Natural Dyes
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Lecture No. # 28

Let us go back to dyeing of synthetic fibres with synthetic dyes, because we have to strike a balance between learning about synthetic dyes and natural dyes. And because in the industry, it is necessary for information to be given to the industry for dyeing natural as well as synthetic fabric with the use of natural or synthetic dyes. So, today's lecture is dedicated to the fact that how do we do dyeing of polyamide fibres in industry, and therefore, we will try to because these fibres are compositionally very different from the fibres that we have been talking about in the case of natural dyeing; that is the natural fibre the cotton silk and wool.

So, the cotton is cellulosic fibre whereas, cotton and wool are protinateous fibre. So, their dyeing methodology their dyeing system and, their dyeing applications are completely different from the dyeing procedure application dye uptake of the synthetic fibres, and polyamide is one of the very prominent synthetic fibre which is very popularly used by the consumers.

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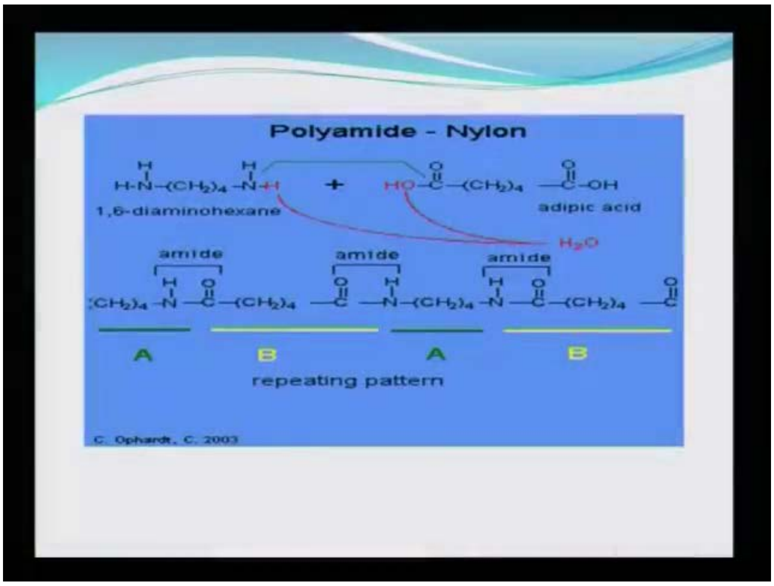

So, trying look at polyamide structure. This is the structure of poly amide, where 1, 6-diaminohexane is condensed with adipic acid and the amide linkages that are formed between the a the molecule. That is diamino compound and the acid by the loss of water molecule is what is actually if the simple condensation product, which is called nylon or polyamide.

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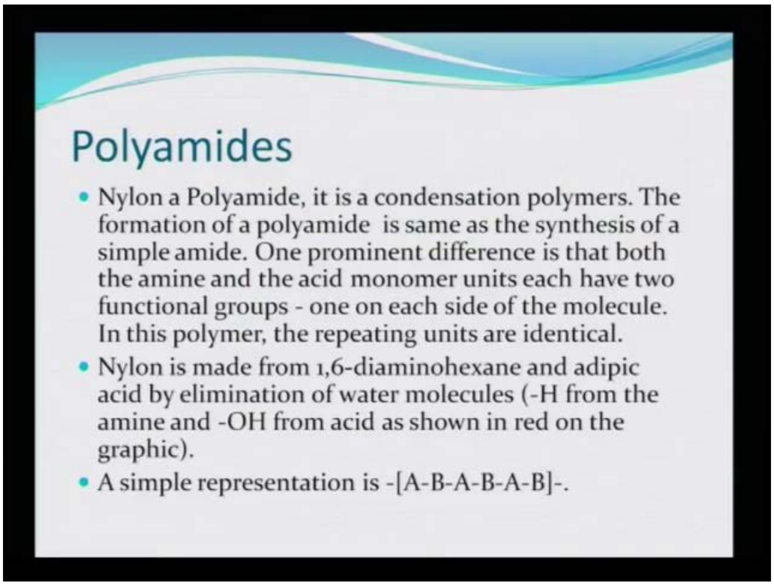

Polyamide, Nylon as one of the representative examples is a polyamide it is a condensation polymer. The formation of a polyamide is same as the synthesis of a simple amide. So, mainly it has the CO NH 2 groups in subsequent orders. One prominent difference is that, both the amine and the acid monomer units each have two functional groups, one on each side of the molecule in this polymer the repeating units are identical. Nylon is made out from 1, 6-diaminohexane and adipic acid by the elimination of water molecule; that is we saw that -H from the amine and -OH from the acid. I have been shown that they are removed and that is the simple representative A and B, and A and B go on linking to each other, that is the structural detail of the polyamide.

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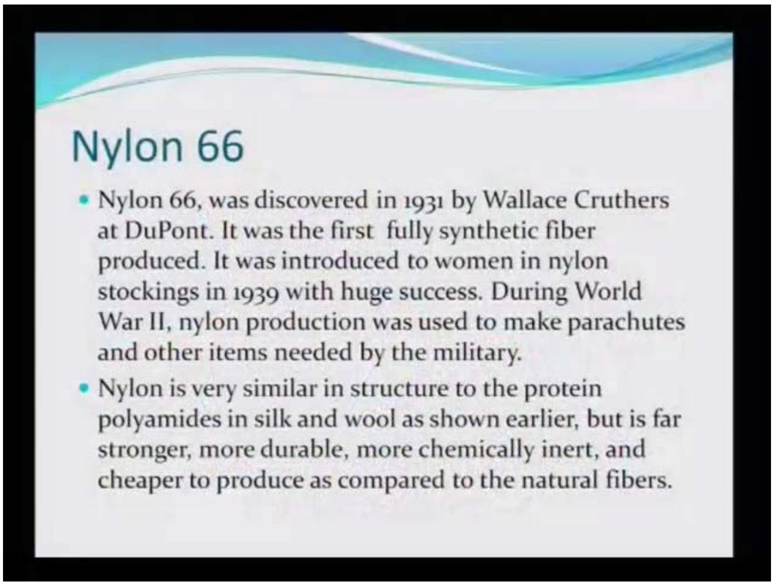

Nylon 66 was discovered in 1931 by Wallace Cruthers at DuPont. It was the first fully synthetic fibre produced. It was introduced to women in Nylon stockings in 1939 with huge success. During World War II nylon protection was used to make parachutes and other items needed by the military.

