Natural Dyes

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Lecture No. # 40

Now, we have come to an end of this course and the last lecture is related to dyeing with azoic dyes. I have been avoiding talking about azo dyes, because we have talked about it, because it was banned, and it was banned, because it was it is hazardous and it is known to be mutagenic allergenic and many other things. But nevertheless you know azo dyes have been used and are being used still in the industry. And so, I thought I would mention this at the end, because I give the least priority to this dye, because of its harmful nature. But nevertheless it has its own role to play in the textile industry. And therefore, a special lecture dedicated just the way we had spoken especially about reactive dyes, about sulphur dyes, about the dying properties of natural dyes, various classes of natural dyes. Similarly, we need to spend some time looking at these azoic dyes, how they are formed and how they are applied.

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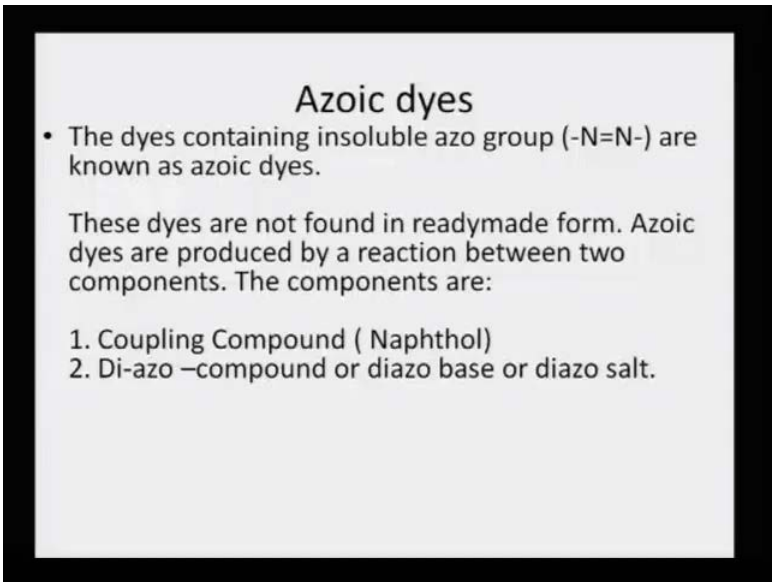

Azoic dyes: The dyes containing insoluble azo bond or group are known as azoic dyes. Now, this N double bond N is a very important chromoforic group in the azo dyes. These

dyes are not found in readymade form. Azoic dyes are produced by a reaction between two components and the components are coupling compound - naphthol and a di-azo - compound or a diazo base or a diazo salt. So, it is actually combination and it is not like any reactive dye, direct dye, acid dye, you know which can be just bought of the shell. It has to be prepared (( )) on the fabric and for that two components are required; one is a naphthol and the other one is a diazo base. And without which if one of them is missing the reaction will not take place and it will not fall into the category of azo dye. So, therefore, azo dyes first thing you have to understand must have an N double bond N linkage. And it is this N double bond N linkage which actually hydrolyzes and gives primary amines and the primary amines are the main culprit of making the azo dyes harmful.

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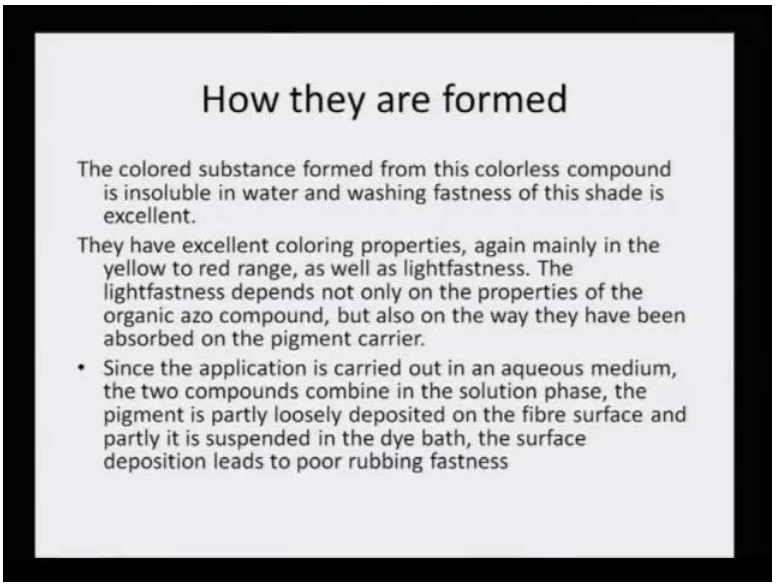

So, looking back at its structure the naphthol part and the diazo base part are two components of the same dye. How they are formed? The colored substance formed from this colorless compound is insoluble in water and washing fastness of this shade is excellent. Obviously, because it does not run off into the water; therefore, if the washing fastness once it adheres to the fabric, the washing fastness is very good. They have excellent coloring properties, again mainly in the yellow to red range, as well as the light fastnesses are also very good. The light fastness depends not only on the property of the organic azo compound, but also on the way they have been adsorbed on the pigment carrier. Since the application is carried out in an aqueous medium, the two compounds

combine in the solution phase, the pigment is partly loosely deposited on the fiber surface and partly it is suspended in the dye bath. The surface deposition leads to poor rubbing fastness.

So, how it occurs? Because the water the dye itself is not so soluble; so, whatever solubilizes gets adsorbed on to the… I mean so there is a part of the dye which is remaining in the aqueous phase and there is part of the dye which is you know suspended in the dye bath. So, the one which is completely dissolved gets in penetrates into the surface and the one which is floating in the dye bath gets adsorbed. So, sometimes what happens that these five fabrics which are dyed by azo dyes have poor rubbing fastness, because they were the dye molecules which are simply adhering or adsorbing on the surface can be just brushed off or rubbed off. So, they do… But the amount of dye which penetrates into the fiber is then cleaning to the fiber very strongly.

