Natural Dyes

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Lecture No. # 18

Today we will study, a little more detail about a very special class of dyes called the vat dyes. I had mentioned fleetingly while, we were doing different types of dyes, structurally different types of dyes as indigo being one of the vat dyes. Today, we will try to look at the process by which this vat dye is actually fermented, and used what are the different parameters for dyeing with vat dye and so on and so forth. You will realize that the, this particular type of dye needs really some special attention. For the simple reason that vat dyes are very popularly used in the industry. Secondly, they have a special kind of processing unlike the direct dyes, and the reactive dyes, and the disperse dyes and so on and so forth or even the natural dyes.

So, whether we take an example of vat dye which is of synthetic origin or a vat dye which is of natural origin, they all go through the similar process of oxidation, reduction and therefore, we will talk more in details about the vat dye.

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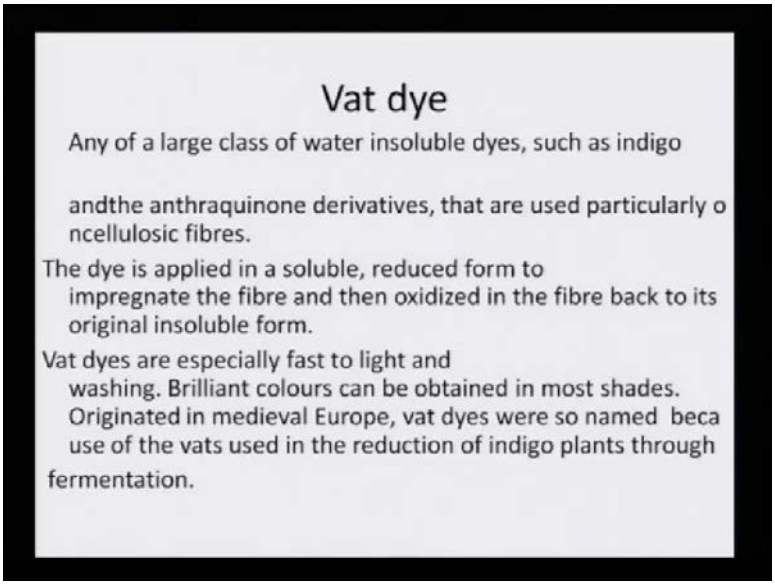

Vat dye: any of a large class of water insoluble dyes such as indigo, and the anthraquinone derivatives, that are used particularly for non cellulosic or cellulosic fiber, that is particularly water insoluble. Vat dye when we talk, we talk in terms of its being water insoluble. Now, if a dye is insoluble, how does it actually get adhered to the fabric. Because so far, we we had been learning about one fact that the dye should be soluble in water or at least in 50 percent methanol water. Then only the dyeing, it fits into the category of being a dye. But here is a dye, under the class of vat dye which is insoluble, but still it is applied, and it is a large class of dye which is being used in the industry.

The dye is applied in a soluble reduced form to impregnate the fiber, and then oxidized in the fiber, back to its original insoluble form. So, it goes through a process in which its solubilizes for a while, gets into the fiber, and then when the fabric is taken out, it is back to its insoluble form. So, that is how this beautiful vat class of dyes are used in industry, as well as in a laboratory, because if this oxidation reduction, and this insolubility, solubility, solubility, insolubility was not functioning accordingly the vat dye would not have been in use.

Vat dyes are especially fast to light and washing. So, they have a very big advantage; although they have a disadvantage of being insoluble, but there is a way to solubilize it, and impregnate on the fiber. And therefore, because it has very good light and wash fastness; it really fits into the best category of dyes. So, if we try to way the advantages and the disadvantages. The advantages of harmoul than the disadvantages; brilliant colors can be obtained in most shades.

So, its not that the vat dye is only associated with indigo and indigo is blue. It could have a variety of color or and they are very bright brilliant color, they are not dull colors; originated in medieval Europe. Vat dyes were so named, because of the vat used in the reduction of indigo plants through fermentation. So, because the vessel that was used was the vat vessel, that is why the name came to be as vat dye. Otherwise, you know this has its own way of in it can be carried out in any type of vessel, but because of that earlier times the name has persistive.

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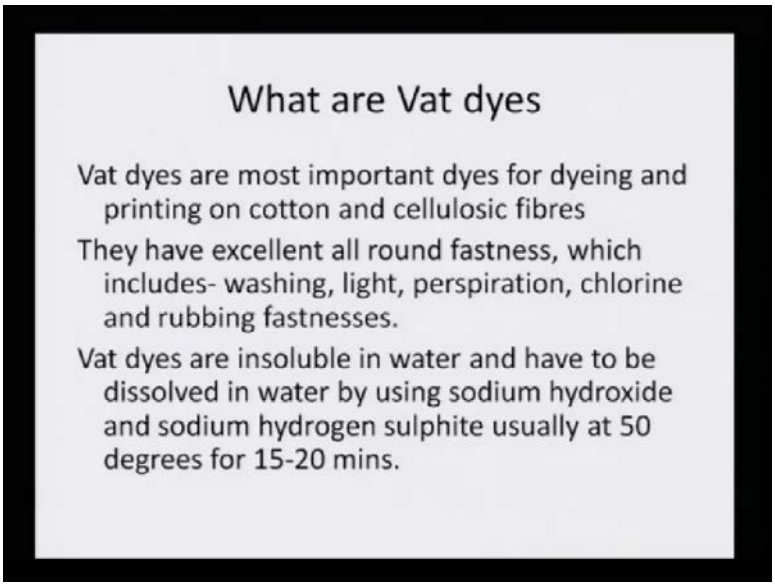