Nylon is very similar in structure to the protein amides in the silk and wool as shown earlier, but is far more stronger, more durable, more chemically inert, and cheaper to produce as compared to the natural fibre, and that was what made the polyamide or the nylon, so popular in the consumer market, because of these properties that it has it is far more stronger, more durable chemically more inert and cheaper to produce. So, what more can one ask. Natural fibres have the little limitation they are not so durable, they have they are not so strong, and they are not chemically inert, they are they get affected by very acidic or very basic condition and so on and so forth, because of the tenderness, but this nylon 66 seems to be a very ideally suited material for consumers.

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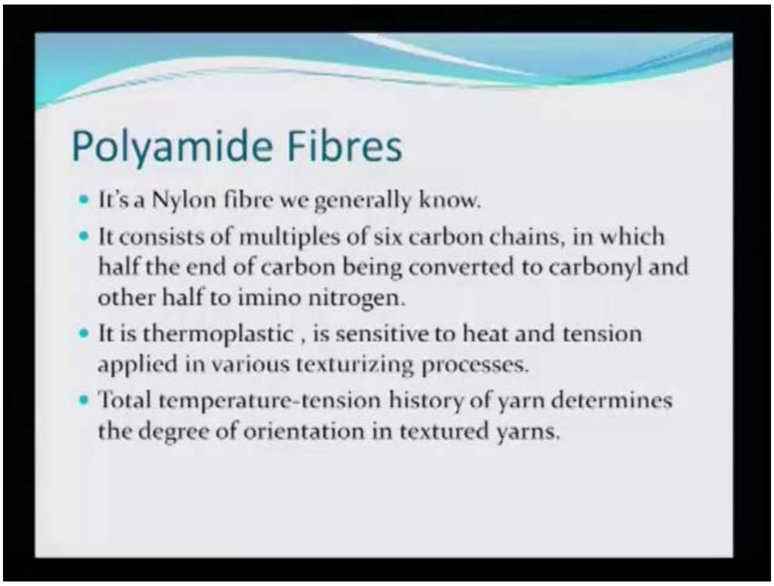

Polyamide Fibres, it is a Nylon fibre we generally know. It consists of multiples of six carbon chain, in which half the end of the carbon being converted to carbonyl and the other half into the imino nitrogen. It is thermoplastic, is sensitive to heat and tension applied in various texturizing processes. So, the total temperature-tension history of yarn determines the degree of orientation in textured yarn. So, you see that it has all very good qualities for the from the stability point of view: it is a thermo plastic material it is sensitive to heat so it can be textured, many designs can be introduced and, this design would depend on the total temperature and the way the yarn has been tensed to see the degree of orientation in the textured yarn. When, we come to dyeing of this very unique material, unique in the sense that it has all the qualities.

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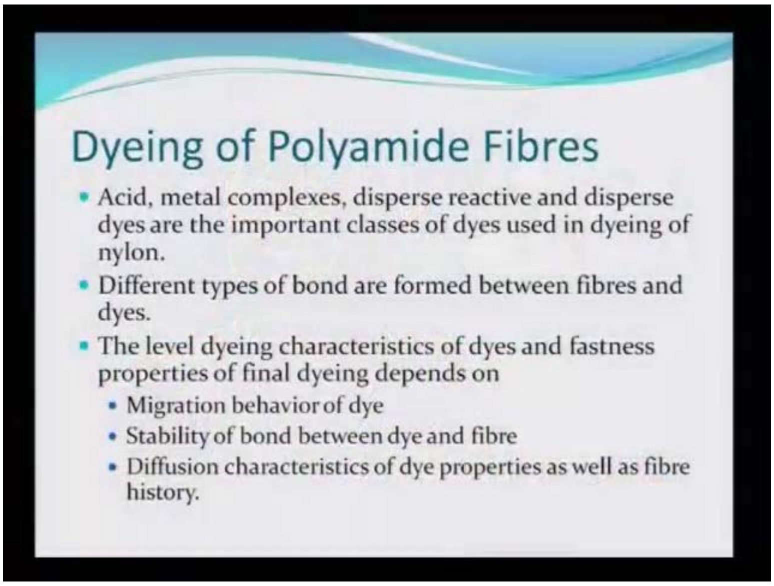

Acid, metal complexes, disperse reactive and disperse dyes are the important classes of dyes used in dyeing of nylon. Now let me tell you that natural dyes do not come into the picture at all when we talk about nylon dye, because the dye uptake phenomena is completely different.

In this case and as we go along you will be able to see why this acid dye or metal complexes or disperse dyes are the only classes of dyes, that are used for polyamide fibre dyeing and why natural dye fails, because there is no mention of any modern dye here and for the simple reason that natural dyes are all modern dyes. Therefore they do not they are not compatible. That is the only word that I can use that natural dye here has no way to be used in polyamide dyeing.

So, we have to now concentrate on the dyes, that can be used that is because we are trying to learn about polyamide fibre dyeing acid dyes, metal complexes disperse reactive dyes and disperse dyes are the only important class of dyes that can be used for nylon dyeing. Different types of bonds are formed between fibre and dyes. The level dyeing characteristics of dyes and fastness properties of final dyeing depend on migration behavior of the dye stability of bond between the dye and the fibre and diffusion characteristic of dye properties as well as fibre history.