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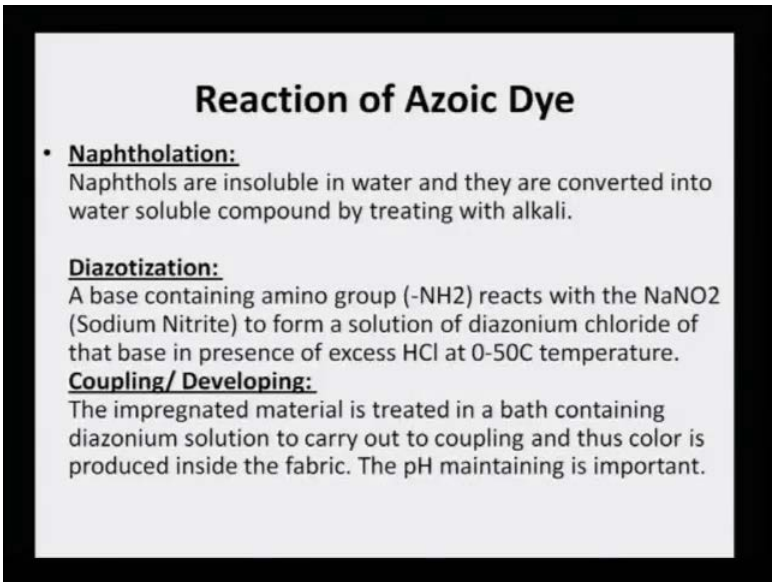

The reaction that takes place between naphthol and diazo base, how does it happen? Naphtholation, the reaction of azoic dye we have to describe it the it happens in three steps. The first step is the naphtholation; naphthols are insoluble in water and they are converted in water soluble compound by treating with alkali. So, these naphthols are then treated with alkali to make it in the soluble form or they are made sodium salt of the OH. So, the OH of the naphthol is converted into O Na. So, that is the step which is called naphtholation. Then comes the next step which is diazotization; diazotization a base

containing amino group reacts with sodium nitrite in the form in acidic medium to form a solution of diazonium chloride of that base in in presence of excess HCL, and the temperature is kept very low between 0 to 5 degrees.

So that, at that low ice temperature - the temperature is maintained and the diazonium salt of the amino compound is then or the base is then made. Finally, the impregnated material is treated in a bath containing diazonium solution to carry out the coupling and thus color is produced inside the fabric. So, this impregnated material is then treated in the bath containing the diazonium solution. So, naphthol is first impregnated on the fabric and this fabric which has naphthol is then dipped into the diazonium solution to carry out the coupling between the naphthol and the diazonium chloride. So, that is the kind of reaction. The pH maintaining is important, why, because this diazonium salt formation takes place in a highly acidic medium and be it has to be under very low temperature otherwise the reaction is very explosive. So, it if the temperature control is very important and the pH is also very important factor.

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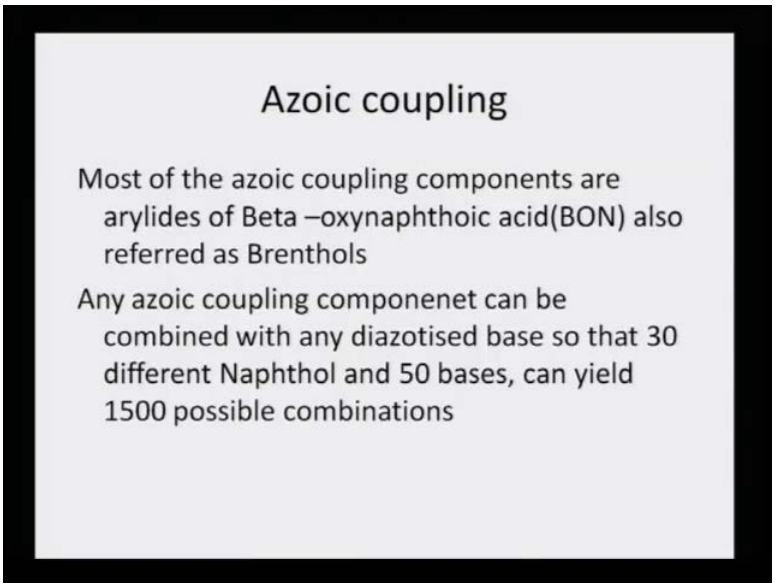

Azoic coupling: Most of the azoic coupling compounds are arylides of beta oxynaphthoic acid also known as brenthols. Any azoic coupling component can be combined with any diazotized base. So that 30 different naphthols and 50 bases can actually yield 1500 possible combination. But not all of them will give the desired shape,

not all of them will have the shades that are some shades will be common. So, that is why you know only handful or couple of azo dyes are actually in picture or in use.

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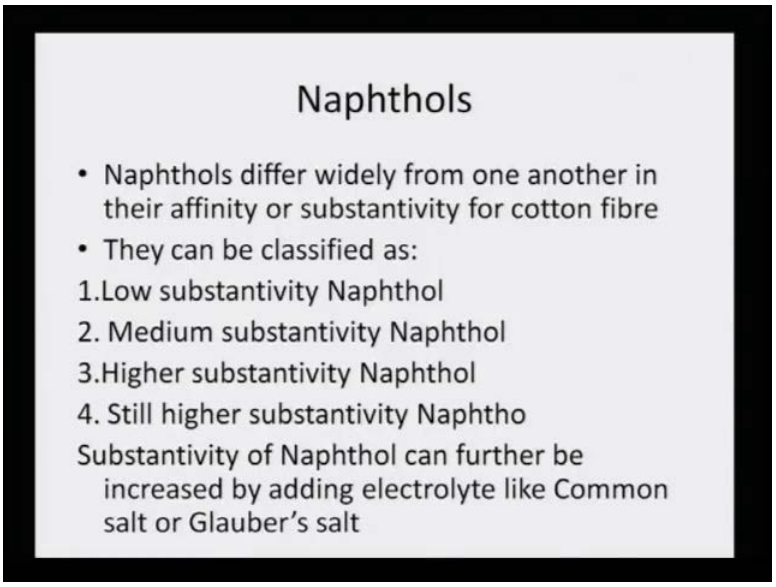

Naphthols differ widely from one another in their affinity or substantivity for cotton fiber. They can be classified as low substantivity naphthol, medium substantivity naphthol, moderate to higher substantivity naphthol or still higher substantivity naphthol. Now, substantivity of naphthol can further be increased by adding electrolytes like common salt or glauber's salt. Now, it is important that these how do they dissolve, how do they come into the solution form and in order to solubilize them, the role of an electrolyte is very important. And that is why some times common salt that is sodium chloride or glauber's salt that is sodium sulphate are added to increase the solubilization and at the same time impregnation, because whatever will be solubilized will get penetrate into the fabric. So, that is what is the most important part and role of the naphthols. And they are of four categories; one with very low substantivity, one with medium substantivity, one with moderate substantivity and one with very high substantivity.