What are vat dyes? Vat dyes are most important dyes for dyeing, and printing on cotton and cellulosic fibers. So, it is as I told you, that when we were talking about natural dyes; I told you the toughest of the tough is the dyeing of cotton. Silk and wool being from the proteinaceous nature can take up natural dye very easily, and I also mentioned that for dyeing cotton many pre treatments like, treatment with tannic acid, and of course, modenting and all that is required only for the dye to be able to adhere. And here is a dye, vat dye which does not require modenting, and is best suited for cotton or cellulosic fiber.

So, another advantage that comes on the side of the vat dyes is that, it is very good for the toughest material that is the cellulosic fiber. They have excellent all-round fastness which includes washing light, perspiration, chlorine and rubbing fastness. So, its not only just the light and wash fastness, it has an overall on all round fastness, it it is one up from the other dyes. So therefore, it is very good washing fastness, light fastness, rubbing fastness, perspiration fastness, fastness and even chlorine reaction. Because sometimes you know, chlorinated water is obtained from the municipal corporation and so, if the dye is reactive towards the chlorine, it will fade off.

But it is able to sustain even such chlorinated water. Nobody treats chlorine on the fabric directly, but it is the chlorinated water sometime from the supply which can create fading in many cases, but vat dyes are resistant to it. Vat dyes are insoluble in water, and have

to be dissolved in water by using sodium hydroxide and sodium hydrogen sulphite usually at 50 degrees for 15 to 20 minutes. So, there is a small procedural, you know process by which this insoluble dye can be solubilized. So, that requires addition of two compounds- one is sodium hydroxide, and the other one is sodium bisulphite or sodium hydrogen sulphite, it is one and the same thing and its slightly warmed up at 50 degrees, and it is kept for 15 to 20 minutes when all of this vat dye can solubilize into the water.

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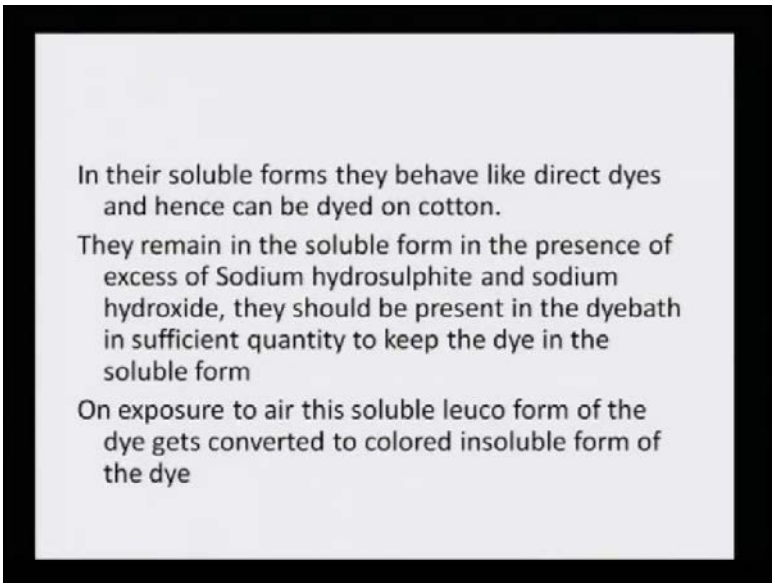

In their soluble forms, they behave like direct dyes, and hence can be dyed on cotton. So, once it solubilizes, the process of dyeing that is the capillary action, the impregnation, the adherence of the dye on to the cotton fabric is very fissile and is similar. To the basic dyeing process that we have learn so far; they remain in the soluble form in the presence of excess of sodium hydrogen sulphite, and sodium hydroxide. They should not be present in the dye bath in sufficient quantity, they should be present in the dye bath in sufficient quantity, to keep the dye in the soluble form.

So, as long as sodium hydroxide and sodium bisulphite is present; it will remain in the soluble form. On exposure to air, this soluble leuco form - leuco means colorless of the dye gets converted to colored insoluble form of the dye. So, it is back to its original form. So, when the dye powder was taken, it needs to be solubilize by two agents that is sodium hydroxide and sodium bisulphate, utter slightly lukewarm temperature for 15 to 20 minutes, and it remains in the soluble form; once it is in the soluble form, it acts like

any direct dye, and it gets impregnated on through the fabric like the normal dyeing process as what would be carried out with any dye, and then once the dyeing process are impregnation or dye up take has been done or dye exhaustion from the dye bath seems to be have taken place, then the fabric is lifted up ,and it is expose to air.

It is this soluble form which then reacts with the oxygen of the air, and it turns the dye into its insoluble form. So, that is the procedure; it is a slightly different procedure from what you have learn so far, but nevertheless it is a very significant procedure.