So, you see these are the three main criteria based on which the fibre will actually take or reject the dye. First is that how easily the dye molecule is migrating. So, its migrating behavior how good is the stability of the bond that is forming between the fibre and the dye, because then only the dye adherence will take place and the third part is the diffusion characteristic, how easily the dye can penetrate or diffuse into the fibre, and what is the rate of the diffusion, whether it is good or bad would decide, whether the dye will be taken up by the nylon fibre or rejected and that is where the natural dyes actually fail the dye diffusion was very poor.

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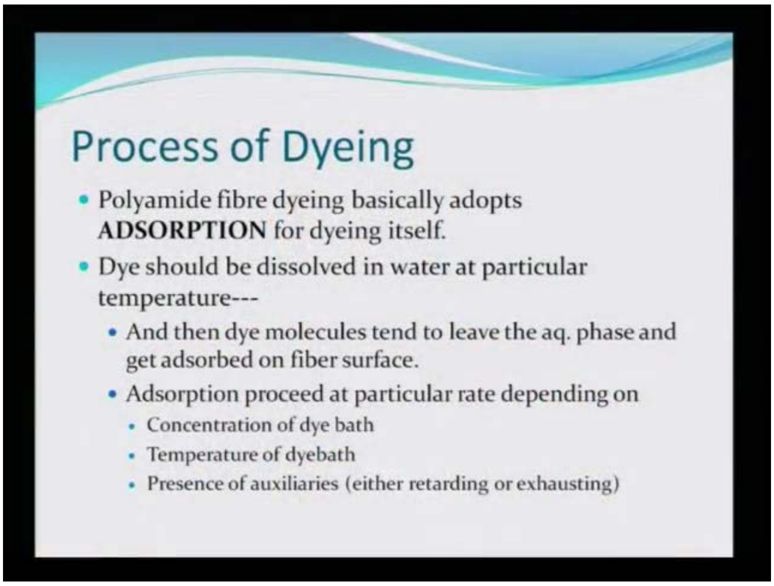

So, the process of dye, polyamide fibre dyeing basically adopts ADSORPTION. So, it is with the help of adsorption on the fabric surface. Dye should be dissolved in water at particular temperature: and then dye molecules tend to leave the aqueous phase and get adsorbed on fibre surface. So, you see that it is just a function of the surface. Adsorption always takes on the surface. So, first thing that must happen is the adsorption of the dye. The adsorption proceeds at particular rate depending on the concentration of the dye bath, the temperature of the dye bath and the presence of auxiliaries either retarding or exhausting agents.

We had if you recall, similar retarding and exhausting agents were used in the case polyester dyeing which we learnt a couple of lectures back. So, there also the first step was the breaking of the dye aggregates that is the salvation, the second step was adsorption and, here the dye adsorption is the first step and then the dye migration and so on and so forth.

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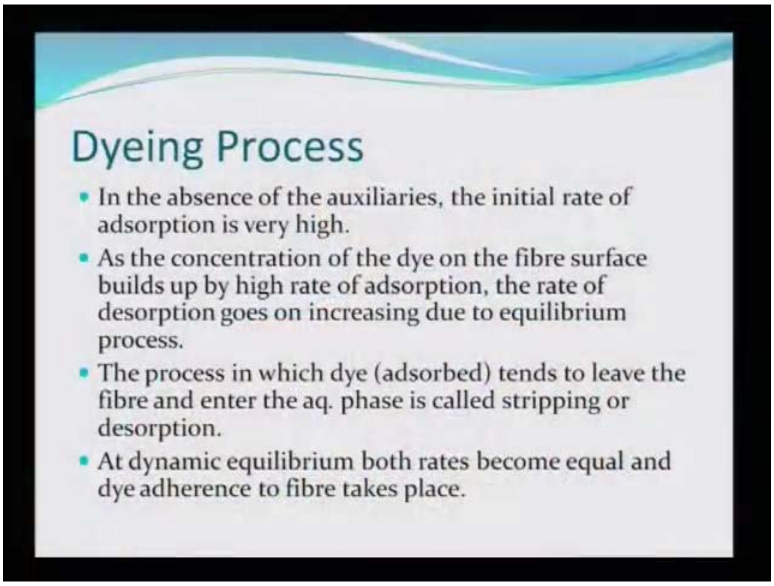

So, in the absence of auxiliaries, the initial rate of adsorption is very high. As the concentration of the dye on the fibre surface builds up by high rate of adsorption, the rate of desorption goes on increasing due to equilibrium process. So, here again there is a forward reaction, where the dye is actually being adsorbed and there is a desorption reaction happening simultaneously after some time, when the concentration of the dye in the fabric has increased enough.

The process in which dye adsorbed tends to leave the fibre and enter the aqueous phase is called stripping or desorption. So, these two processes which are actually going in opposite direction; one is the dye entrance and the other one is the dye stripping or the desorption, are taking place simultaneously and because of that there is an equilibrium established and therefore, it is important to see that this equilibrium moves in the forward direction rather than in the backward direction. Otherwise all the dyes that has been taken up by the fibre will be ah you know desorp or stripped off by the fibre.

So, at dynamic equilibrium both rates become equal and dye adherence to the fibre then takes place. So, if that does not happen the rate of forward reaction will not go further beyond and therefore, at this you know situation when there is enough amount of dye in the concentration within the fibre, not adsorbed first it is adsorbed then it moves inside and that is where when it is moving inside it is also moving outside. So, there is a dynamic equilibrium and at that point the dye adherence start taking place and the dye starts chemically reacting with the fibre.