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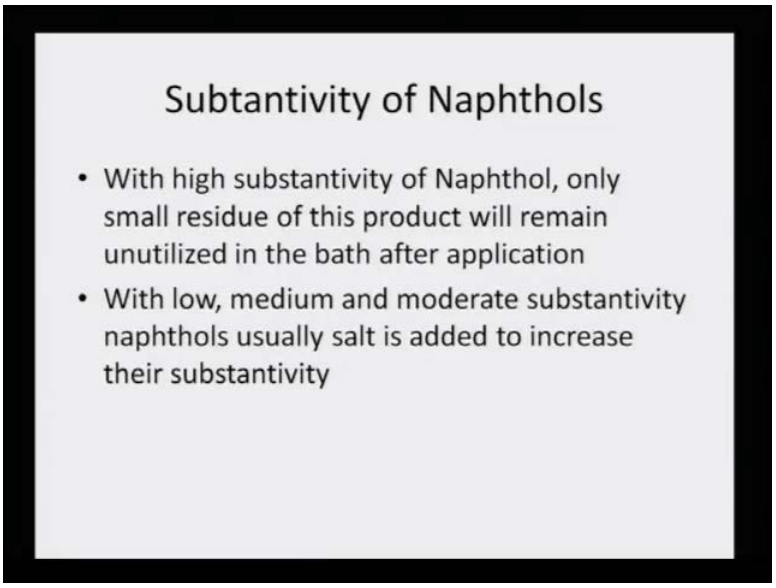

Substantively of naphthols: Why is it important to discuss so much about it? That is because with high substantivity of naphthol, only small residues of the product will remain unutilized in the bath after application. Because most of it if it is in the soluble state will get you know penetrated into the fabric; just the way if you recall, sulphonation helps in increasing the solubility. Similarly, here the OH of the naphthol, the more it is converted into O Na, the better it is for it to get solubilized and the more it solubilizes the more it penetrates into the fabric. Because now, as much naphthol that has reached into the fabric will now react with the diazo base. Because when it is dipped into the di diazonium chloride base bath, it will then react with the the two will react and will then form the azo dye or the azo dyed fabric. With low, medium and moderate substantivity naphthols usually salt is added to increase their substantivity. So, the role of addition of sodium chloride and sodium sulphate should be understood very clearly.

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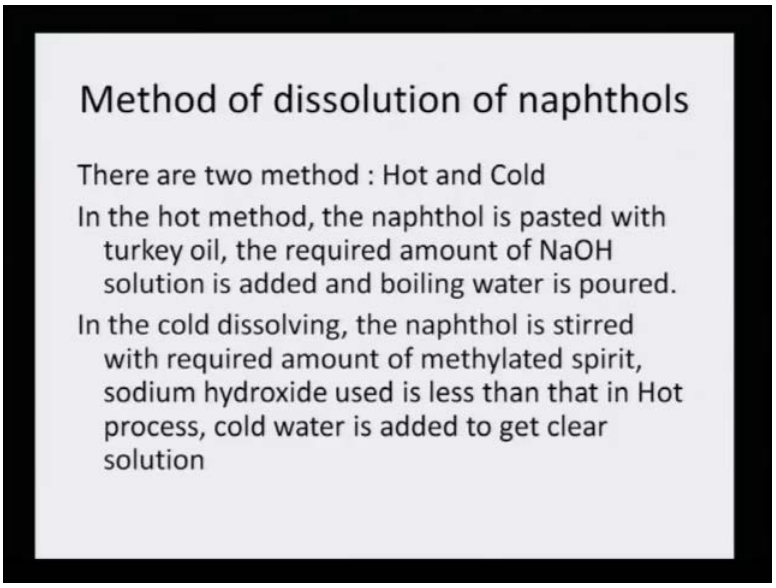

Now, method of dissolution of naphthol; we have just talked about the fact that naphthols are insoluble in water. So, there has to be some method of repairing this naphthol solution. So that it the the substantivity can be enhanced. There are two methods; one is a hot method and the other one is a cold method. In the hot method, the naphthol is pasted with turkey oil, the required amount of NaOH solution is added and boiling water is poured. So, there if one has to use turkey oil, but before that it is, you know, the first step paste of naphthol with turkey oil is made to that hot sodium hydroxide is added and further more boiling water is then added. So that it makes an even solution of the naphthol. This is the hot method.

In the cold method, dissolving the naphthol is stirred with required amount of methylated spirit, sodium hydroxide used is less than what it is in the process of hot process and cold water is then finally added to get clear solution. So, in the hot case, it is the or the hot method of dissolution, it is the use of turkey oil followed by NaOH. But a large amount of NaOH has to be added, and then finally boiling water is added. Whereas in the cold method, the naphthol is first dissolved in methylated spirit and with less amount of NaOH it can be dissolved and finally, cold water is added. And in this process, the amount of NaOH required is relatively less as compared to the hot process.