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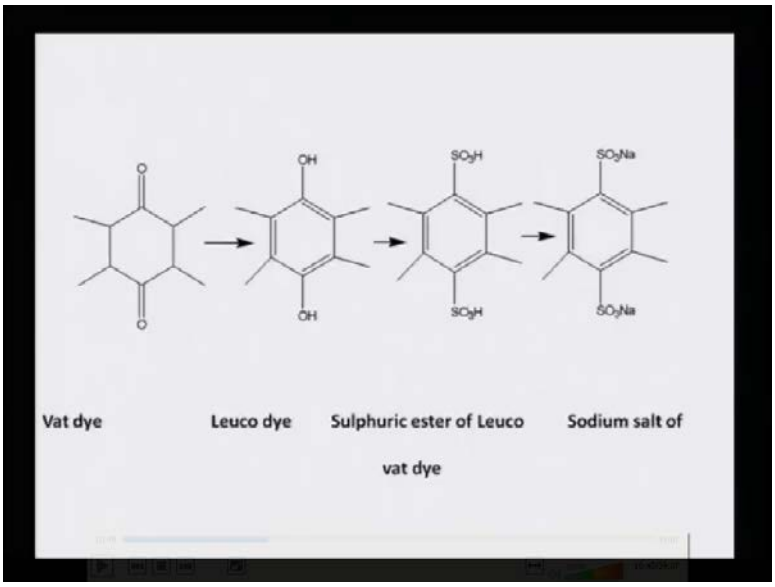

Now, this is how the vat dye is the carbonyl containing group which is in the leuco form when it is treated with the sodium hydroxide, it enolises and it forms like a benzenoid dye alcohol, and this is then, a the leuco vat acid, then when reacts with sodium bisulphite to form the sulphuric ester of the leuco vat dye; and when we add sodium hydroxide, it converts, because this is an acid. And so, it will form a salt with sodium hydroxide which is a base.

So, these are the various structures; the vat dye has the carbonyl group, the leuco dye which goes into the soluble form is the hydroxy compound which immediately reacts with the sodium bisulphite to form the sulphuric ester of the leuco acid, leuco vat dye and then finally, with sodium hydroxide it forms a salt of the sodium sodium salt of the vat dye. So, this is how it the structures change from from one to another, and how it solubilizes in the medium.

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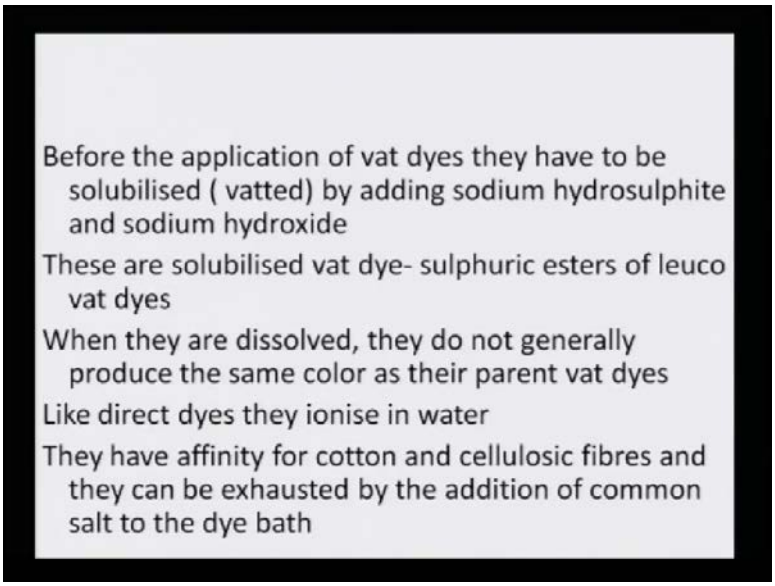

Before the application of the vat dyes; they have to be solubilized that is vatted by adding sodium hydrosulphite and sodium hydroxide. So, it needs to be understood very clearly, that in order to convert the vat dye from insoluble form to soluble form, these two reagents are absolutely mandatory. Without the addition of these two, the dye will not solubilize in water. And if it does not solubilize in water, it cannot react with the fabric. These are solubilize vat dyes, sulphuric ester of the leuco vat dyes when they are dissolved, they do not generally produce the same color as they parent vat dyes.

So, in the leuco form, it is a very undefined kind of a color or rather the blue color suppose, if we take the example of indigo; since, to be absolutely faded and it has a yellowish, greenish, undefined, you know fluorescent kind of a color. But once, it is exposed back into the air, it gets the blue color on the fabric. So, the blue color which was initially in the dye state is now on the dye fabric. Like direct dyes they ionize in water; they have affinity for cotton and cellulosic fibres, and they can be exhausted by addition of common salt to the dye bath.

And the best way to exhaust these dyes are to see that maximum dye has been taken up by the fabric, common salt is also added, because it acts like a leveling agent. We had learnt about modifiers and leveling agents and so on. Now common salt, glauber salt these are all modifiers or leveling agents. So, with the help of the leveling agent maximum amount of a solubilized, leuco form of the vat dye enters into the fabric.