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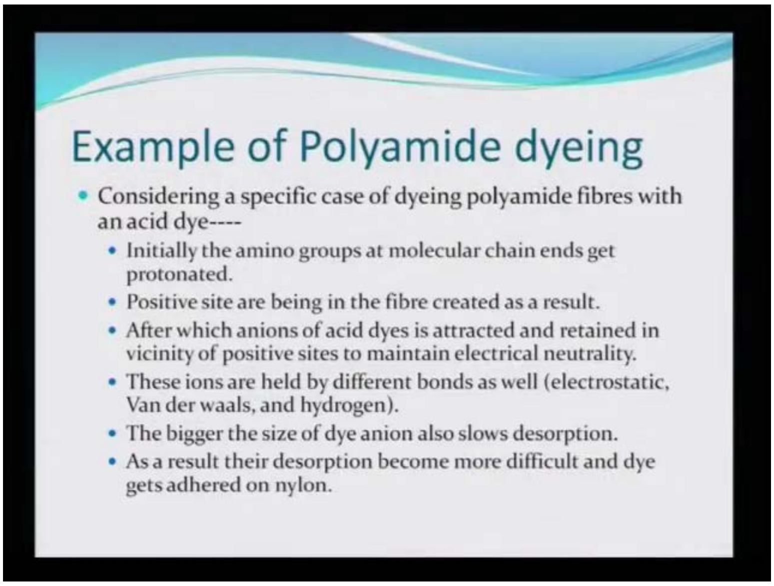

Example of you know if we try to you know take deeper look at that dyeing process; Consider a specific case of dyeing polyamide fibres with an acid dye. Suppose if we take a acid dye how will that behave in this situation. Initially the amino groups at molecular chain ends get protonated. Positive sites are being in the fibre created as a result. After which anions of the acid dye is attracted and retained in the vicinity of the positive sites to maintain electrical neutrality.

The ions are held by different bonds as well as by electrostatic, Van der waals and hydrogen bonding. Which have all three of them are weak bonds, but nevertheless if there are hundreds of these weak bond that itself will strengthen. The bigger the size of the dye anion also slow desorption will occur, as a result their desorption becomes more difficult and dye gets adhered on nylon. So, the whole process is supposed if there is an acid dye. The first thing that happens in the system is that the amino end of the nylon gets protonated, once that is protonated the it creates a positive site in the fibre and to which the anion of the acid that is the CO O minus group or the sulphonic acid SO3 minus group anion, will then go very close to that now here is a positive charge here is the negative charge. So, because of the you know electro static attraction they will be there so, that will also create a electrical neutrality. Otherwise the system will be either acidic or basic. These ions are held by different bonds such as Vander Waals forces, electro static forces and hydrogen bonding. So therefore, this desorption process is very facile.

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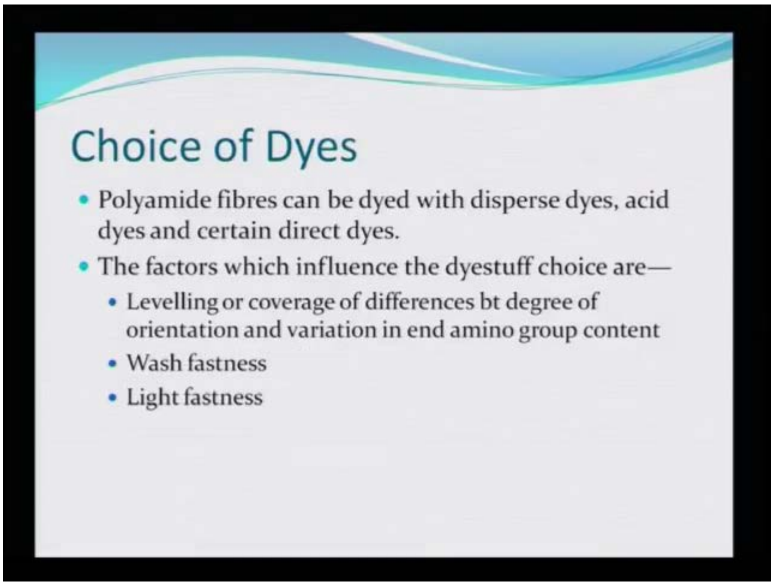

Now when we try to look at the choice of dyes the polyamide fibre can be dyed with disperse dyes, acid dyes and certain direct dyes. Also, there are a few factors which influence the dye stuff choice that is leveling or coverage of differences between degree of orientation and variation in end amino group content. Wash fastness and light fastness, any dye any dyeing process will be only considered worthwhile, if the wash fastness and light fastness are good for the dyed fabric. Otherwise the process fails and that is why natural dye fails, because it did not have a good dye adherence, as a result the dye washed off.

So, the fabric remain faded and it did not take up the dye, but if we have to look at the dying of polyamide fibre we have to keep a few points very clearly in mind that the factors that actually if a influence the dye stuff choice should be that which type of dye is structurally compatible with the structure of the nylon dye.

We just now learnt that if we take an example of the acid dye. The first thing that happens is the protonation of the amino group, because there is an anion and the cation in the acid dye the anionic part goes and sits near the protonated end of the nylon. Now because they are in close vicinity, the dye molecule starts migrating and the desorption has to be slower in order for the dye to retain in the fabric. Then only the dye adherence and the electro static forces and the electrical neutrality and the Vander Waals forces and the hydrogen bonding all will take place.

If the dye does not remain there if it runs out if it strips off. Then, where will be the possibility for any kind of wander wall forces or hydrogen bonding. So, that is why the main in factor that influences the dye stuff choice is the leveling of coverage of differences between degree of orientation and variation in the end amino group content and, that is what because that is the starting point.