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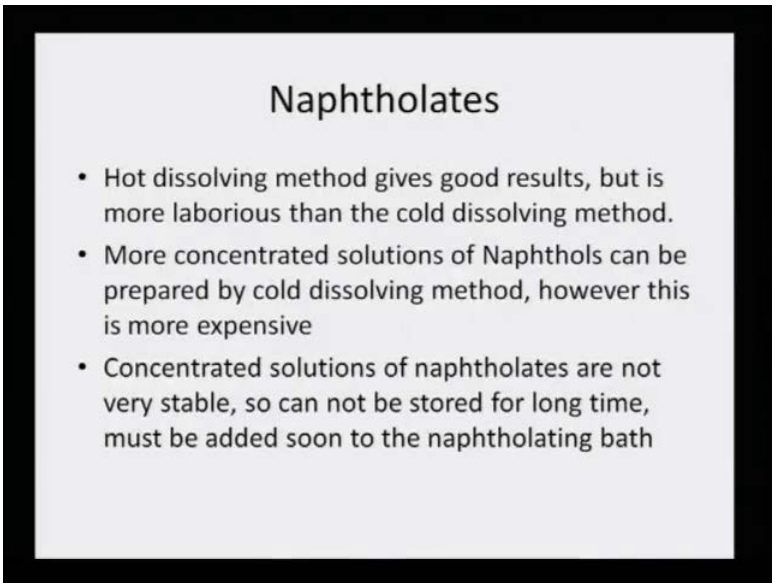

When this naphtholate that is the sodium salt of the naphthol is already prepared by hot dissolving method gives good result, but is more laborious than the cold dissolving method; obviously, because of the you know step being more. More concentrated solutions of naphthol can be prepared by cold dissolving method; however, this is more expensive. So, if you one tries to look at the two methods - the hot and the cold method of dissolution of naphthol, each one each one has its own advantage and each one has its own disadvantage. So, one has to out way which one is giving the best result.

In the hot process it is laborious as compared to the cold process. But the results are very good. Whereas, in the more concentrated solution can be prepared by cold rather than the hot method, and therefore, it is more expensive. Concentrated solutions of naphtholates are not very stable. So, cannot be stored for long time and must be added soon to the naphtholating bath. So, it is not that you make a sodium salt and just set with it. It has to be used immediately otherwise it gets destroyed or deactivated.

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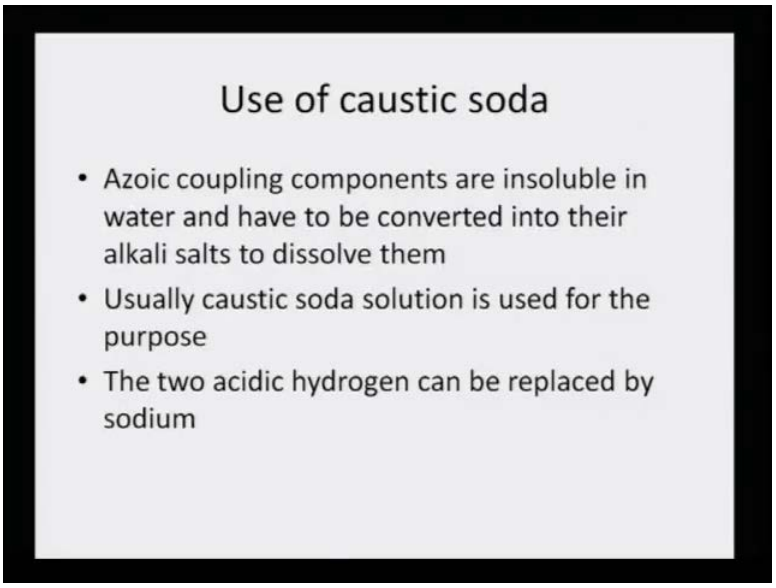

Use of caustic soda: Now, you know that sodium hydroxide we have been talking is a very crucial component in converting the naphthols to their sodium salts. So, azoic coupling components are insoluble in water and have to be converted to their alkali salts to dissolve them. So, it is important that the role of each chemical, why is it added, what is the role, and in this you know that naphthols for say are insoluble, and they need to be solubilized in order to impregnated the naphthols on the fabric. So, for that NaOH has a very crucial role, because the OH of the naphthol is converted into O Na salt. Causing usually caustic soda solution is used for the for this purpose. The two acidic hydrogen can be replaced by the sodium, so as many OH that are present on the naphthol; that many Na's will be replaced. So, it will become O Na now.

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High degree of brightness: Because of high degree of brightness, ease of application and excellent fastness properties except sometimes the rubbing fastness which can be improved by using certain auxiliaries, azoic combinations that is the naphthol and the bases are widely used in printing on cellulose fiber fabrics as well. Because you see it is not only meant for dyeing, it is also a very good material for printing. And the characteristic that it has why it is you know still regarded and used, and is still one of the best dyes, although it has its own harmful effects. But in terms of its brightness, in terms of the ease of application and excellent fastness properties except for poor rubbing fastness in a few cases where it is adhering, the extra naphthol is just adhering to the surface. There only there is a poor rubbing fastness otherwise all other light fastness and perspiration fastness, rubbing fastness and the other characteristics are washing fastness are very good.

So, if one has to take an overview of this azoic dyes and their dyeing property, they will still be regarded as one of the better ones. Azoic dyes are used for producing bright shades of color such as orange, red, scarlet, navy blue and black color. So, you see they have a whole range of color and it is because as I told you there are 30 popular naphthol bases and 50 sorry 30 naphthols and 50 bases. So, the combination could be a huge number and because of this permutation and combination it is possible to have a variety of color ranging from orange to red to scarlet to navy blue and black as well. You saw that you know this kind of you know, huge variation in color, huge variety in color was

not so popularly seen in any other class of dyes. So, there also they have an edge over other dyes.

