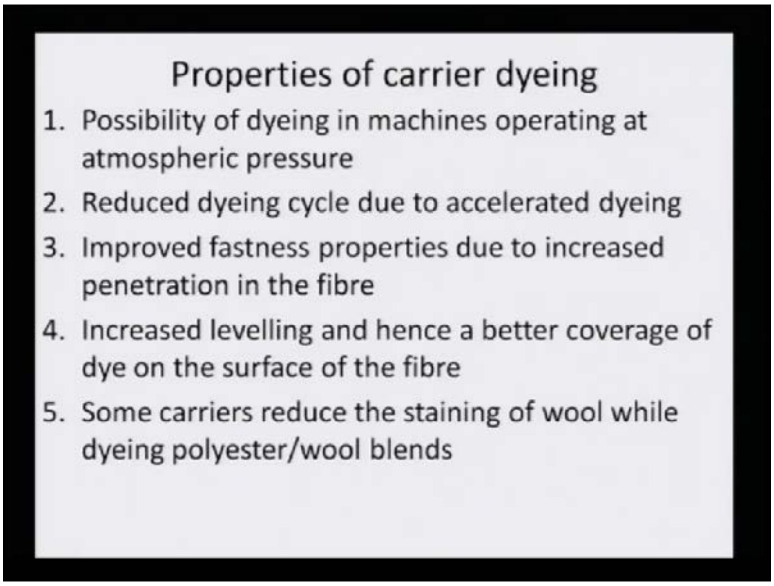

Properties of carrier dyeing: Possibility of dyeing in machines operating at atmospheric pressure, because in that case we can do this otherwise pressure and high temperature is required to dye polyester. And that was because of the insolubility of the dispersed dye and the compactness and hydrophobicity of the... So, it needs to be done with great force and at high temperature, but with this carrier use of carriers swelling agents; it is possible to do this dyeing at atmospheric pressure.

Reduced dyeing cycle due to accelerated dyeing and it also reduces the number of time it has to go through that cycle. Improved fastness properties due to increased penetration in the fibre and therefore because more and more dye is entering the fibre core, the fastness property automatically becomes better. Increase leveling and hence a better coverage of the dye on the surface of the fibre. So, it because it is happening in a very uniform manner with the help of the carrier all of it is getting swollen to the same extend. It is having a leveling of dyes on an even ground and even surfacing and therefore, it has a better coverage of the dye on to the surface.

Some carriers reduce the staining of wool while dyeing polyester wool blends. So, even when some of them also have a good effect that they do not let the dye bleed, because I as we were seen that when we were trying to understand the fastness property. The way rubbing fastness and the washing fastness were certain… That any dye which is leaving the dyed fabric must not get on to another fibre. So, that staining also can be controlled by using some carriers. So, that is they have a dual role and more, so much for the diffusion of the dye, they play a very important role.

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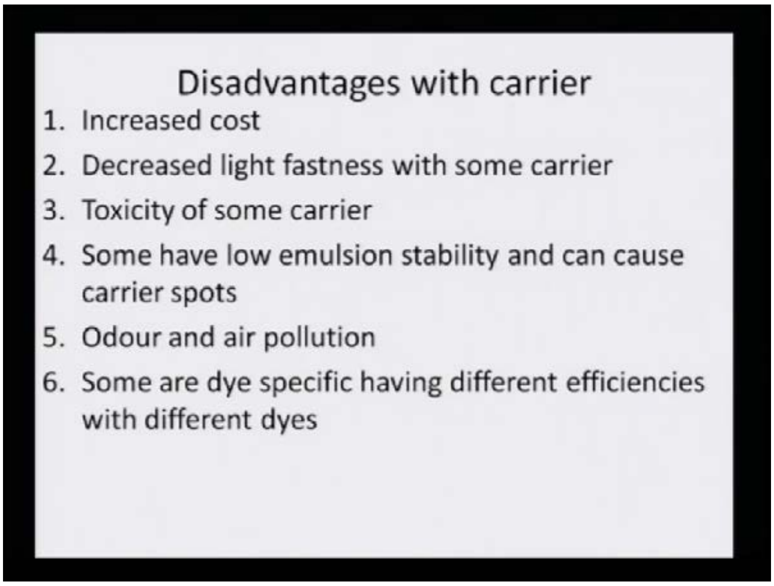

However, some of the carriers have equal disadvantages also. You see every chemical which is used for some usefulness is not necessarily 100 percent useful. It may have certain disadvantages and what are the disadvantages that are related to carrier or increased cost, decreases light fastness with some carriers, toxicity of some carriers, because all these phenolic compounds are fairley you know into the category of toxine. Some have low emulsion stability and can cause carriers spots. So, they can call you know some patchiness on the dyed fabric and that is undesirable. So, these are certain disadvantages with using these phenolic compounds, and of course phenolic compounds have terrible odour. So, there is air pollution, there is people who are working with these have to you know in hale a lot of phenolic compounds, some are dyes specific having different efficiency with different dyes.

So, as what we saw that these ionisable group one like benzoic acid, sulphonic acid are not as good as the ortho phenyl, phenol or just the phenol or para phenyl phenol or meta cresol and so on. So, these everywhere you saw dispersing agents, swelling agents carriers, these are all having their own choices and advantages. It is not that one group, one compound is (( )) proof. So, one has to do a lot of permutation, combination and particularly for dyeing in this particular method; it is extremely important to keep these things in mind.

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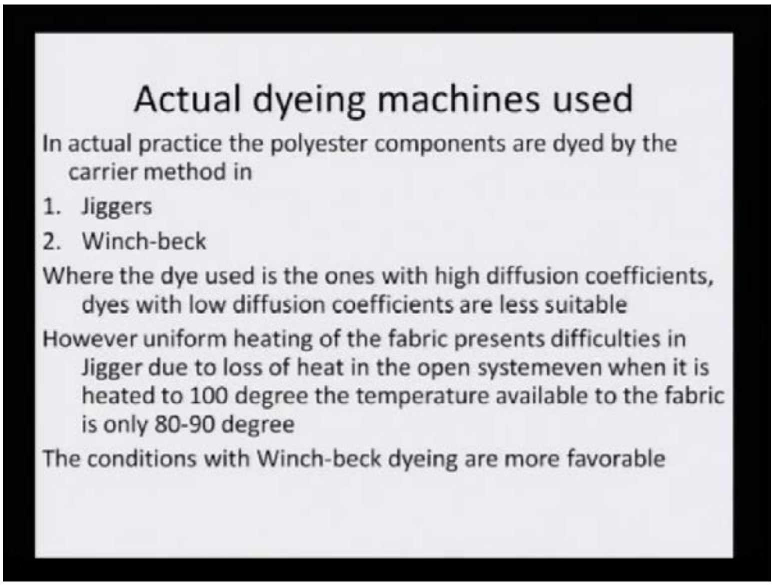

In actual practice the polyester components are dyed by carrier mentioned in the earlier by Jigger or by Winch-beck. We have already discussed Jigger and Winch when we were doing dyeing machine. So, I will not go in to the detail and the conditions are that you know it is kept at high temperature. So, if we now have to conclude this chapter, we understand that the same Jigger machine, the same Winch can be used for dyeing polyester blends, but with the help of dispersing agent and with the help of carriers.