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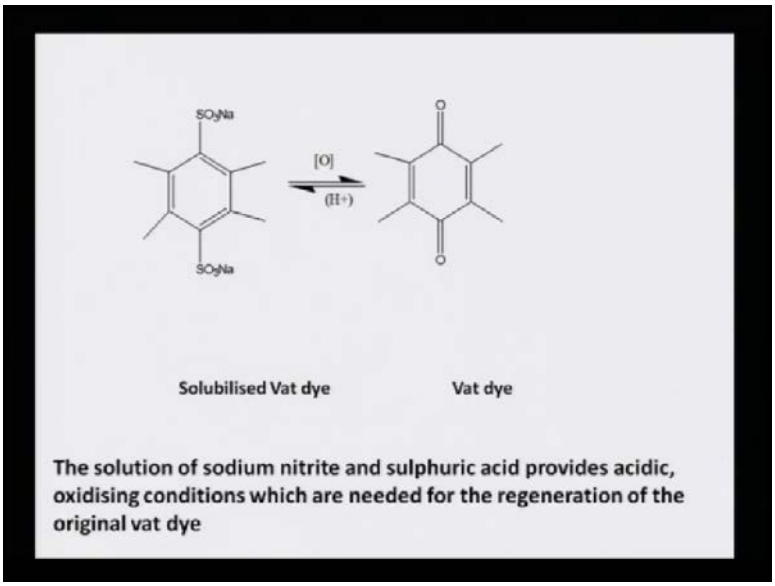

Now, this is what the sodium salt of the sulphuric ester of the leuco dye; when it is exposed to oxygen, it gets converted into the initial carbonyl insoluble compound which is the vat dye. But now, it is on to the fabric. So, the powder has now gone transferred to the fabric through this insoluble, soluble and insoluble state or we can say that from vat dye to leuco form, and from leuco form to vat dye again. The solution of sodium nitrite and sulphuric acids are sometimes added to which provides acidic oxidizing conditions which are needed to regenerate the original vat dye.

So sometimes, if the procedure has to be enhanced or esten or a has to be carried out in a faster manner, it is possible to that with the help of addition of sodium nitrite and sulphuric acid which are nothing but oxidizing agent, and they facilitate this oxidation, if the air oxidation or air oxygen is not sufficient.

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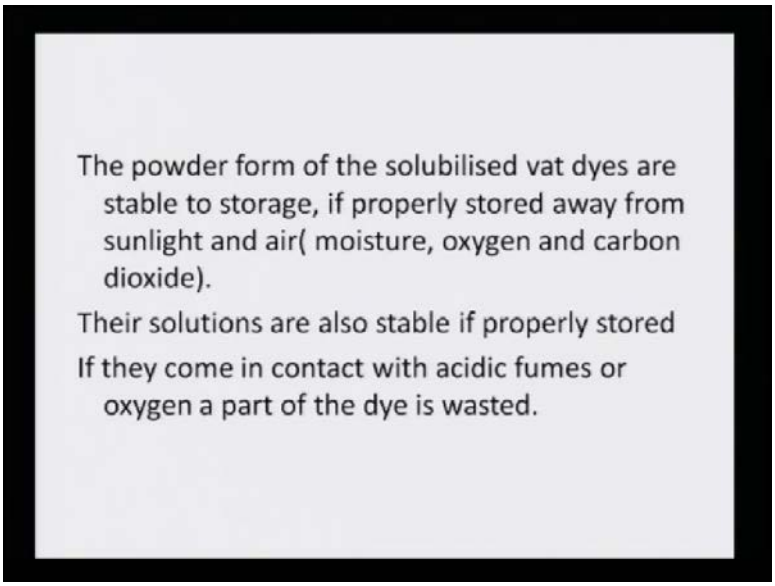

The powder form of the solubilized vat dyes is stable to storage; if properly stored away from sunlight and air. Moisture, oxygen and carbon dioxide can be detrimental. So, this is a very stable dye, it if it is stored properly, it can be kept for very long times, be it natural dye or be it synthetic vat dye. Their solutions are also stable, if properly stored; if they come in contact with acidic fumes or oxygen apart of the dye is wasted. So, one has to keep in mind that oxygen and moisture should be avoided, even the paste can be kept. You know, the leuco form paste can be stored and in many cases some dyers ask for the leuco form directly.

Because they do not want to go through this process of solubilizing them; and therefore, they ask the suppliers to give the dye not in the powdered insoluble form, but in the soluble leuco form. So, these solutions are also very stable provided, they are not exposed to the air. Because if they come in contact with the air, we have seen that the oxidation occurs; and it gets converted into the vat dye that is the insoluble dye carbonyl compound.

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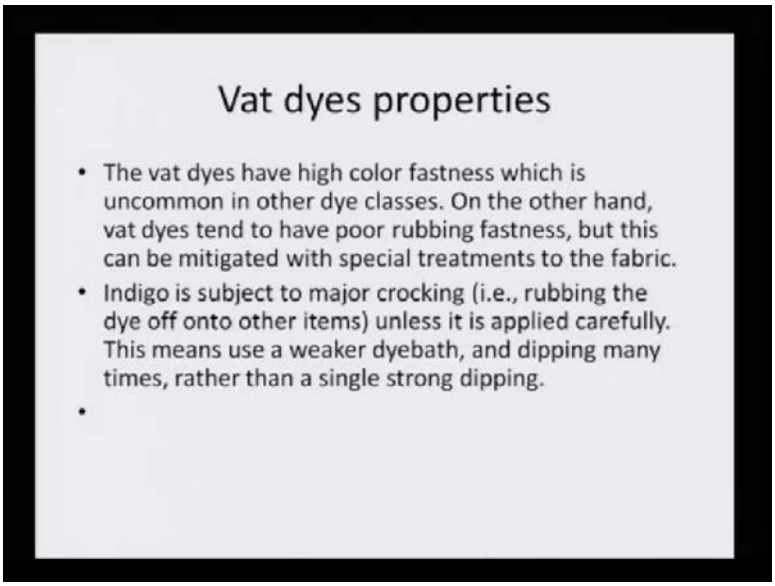