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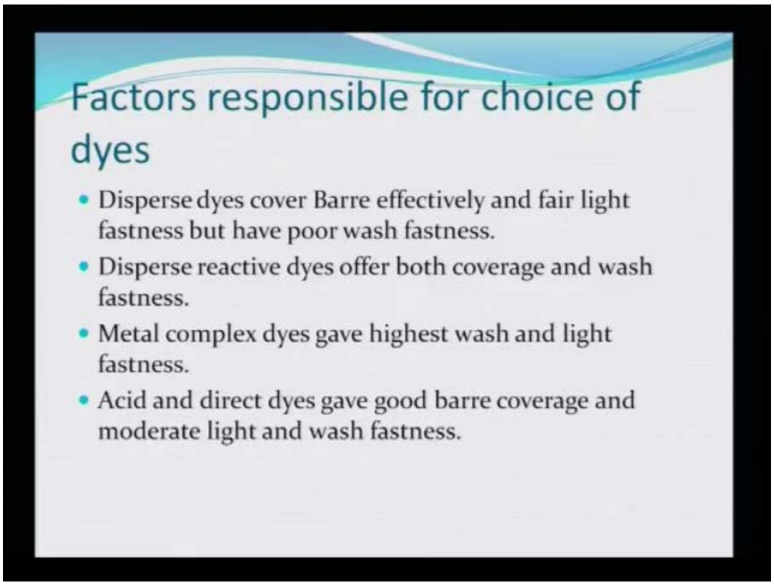

So, that is what makes a lot of difference what other factors that is responsible for the choice of the dye. Disperse dye cover Barre effectively and fair light fastness, but have poor washing, wash fastness. Disperse reactive dyes offer both coverage and wash fastness coverage is also termed as Barre; that means, how much portion of the surface of the fibre has been affected by the dye presence of the dye. So, that is referred as Barre or Barre. So, if we look at simple disperse dyes they have good light fastness, but poor washing fastness and they have some what you know medium type of coverage possibility.

Whereas disperse reactive dyes have both coverage good coverage and good wash fastness. Metal complex dyes have highest wash fastness and light fastness. So, these metal complex dyes which are synthetic dyes, we are talking only in terms of synthetic dyes, this category of disperse dyes disperse reactive dyes, metal complex dyes and acid and direct dyes are only categories of synthetic dyes, we are not talking natural dyes because natural dyes have been rejected in the case of polyamide dyeing.

So, coming back to metal complex dyes, they have highest wash and light fastness whereas, acid and direct dyes gave good Barre coverage and moderate light and wash fastness. So, one has to now again it is all structure related you have understood one thing that structures play a very big role and I gave you an example with the help of an acid dye example, that how this is all possible because of the structural detail of a dye, because we know the structural detail of the nylon, there is an end group which is amino group, there is another end group which is a carboxylic group and all the amide linkages; amide linkages in between help in all those small different types of electro static attraction of Vander Waals forces or hydrogen bonding and all that.

To you know bring the dye and the fabric together, but the initial bringing up is all related to the structure of the dye and to the structure of the polyamide. So, these are the various facts I mean each dye has its own coverage possibility each dye has its own reactivity and the reactivity related to its being adhering. Adhering is only though this physical method; that is the hydrogen bonding and so on. So, because these are of weak nature, but they are in huge number.

Therefore, the dye is sitting there because of the electro static attraction and these disperse dyes are disperse reactive dyes have different kind of compatibility; because of their difference is structure. So, whether it is metal complex dyes, whether it is disperse dyes, whether it is disperse reactive dyes, whether it is acid dyes or whether it is direct dye all have different structures therefore, all have different kind of reactivity with the polyamide fibre.

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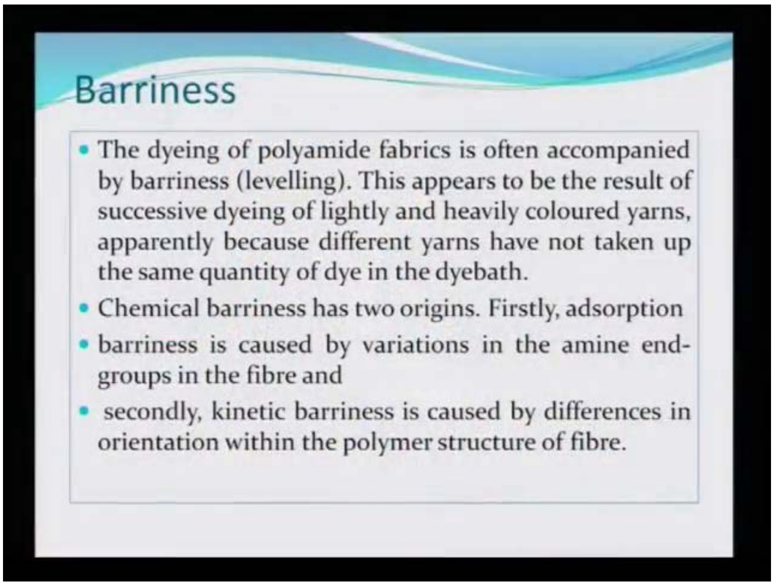

Barriness, let us learn this new term a little more in detail the dyeing of poly amide fabric is often accompanied by barriness or leveling. This appears to be the result of successive dyeing of lightly and heavily colored yarns. Apparently because different yarns have not taken up the same quantity of dye in the dye bath, chemical barriness has two origin.

Firstly, adsorption barriness is caused by variation in the amine end groups of the fibre and secondly kinetic barriness is caused by the differences in the orientation within the polymer structure of the fibre. So, you see that even the leveling or the coverage or the equalness of the dye uptake at various position of the fibre would depend on the fact that how is this dye (( )).

What is the structure of the nylon and the chemical barriness has two main origins that is one is caused where is the amino group is it and how is it located and the second one is that the orientation of these molecules and the polymer structure of the fibre, how is it if the yarn is twisted the dyeing will be uneven because the amide groups are now inward outward. So, that is what is causing the non you non evenness or non leveling of the coverage area of the surface.