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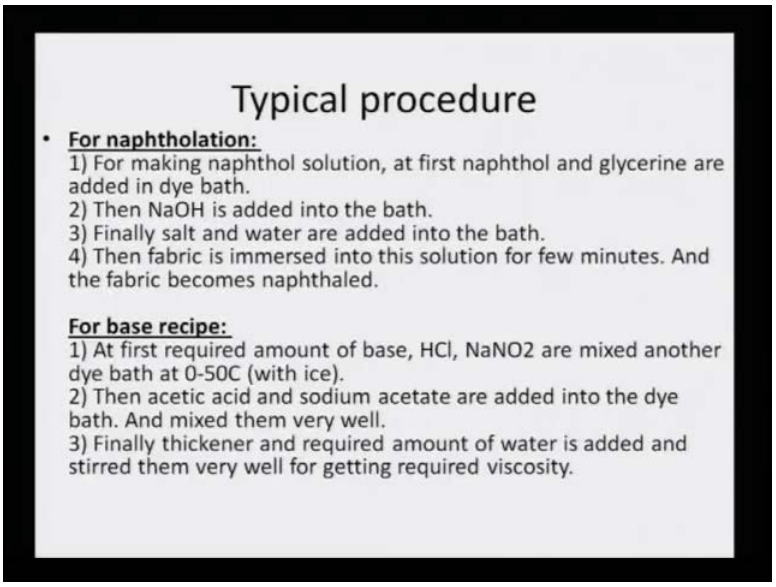

A typical procedure for naphtholation is for making naphthol solution, at at first naphthol and glycerin added to a dye bath, then NaOH is added. So, sometimes even glycerin can be added instead of the any other turkey oil or something like that. Then NaOH is added into the bath, finally salt and water are added into the bath. So, salt is now acting like an electrolyte, then fabric is immersed into the solution for a few minutes and the fabric becomes naphtholated. So, this is the procedure for making the fabric naphtholation.

Then for the base, what is the recipe, let us take a look. At first required amount of base, HCL and sodium nitrite are mixed with each other at 0 to 5 degrees with ice, then acidic acid and sodium acetate are added into the dye bath and mix them very well. Finally a thickener and required amount of water is added and stirred them very well for getting the required viscosity. So, this is a very simplified procedure, just to make you understand that how the naphtholation of the fabric is done and how the diazotization is done separately and then the to the diazonium dye bath, the naphtholated fabric is immersed.

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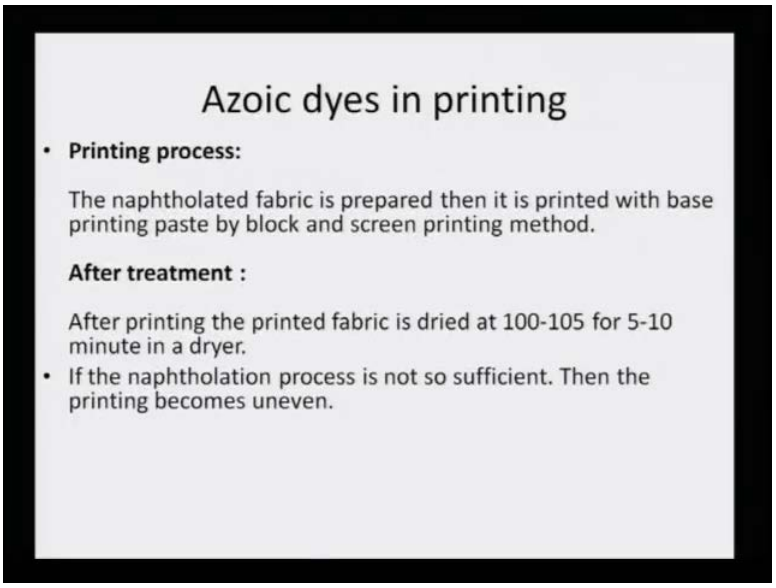

Azoic dyes as I mentioned a while ago are also very useful in printing. Printing process ideally has the naphtholated fabric is prepared then it is printed with base printing paste by block or by screen printing method. So, it is very simple. First the fabric is, you know treated with the naphthol which we call as naphtholation of the fabric. Once that is done then printing with blocks or screen printing is done with the base compound. So, it is very simple and yet you know the color is so bright and nice and with best of the fastness properties.

However, this printing requires a an after treatment as well. After printing, the printed fabric is dried with at about 100 to 105 for 5 to 10 minutes in a drier. If the naphtholation process is not sufficient then the printing becomes uneven. So, now you know that naphtholation process is the bottleneck. For any process to be able to go successfully it should have a smooth path and if there are narrow paths, those narrow paths have to be taken into account more seriously than the other ones. And naphtholation does is the most crucial step, be it dyeing with azo dye or be it printing with azo dye. I want to again emphasize that naphtholation of the fabric is the most crucial step.

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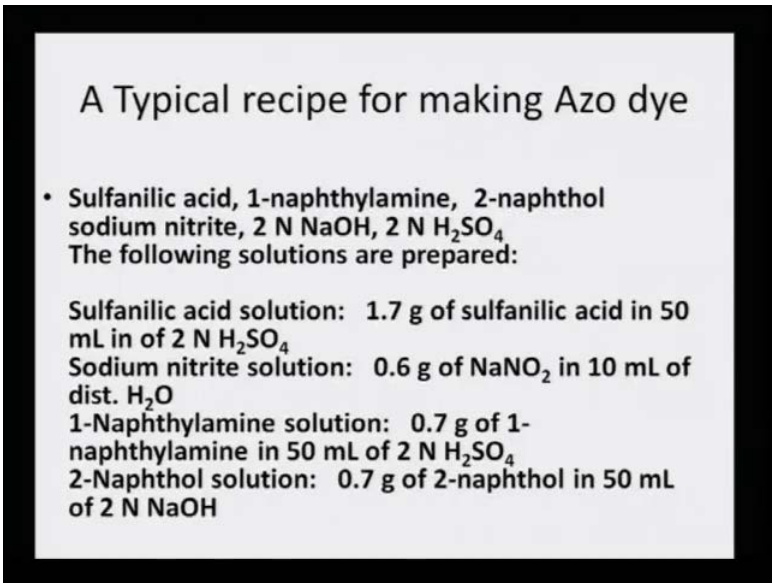

A typical recipe for making azo dye is that one can take sulfanilic acid 1-Naphthylamine as the amino base 2-Naphthol sodium nitrite, 2 N NaOH, 2 N Sulphuric acid. And the following solutions are then prepared; the sulfanilic acid solution is prepared by taking 1.7 gram. This is a laboratory method that I am discussing, so that you know you can even do this experiment even by yourself and you get an idea how dyes are made. 1.7 gram of sulfanilic acid in 50 ml of 2 N Sulphuric acid is prepared; sodium nitrite solution - 0.6 gram of sodium nitrite in 10 ml of distilled water is prepared; 1 naphtholamine solution is prepared by using 0.7 gram of 1 naphthylamine in 50 ml of sulphuric acid. So, you see that sulphonylic acid solution and naphthylamine acid solution are all made in acidic medium. The 2-naphthol solution is made in the base. So, one is completely in the acidic medium and the other one is completely in the basic medium. And the role of the base here is that it utilizes the NaOH Na hydrolyzes the OH of the naphthols and converts into them into ONa. So, that it is more reactive.