Vat dye properties: the vat dyes have high color fastness which is uncommon to other dye classes; on the other hand, vat dyes tend to have poor rubbing fastness, but this can be mitigated with special treatments to the fabric. The although it has good rubbing fastness, but in few cases of the vat dyes, it may have a bit of a problem with the rubbing fastness. Indigo is subject to major crocking that is rubbing the dye off onto other items, unless it is applied carefully. One such example, which has poor rubbing fastness are not so appreciably, high rubbing fastness is indigo dye, because it rubs of the dye as it is in the insoluble vat form. Unless it is applied carefully; this means use a weaker dye bath and dipping many times rather than a single strong dipping.

So, by doing repeated dyeing; the impregnation is enhanced. And the surface dye content is less in. And therefore, using a weaker dye bath that means, having lesser concentration of the dye in one group, but doing several times dyeing, that is over dyeing or repeated dyeing and that creates more and more color within the fabric rather than on the surface. Because the one which comes on the surface is actually what is rubbed of. So, therefore, that can be you know, mitigated or that this drawback can be overcome; and they the application process only changes in this case, because if the application is done in a good manner, in a manner which will only let the dye be within the fabric and not a you know on to the surface of the fabric, it will avoid the rubbing fastness to be poor.

Vat dyeing - after dyeing in a bath containing the vat plus sodium hydrosulphite plus sodium hydroxide exhaustion of the dye on to the fabric. The dyed material is removed, squeezed and exposed to air when the leuco vat dye is converted to insoluble dye form. So, this is what the entire procedure is, we have understood that this is definitely very different from the normal basic dyeing that we covered in the in the lecture, that we covered for basic dyeing material, we also took a look at the typical dyeing material process for cotton and silk.

But this particular process is quite different, and this kind of, you know treatment of the dye powdered is necessary for the solubilization of the vat dyes. Sometimes other oxidizing agents like, sodium borate, hydrogen peroxide or potassium dichromate may be used to esten the oxidation. So, as I told you, if the air is not sufficient; if the oxygen in the air is not sufficient. Then other oxidizing agents like, potassium dichromate or hydrogen peroxide or sodium borate which are all sources of oxidant.

Can act as a oxidative material for enhancing the oxidation process of the leuco vat dye to the vat dye. Now, let me mention here. The potassium dichromate is not acting like mordent in this case, but it is rather acting like an oxidizing agent only.

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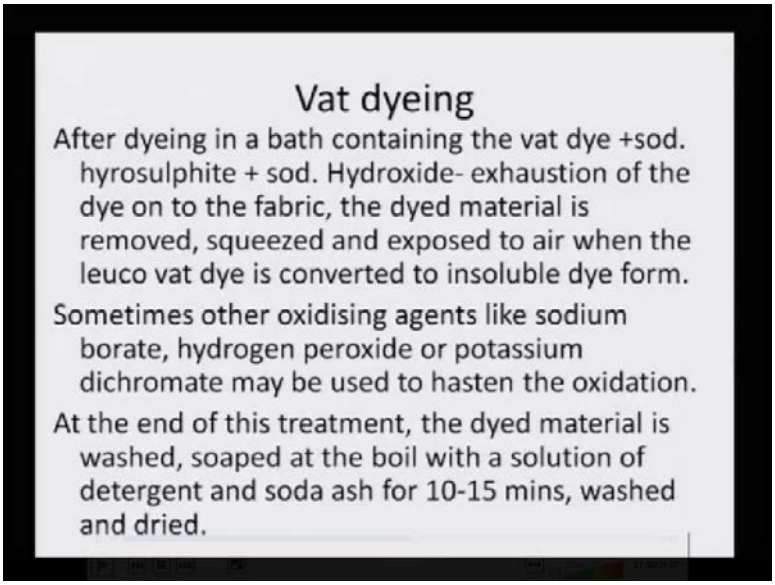

At the end of this treatment, the dyed material is washed soaped to the boil with the solution of detergent, and soda ash for 10 to 15 minutes, again washed and dried. So, that is all the dyeing process is all about when we do vat dyeing. But one has to remember,

that at what time the leuco must be exposed to the air is a crucial decision; whether, the dye extortion is complete or not, but there is a flexibility to actually do re dyeing several times, before the final treatment.

That is the treatment with washing of detergent, and soda ash, and so on and so forth. Till then, we can do several dipping, and if we keep the weak solution of the vat dye that is the leuco form, it is possible to gradually do the the extraction or exhaustion of the dye on to the fabric. And that will be acting in a more facile and more advantageous way, then just by dipping once. So, it is a common sense that every sof surface has a capacity to absorb at a particular time after which it forms an equilibrium.

Now, if the equilibrium is reached, then it will go backward, forward; that means, the dye up take will not be further facilitated. But if this process, every time there is some equilibrium moving towards the dye uptake, if this is facilitated for 2 to 3 to 4 times that more and more and more dye will be impregnated on the fabric. So, instead of making just one dip in a strong solution of the vat dye; the other alternative is to make several dips 2 to 3 to 4 dips in a slightly vicar solution. So that more and more and more dye can be taken up.