So, therefore because this is not like chemical dyeing that there is a direct bond formation covalent bond or coordinate bond formation with the metal and the fibre and this and that it is very different and because of this difference and only physical adsorption bringing the dye aggregate closer to the fabric as far as possible the protonation of the fabric and so on causes this a dye to come closeness.

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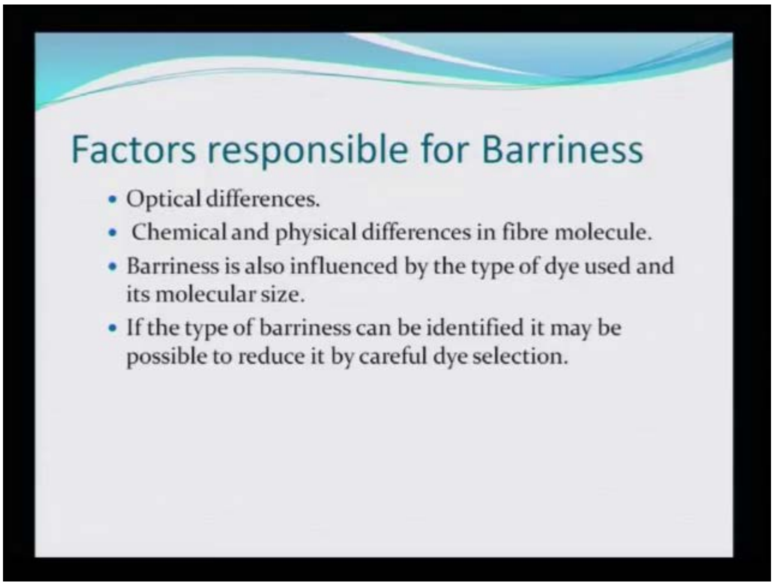

Factors responsible for Barriness: optical differences chemical and physical differences in the fibre molecule. Barriness is also influence by the type of dye used and its molecular structure or molecular size. If the type of barriness can be identified may it may be possible to reduce it by careful dye selection. So, now, if we know that a particular dye say for example, natural dye is not having a good coverage or leveling we will not use it.

So, we will reject that dye, but among the direct dye, acid dye, metal complex dye, disperse reactive dye and disperse dye we will choose that particular type of dye which will have evenness or barriness, which is ah causing even dye uptake. And this can be figured out by optical difference, because one place the dye will be taken up largely more dye aggregate will be there, so even the dye choice molecular size of the dye if the molecule is too large again the you know diffusion will be a problem. So, all these can control the barriness.

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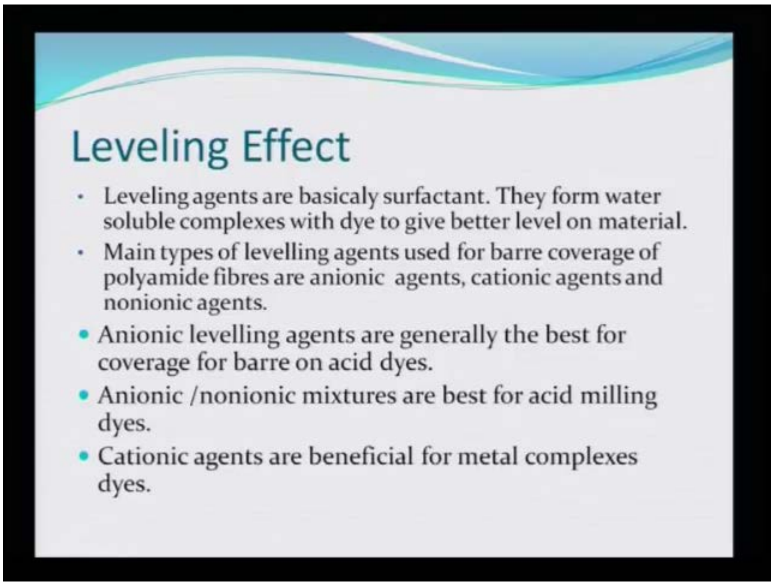

Leveling Effect are basically surfactant they form water soluble complexes with dye to give better level or material. Many types of leveling agents used for barre coverage.barre coverage of the poly amide fibres are anionic agents cationic agents and non ionic agents anionic leveling agents are generally the best for coverage for barre on acid dyes, anionic and non anionic mixtures are best for acid milling dyes and cationic agents are beneficial for metal complexes dyes.

So, now, in order to remove this problem of barre coverage there are leveling agents and these leveling agents are nothing, but surfactants and the role of surfactant is that they try to dissolve the dye as good or as nicely as possible. So, that there is a better level of dye infusion or diffusion main types of leveling agents are you know they can be anionic agents cationic agents or non anionic agents.

An anionic agent are best meant for acid dyes. So, if we use acid dyes in place we along with anionic leveling agents it is the best combination, because that starts promoting or protonating the amino group of the nylon 66, similarly cationic agents are good for metal complexes because they start initiating the reaction by protonation.