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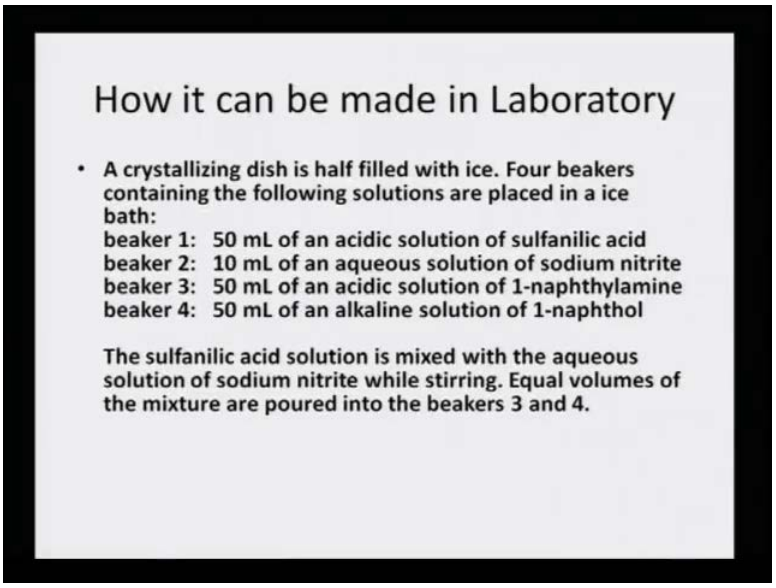

How it can be made in the laboratory: A crystallization dish is half filled with ice. Four beakers containing the following solutions are placed in the ice bath. Beaker 1 has acidic solution of sulfanilic acid, beaker 2 has an aqueous solution of sodium nitrite, beaker 3 has acidic solution of naphthylamine and beaker 4 has alkaline solution of 1-naphthol. The sulfanilic acid solution is mixed with aqueous solution of sodium nitrite while stirring. Equal volumes of the mixtures are poured into the beaker 3 and 4 which has one naphthylamine and 1-naphthol.

So, that is how in such a simple method of making azoic dyes nevertheless you know it is to be understood that when it comes to dyeing with fabric. This naphthol has to be impregnated on the fabric. Whereas, the diazonium salt is prepared separately in a diazonium bath and the naphtholated fabric is then immersed into it and the reaction takes place inceptive. Then we go on to see how this dyeing of cotton takes place with azo dyes.

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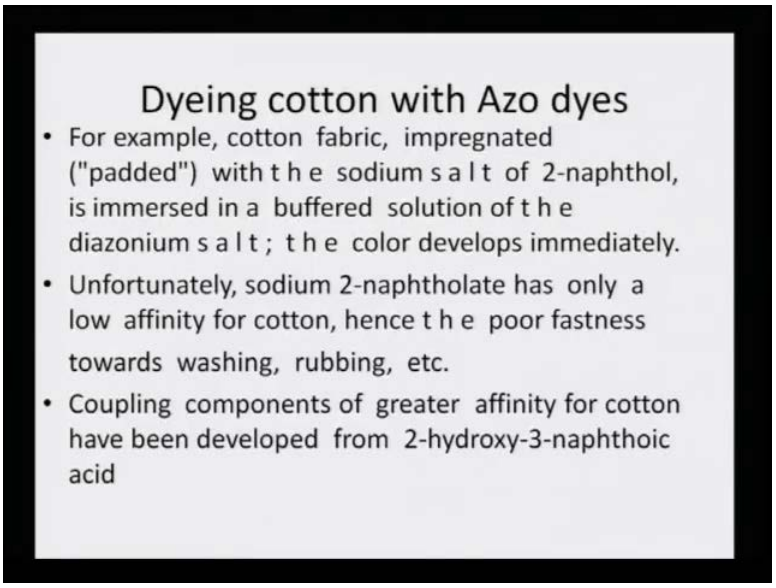

For example, cotton fabric, impregnated or padded with the sodium salt solution of 2-naphthol is immersed in a buffered solution of the diazonium salt; the color develops immediately. Unfortunately, sodium 2-naphthalene has only a low affinity for cotton, hence the poor fastness towards washing and rubbing. So, 2-naphthol is not one of the best naphthols, there are other very good naphthols which have good affinity for cotton, those must be used. So, but I am giving you an idea that how important is the role of naphthol in this azo dyeing. And if the naphthol makes a good naphtholate and the naphtholate has good substantivity then only it will be taken up by the fabric. Coupling components of greater affinity for cotton have been developed and 2-hydroxyl 3-naphthenic acid is better than 2-naphthol.