You can understand in one, simple way that suppose if from a weak solution. Every time 10 grams of the dye are taken up by the fabric, and we make 5 such dips. So, every time 10 grams will be taken up, because of the weak solution, it cannot take up more. So, it will in one goal, a it will take only 10 grams and thus 10 into 5 is 50 grams will be finally, taken up by the fabric. Because it gets time two, you know equilibriate, and then come back to its normal position where it is ready to take, more and more every subsequent time. We service if we take an example, where we take a stronger solution and make only one single dip. What will happen? It will take up once only 30 grams.

So, eventually that one dip has got 30 grams of vat dye on the fabric; whereas, the 5 time dip fabric will have 50 grams of dye; obviously, the color will be brighten, in the later case, and that is the kind of example that I am trying to explain to you. Dipping once is not an advantageous situation, dipping several times is possible, but this should be done before the final treatment or the final wash, soda wash and detergent washes carried out. All the re dyeing can be dump several times as perception the dyers choice of the color,

but once it is exposed, it needs to be or once it is washed and finally, settled it cannot be re dyed.

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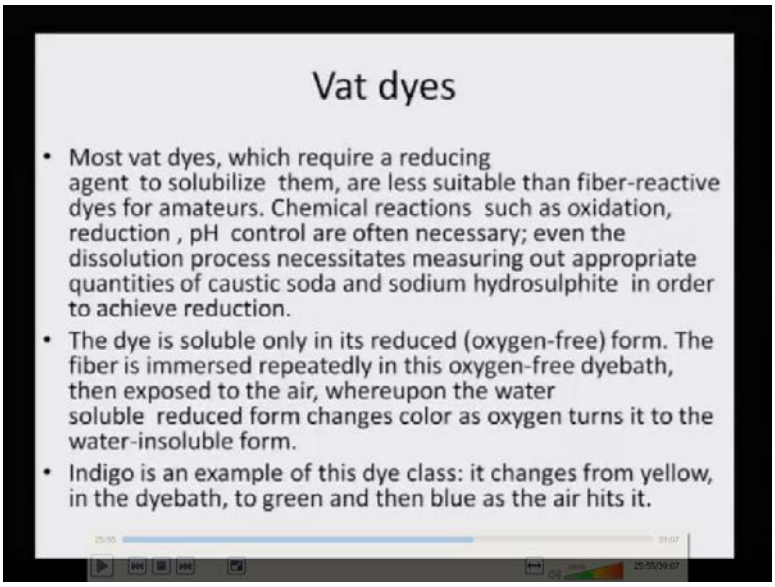

Vat dyes: most vat dyes which require a reducing agent to solubilize them are less suitable, then fibre reactive dyes for amateurs. Chemical reactions such as oxidation, reduction, pH control are often necessary. Even the dissolution process necessitates measuring out appropriate quantities of caustic soda and sodium hydrogen sulphite, in order to achieve reduction. So, all this is a very tricky process; its not so simple. That you can solubilize the vat dye into the leuco dye, just by adding this and this, and that is it. All the measurements have to be done in stoicometric ratio, only then all the vat dye will be in the leuco form, because it is equimolar quantities of the sodium hydroxide, and sodium bisulphite should be added.

The dye is soluble, only in its reduced that is the oxygen free form. The fiber is immersed repeatedly in the oxygen free dye bath, then exposed to the air, whereupon the water soluble reduced form changes color as oxygen turns it to the water insoluble form. So, we saw that how from the sodium salt of the sulphuric acid ester of the gluco dye, it got converted into the dye carbonyl molecule and that was the insoluble form. Indigo is an example of this dye; it changes from yellow in the dye bath to green, and then blue as the air hits it. So, as I told you, that when it is in the leuco form it has a very undefined kind of a greenish yellow color.

But once it comes on to the fabric after the exposure to the air, it takes up the bright blue color of the indigo. So, indigo example, I am taking again a again and again, because it is an representative of the vat dye. And since, you all have seen indigo; it is easy to understand and to correlate what is the dye we are talking about.

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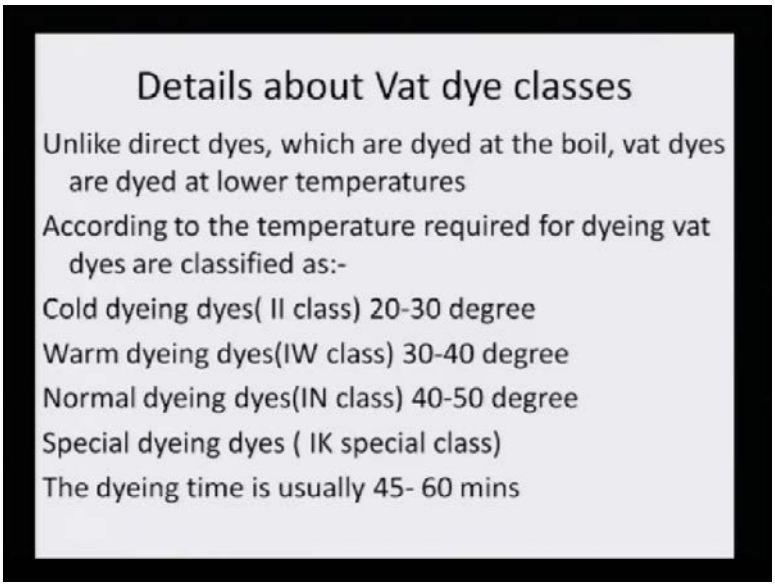

Details about vat dye classes. Unlike direct dyes which are dye dyed at the boil, vat dyes are dyed at lower temperature. So, the you must know that we do not need heating up to 80 degrees, we had discussed the boiling point a of water, as a temperature, a slightly below the boiling point that most of the dyes be its synthetic or natural dye or actually dyed. But here, we work only at very ambient temperature or luec warm temperature and lower temperatures. According to temperature required for dyeing vat dyes; they are classified as cold dyeing dyes which is class two, and for class two we just required 20 to 30 degrees are room temperature.