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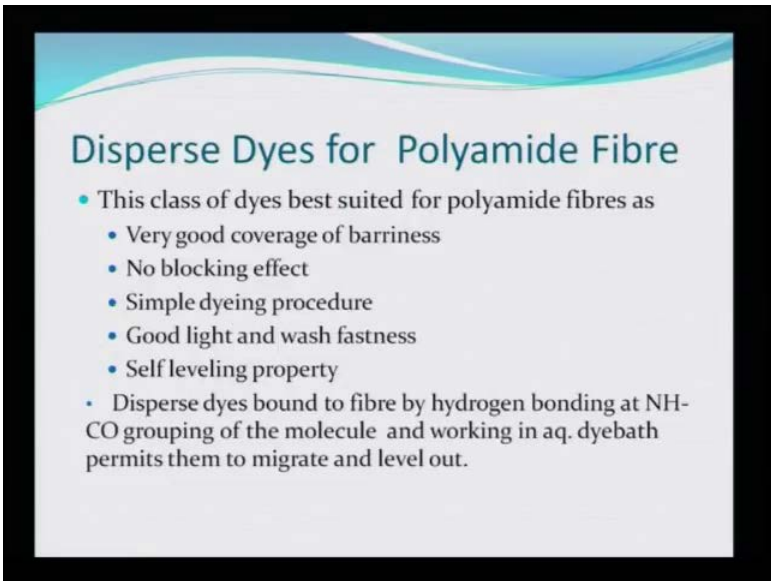

Disperse Dyes for Polyamide Fibre, this class of dyes best suited for amide polyamide fibre as very good coverage of barriness, no blocking effect, simple dyeing procedure, good light and wash fastness, self leveling properties. Disperse dyes bound to fibre hydrogen bonding at NH-CO grouping of the molecule and working in aqueous dye bath permit them to migrate and level out.

So, since disperse dyes seem to the best compatible choice for poly amide fibre there is very good coverage of the barriness the there are no blocks. So, the dye aggregates do not form the migration of the dye takes in a very facile manner and the procedure of dyeing is also very simplified. And more so, much and most importantly the wash fastness and the light fastness is very good, because for every kind of dyeing procedure be it natural dyeing with on natural fibres or be it synthetic dyeing with synthetic dyes on synthetic fibres both need one basic criteria, that the dyed fabric should have good fastness property light and washing fastness.

These are the two main basic criteria for a dyed fabric to be a certain as a good dyed fabric only on these two parameters one can judge them. So, and the self leveling property of the dye will also be an added advantage because it will not create any barriness and therefore, this is possible that these disperse dyes are actually hydrogen bonded only by this weak bonding, but nevertheless because there are huge number of hydrogen bonding therefore, it is a good option to hold up the dye at the situation.

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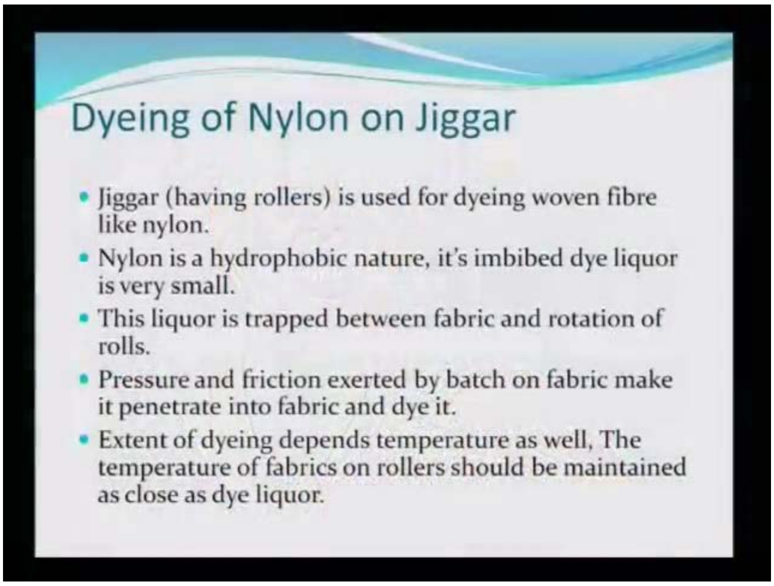

Dyeing of Nylon on Jiggar; Let us now look at what is the machine that can be used for dyeing of nylon. Jiggar - having rollers, is used for dyeing woven fibre like nylon. Nylon is a hydrophobic is hydrophobic in nature, it is imbibed dye liquor is very small. This liquor is trapped between fabric and rotation of the rolls. Pressure and friction exerted by batch on fabric make it penetrate into the fabric and dye it. Extent of dyeing depends temperature depends on temperature as well. The temperature of fabric on rollers should be maintained as close as dye liquor.

So, if the temperature is kept at little high and because they are moving in the roller it is possible to use Jiggar for nylon dyeing, but in general nylon is hydrophobic in nature. So, that is it is not water loving. So, therefore, the dye liquor that goes into the fabric by the mode of adsorption is very small. But this liquor that goes liquid means dye solution which goes get strapped between the fibre and the rotation. And therefore, it remains there for some time in close proximity with the fabric and that is what creates you know to for it to get adsorbed and initially once that the adsorption takes place it starts diffusing inwardly to get into the core.

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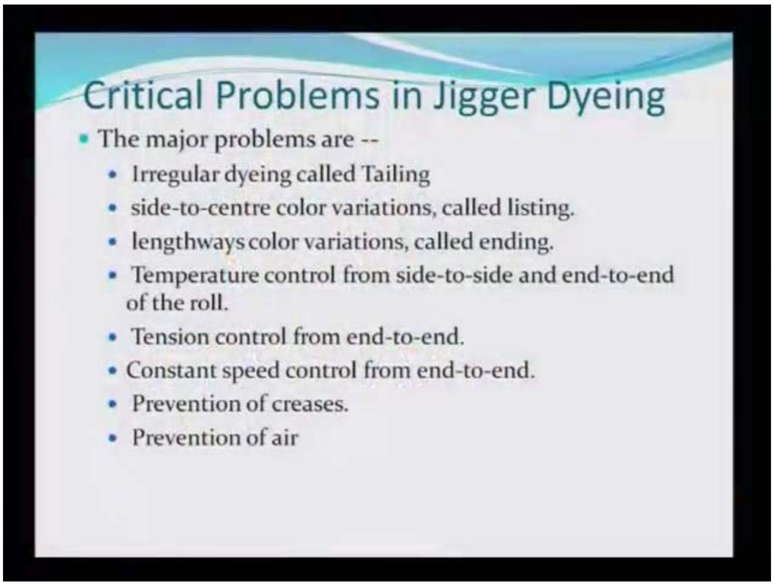

Critical points on Jiggar dyeing, the major problems that one actually comes across while dyeing on nylon although it is possible to dye on Jiggar. Irregular dying called tailing, side to centre color variation called listing, length ways color variation called ending, temperature control from side to side and end to end of the roll, tension control from end to end, constant speed control from end to end, prevention of creases prevention of air so these are the major problem that one figures out because Jiggars are open Jiggars and they.