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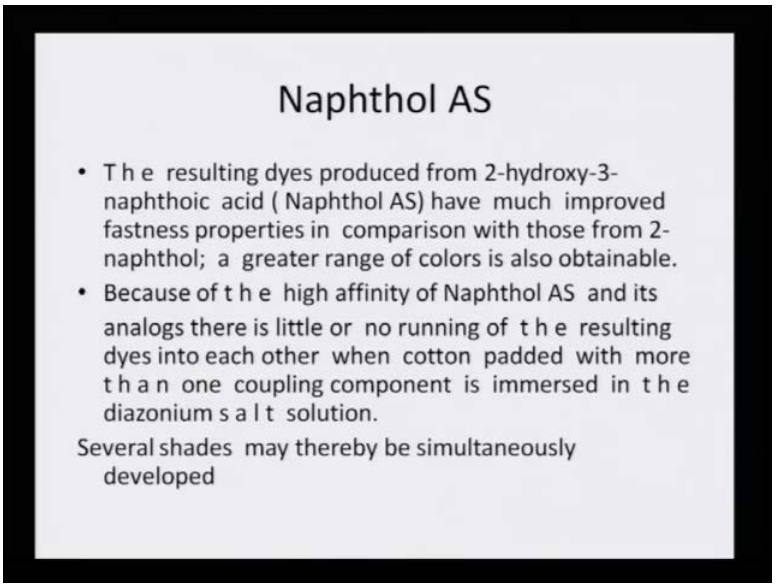

Naphthol AS: The resulting dyes produced from the 2-hydroxy 3-naphthoic acid that is naphthol AS is the common name have much improved fastness properties in comparison with those from the 2-naphthol; a greater range of color is obtainable. Because of the high affinity of naphthol AS and its analog there is little or no running of the resulting dyes into each other when cotton padded with more than one coupling component is immersed in the diazonium salt solution. Several shades may thereby be simultaneously developed. So, you see that just by changing the naphthol variety from 2-naphthol to 3-hydroxy sorry changing from 2-naphthol to 2-hydroxy 3-naphthoic acid that is naphthol AS the whole chemistry of the naphtholation has changed and it has enhanced the property of the fastness, giving greater color range and because now this naphthol has better affinity.

So, what does it boil down to? It boils down to the fact that fiber affinity of the naphthol variety is of ultimate importance. Because unless and until that is achieved the naphthol will not impregnate, and the reaction with the diazonium salt which is the subsequent step will not happen efficiently, and there will be lot of naphthol remaining un-reacted. And in case of naphthol AS which is generated which is the other name for 2-hydroxy 3-naphthoic acid. The property enhancement is really advantageous for the people who use azoic dyes.

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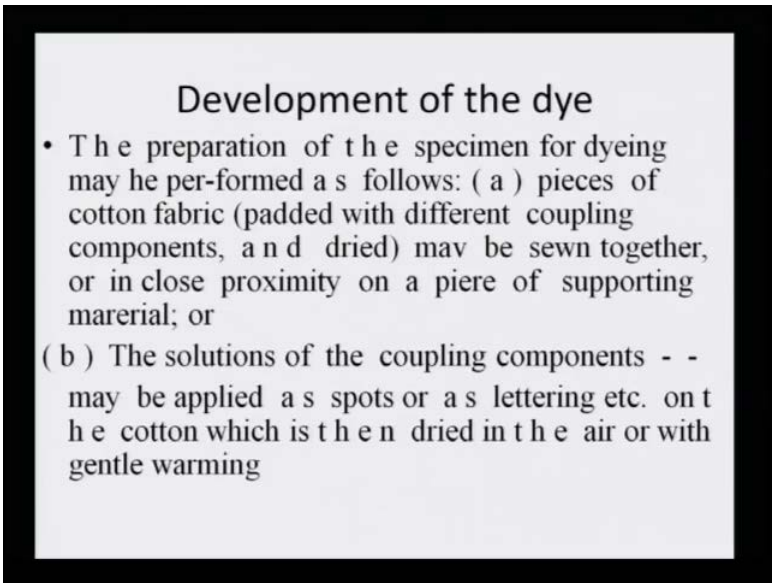

Development of the dye: The preparation of the specimen for dyeing may be performed as follows; the pieces of cotton fabric padded with different coupling components or dried and may be sewn together and in close proximity with the piece of supporting material, the solutions of the coupling components may be applied as spots or as lettering and the cotton which is then dried in air will with gentle warming. So, that the development of color is very simple as what you will see. It is the naphthols reaction and fine and subsequent reaction with the diazonium which makes all the difference.

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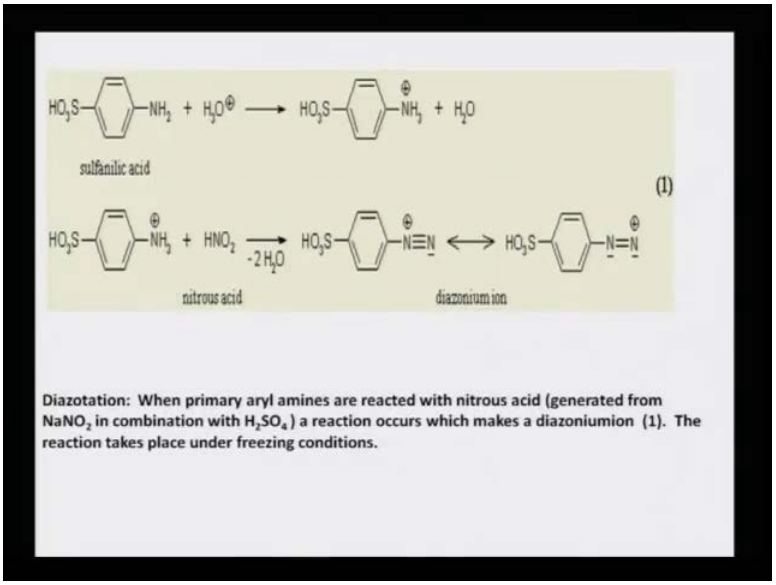

Now, if we try to take a look at the sulfanilic acid reaction. The first step that happens in the diazotation is that the primary aryl amine that is the sulfonilic acid is first reacted with the hydronium ion to form the NH 3 plus. Now, this NH 3 plus then gets diazotized with the sodium nitrite sulphuric acid reaction which creates nitrous acid, which produces nitrous acid, and by the elimination of two water molecules it gives rise to the diazonium salt. Now, you see that it the molecule has N double bond N. Now, this is what is ready now for the coupling of the naphthol from the other end from the nitrogen end. And this this particularly is what happens. So, I wanted to show you that the chemistry is so simple, but yet it is intricate and the only important point that needs to be remembered is the fact that the diazonium ion must be prepared at a very low temperature between 0 to 5 degrees.