Warm dyeing dyes which is IW class of vat dyes requires 30 to 40 degrees only of temperature. Normal dyeing dyes that is IN class of vat dyes requires 40 to 50 degrees, and special dyeing dyes that is IK special class requires the temperature to be something according to what is prescribed on the packet. The dyeing time is usually 45 minutes to 60 minutes. So that means, within an hour the vat dye is already taken up by the fabric. That is why its compatibility, its suitability for cotton dyeing is very very advantageous for the dyers.

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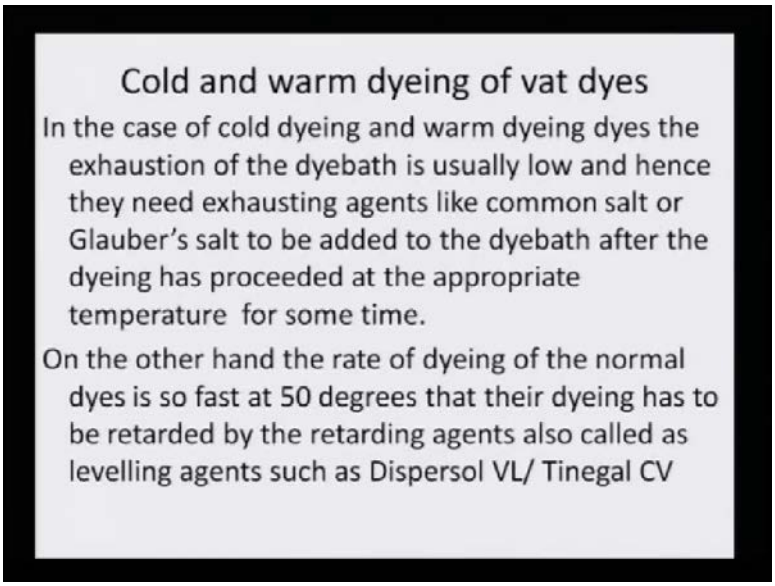

Cold and warm dyeing of the vat dyes. In the case of cold dyeing and warm dyeing dyes, the extortion of the dye bath is usually low; and hence, they need exhausting agents like common salt and glauber's salt to be added to the dye bath; after the dyeing has proceeded at the appropriate temperature for some time. So, these kind of modifiers, these kind of dye enhancers are to be added, because there is no other agency that can you know speeden up the, and they also act like a leveling agent or a balancing agent and cause evenness in the dye up take.

Otherwise what will happen, because these are basically electro lights. Sodium chlorite common salt is NACL NA plus CL minus, glauber salt is sodium sulphate which is NA 2 plus SO 4 minus minus. So, these are nothing but electro lights. And the presence of electro light actually creates a kind of a, you know situation where the equilibrium is achieved in a more facile manner. On the other hand, the rate of dyeing of the normal dyes is so fast at 50 degrees, that their dyeing has to be retarded by the retarding agents also called as leveling agents. So, sometimes this dye up take is very very fast.

Even that is not very good, because it will cause un evenness, because the motion of the fabric may not match with the speed of the uptake. So, in some places the dye uptake will be more, and in the other places the dye uptake will be poor. So, even that situation is not a good situation or a happy situation. So, there in order to slow down the process of the dye uptake, some leveling agents like dispersal VL tini gal VL CV are added. So,

that the up take is slow, and it matches with the motion of the dyeing. Because if this is not compatible, if they are not of the same order there will be patchiness, that will occur on the dyed fabric.

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Some trade names of the dyed fabric are, these are all commercial synthetic vat dyes. We already know indigo, asethin and cum, such dyes are from the natural class of dyes, but amarnthrene, benzanthrene, calconoid, carbenthrene, indanthrene, navidon, navinon, solanthrene, supranthrene these are different types of vat dyes which are synthetically produced and they have been in use in the in the dyeing industry for a very very long time.

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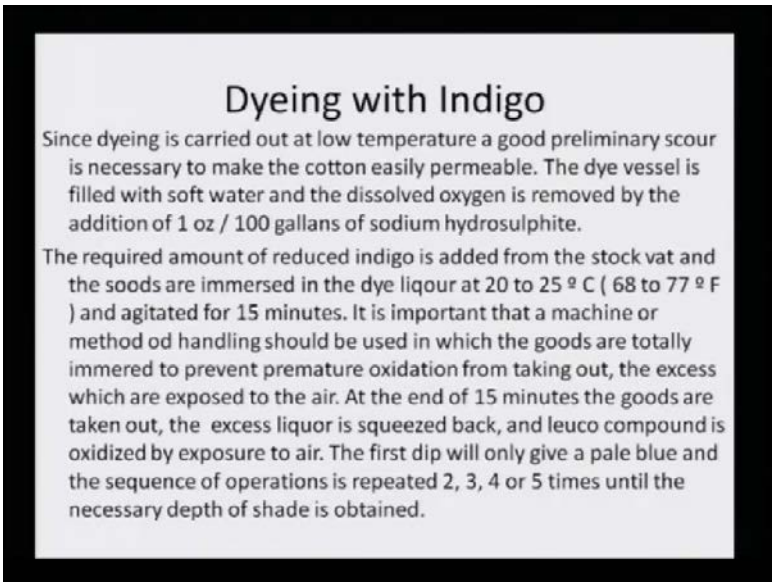