Therefore there is irregular dyeing what happens from the side that dyes will penetrate and towards the centre there will be lesser amount of dye that would reach. Therefore, side to centre color will show a variation and this is called listing length wise also the color variation. Will be there initially the color taken up will be larger and then it will be lesser and lesser, so that is called ending. Temperature control from side to side because whatever be the temperature of the liquid and whatever be the temperature of the roller.

But there is always a variation because there is air in between and therefore, prevention of air should be there which is causing the difference in temperature. When the temperatures are similar, the dye uptake will be similar. But that does not happen in an open system the sides are more ah you know accessible to air and in the centre there is more of the dye solution and so on and so forth.

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After Treatments are required for any dyeing you saw that we also took care of the dye fixing in the case of natural dyeing. Similarly, the wet fastness of acid dye on nylon can be considerably increased by an after treatment involving: Treatment with 20 percent tannic acid with the weight of the fabric or and 4 percent formic acid with the weight of the fabric at 95 degrees for 30 minutes and treat or we can even do treatment with 1 percent weight of the fabric with tartar emetic that is potassium antimonyl tartarate at 90 degrees for 15 minutes.

So, these are the two treatments which can help the poly amide nylon to keep the or retain the dye. So, either we use a tannic acid treatment of 20 percent with 4 percent formic acid combination at 95 degrees for 30 minutes or a treatment with 1 percent with tartar emetic which is potassium antimonyl tartarate at 90 degrees for 15 minutes. So, at very high temperature, these treatments after treatments are required in order to retain the dye that has diffused into the nylon fabric. So, that they do not run off after washing.

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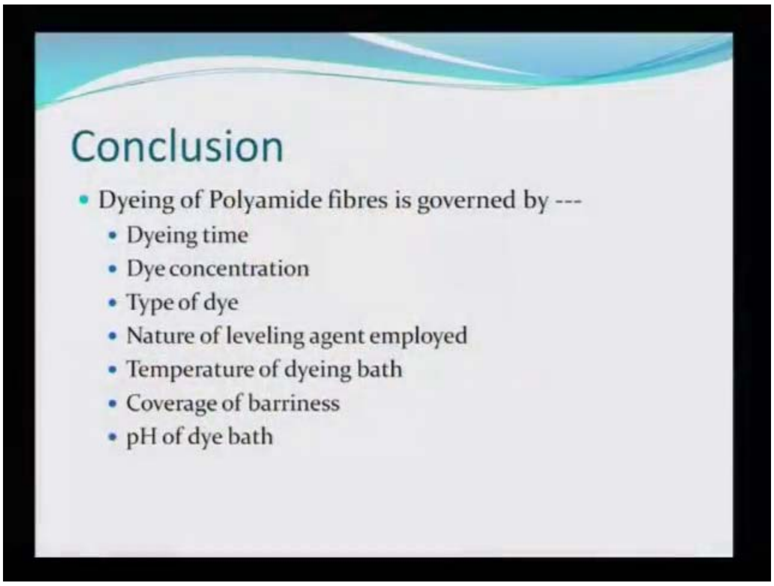

So, if we have to conclude we will say dyeing of polyamide fibre is governed by the dyeing time, the dyeing concentration, the nature of the dye, the type of the dye, nature of leveling agent employed, temperature of the dyeing bath, coverage of barriness and pH of the dye bath you see unless and until. These factors, that is the dye, dyeing time you know it is not fast process, adsorption, diffusion, retention and then you know to break this equilibrium all requires its time consuming, and therefore, the dyeing time is very important in the case of polyamide fibres.

Similarly, dye concentrations you know if we have very weak dye solution. It will be ah causing very light coloration to the nylon fibre. Why because as it is hydrophobic dyes are water soluble how to let this little dye get into the fabric and what kind of coloration will it provide. So, dye concentration must be very high. Then type of dye because we saw that there were several options disperse dyes disperses reactive dyes acid dyes metal complex dyes direct dyes so and acid dyes.

So, these many from these many options what is the best category of dye. That should be used and we saw that disperse dye disperse reactive dyes are the best, because they provide good wash fastness good light fastness they have good barre coverage they have good you know ah fast reaction time and they are with held by the hydrogen bonding. So, that you know they do not run off there is a kind of weak bonding. But still nevertheless they are held the dye molecule and the fibre have a kind of a hydrogen bonding and that is possible, because of the carbonyl and the NH 2 group that are present in the amide linkages of the nylon fibre.

So, that is the type of dye is very important. Again the nature of leveling agent employed, because it is the leveling agent which is the surfactant. Which actually you know keeps them together, if this leveling reagent does not participate then the dye dissolution will be a problem the you know the initial protonation of the amino group in the case of acid dyes and so on and so forth will not take place and the barriness will enhance.

So, therefore, it keeps the barriness or the coverage of the barriness lower. Nature of leveling agent is therefore; very important whether it is anionic cationic which dye is being used first thing is the choice of dye and accordingly the choice of the leveling agent will be followed by that. Then the temperature of the dye bath also has the very big impact. So, therefore, the pH and the covering of barriness in the case of polyamide are very important factors. So, today we finished the chapter on dyeing with polyamides and the synthetic dyes were used.