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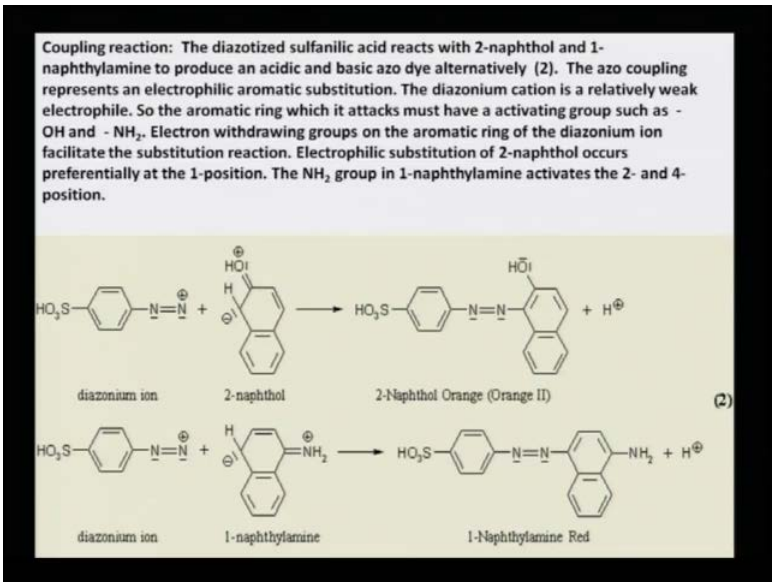

Then subsequent coupling step: The diazotized sulfanilic acid reacts with the with 2-naphthol and 1-naphthylamine to produce an acidic and basic azo dye alternatively; two dyes are happening of prepared in the same type or diazotized bath. The azo coupling represents and electrophilic aromatic substitution. The diazonium cation is a relatively weak electrophyl. So, the aromatic ring which is attacked must have an activating group such as OH or NH 2. Electron withdrawing groups on the aromatic ring on the diazonium facilitate the substitution reaction. Electrophonic substitution of 2-naphthol occurs preferentially at the position 1. The amino group in the 1-naphthylamine activates and the 2 and 4 position.

So, you see that the entire reaction is all driven by the functional groups that are present on the naphthols. If there is a naphthol you know which is having an amino group that is 1-naphthylamine. It will react and form 1-naphthylamine red molecule, whereas if the diazonium the same diazonium reacts with 2-naphthol it gives 2-naphthol orange, and therefore you can understand that why the two different molecule red and orange have formed. Because 2-naphthol and 1-naphthylamine have just only at difference of one extra NH 2, now this extra NH 2 is is the one which is electron donating and it is therefore changing the entire electronic situation of the diazonium salt and the subsequent dye that is formed.

So, this is what I wanted to make you understand that these structures are very important to understand, because the chemistry is very simple. The formation of the naphthol to naphtholate or the formation of the base that is 1-naphthylamine to get converted into its subsequent dye is not very difficult, but one needs to understand how the diazonium salt forms, how the naphtholation takes place and so on and so forth.

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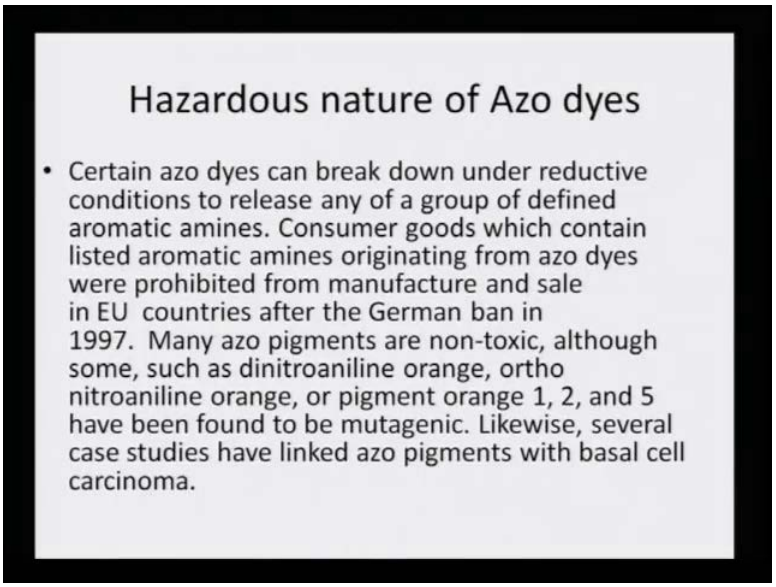

But when we talk about azo dyes we cannot end the story without talking about the hazardous nature of the dye, and therefore I took it as the last lecture. Certain azo dyes can break down under reductive conditions to release any or a group of defined aromatic amines. Consumption consumer goods which contain listed aromatic amines are in originating from azo dyes were prohibited from manufacture and sale in the European

union countries, after the German ban came into existence in 1997. Many azo pigments are non toxic although some, such as dinitroaniline orange, orthonitroaniline orange or pigment orange 1, 2, 5, and 1, 2 and 5 have been found to be mutagenic. Likewise several case studies have been linked to azo pigments with many types of carcinoma which is another type of cancer.

So, whether it is you know really right to use azo dyes or not is left to the users. But definitely a large number of azo dyes have been banned, because it is if I go back to the structure I will be able to explain to you that it is the cleavage of this N double bond N which then releases the primary amines, and it is these primary amines which are extremely hazardous, and these are the ones it is not the azo dye for say, but because the azo dye undergoes reductive cleavage very readily. It produces two sets of primary amines and both the sets could be hazardous or could be you know safe. So, there are some azo dyes which are safe, but there are a large number of azo dyes which are not so safe. So, it is up to you to decide, but nevertheless as a part of the curriculum the dye chapter would would not have been completed or the lecture series on dye would not have been completed without the incorporation or without talking about azo dyes.

So, with this we have come to an end of this course. I hope that you enjoyed and I tried to impart as much information which was possible related to dyes, synthetic dyes, natural dyes, and of course primary emphasis was on natural dyes and natural dyeing processes. Nevertheless we tried to cover most of the dye classes and the dyeing methods with different fibers, natural and synthetic. So, with this we have come to an end of this course.