Dyeing with indigo – since, dyeing is carried out at low temperature, a good preliminary scouring is necessary to make the cotton easily permeable; the dye vessel is filled with soft water and dissolved oxygen is removed by the addition of one arms or 100 gallons of sodium hydrosulphite. So, in order to keep the situation as a redacting atmosphere, sodium hydrogen sulphite must be added first. The required amount of the reduced indigo is added from the stock vat, and the soods are immersed in the dye liquor at 20 to 25 degrees, an agitated for 15 minutes; it is important that a machine or a method of handling should be used in which the goods are totally immersed to prevent, premature, oxidation from taking out.

The excess which are exposed to the air; at the end of 15 minutes the goods are taken out, the excess liquor is squeezed back, and the leuco compound are oxidized by exposure to air. The first dip will only give a pale blue, and the sequence of operation is repeated 2, 3, 4 times until necessary depth of the shade is obtained. So, we just took the example in much detail to make you understand, that this is the entire process of dyeing with indigo. That be it natural indigo, be its synthetic indigo, structurally more or less they are the same, we have looked into that and indigo at class of dyes we have studied in details.

And in this case, first the water that is to be prepared for dissolving this vat dye, indigo dye must have sodium hydrogen sulphites. So that it is under the reduction or reduced

state or as a source of hydrogen. And to that when the vat dye is added, if its converted into the leuco dye, and then the fabric is slowly immersed into it after 15, 20 minutes, it is spell that the dye up take must have taken place; one thing that has to be kept in mind that all along the fabric should be within the surface of the dye solution or below the surface. If it rises above the surface which is a normal tendency, because fabrics are lighter in density, then the solution what will happen the portion which is come up will get exposed to the air, and will get into blue form. And this will cause patchiness.

So, in order to avoid patchiness, all along when the fabric is in the solution, it must be completely immersed in the solution, and must be rotated all the way. And when it is taken out all the excess dye solution should be squeezed out and that should not remain and then the finally, it is kind of check whether it is the desired color or not otherwise 2, 3, 4, 5 dips can be carried out before the final treatment on washing of the detergent and soda wash treatment is done.

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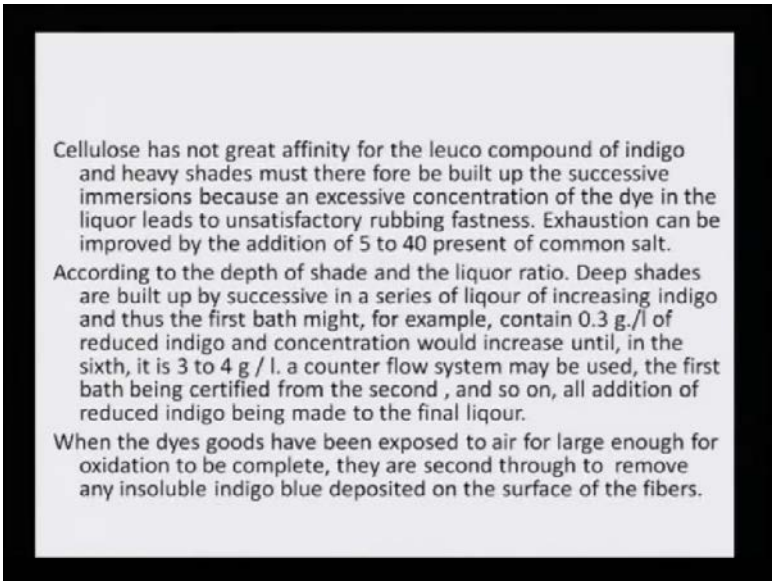

Cellulose has not great affinity for leuco compounds of indigo and heavy shades must therefore be built up by successive immersion, because an excessive concentration of the dye in the liquor leads to unsatisfactory rubbing fastness. We just took a that into consideration; exhaustion can improve by the addition of 5 to 40 percent of common salt that is with when an electro light is added as a leveling agent. According to the depth of the shade, and the liquor ratio deep shades are built up by successive in a series of liquor

of increasing indigo, and thus the first bath might for example, have 0.3 gram perception liter of reduced indigo, and concentration increase until in the sixth it is 3 to 4 gram.

So, initially weaker solutions have used, and then finally, the concentration of the indigo solution in the second, and the third, and the subsequent or enhanced. A counter flow system may be used; the first bath being certified from the second and the so on, and every addition of the reduced indigo can be increased subsequently. When the dye goods have been exposed to air for large enough for oxidation to be complete, they are second through the to remove the insoluble indigo blue deposited on the surface of the fibers. So, then finally, it is exposed to the, you know oxidation part, and then it is actually conformed that the fabric is dyed.