Natural Dyes

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Lecture No. # 31

Having learnt so much about natural dyes, it is time to take a look at some of the synthetic dyes their structure, their history, and their compatibility with different synthetic fibers and natural fibers. So, I thought of dedicating one full lecture on the reactive dyes, we have just spoken about the wool dyeing and how the wool can be dyed with the reactive dyes. So, what is the basic chemistry of reactive dyes? Why the name reactive, and all these details, let us try to take an overview about the dyeing application with reactive dyes.

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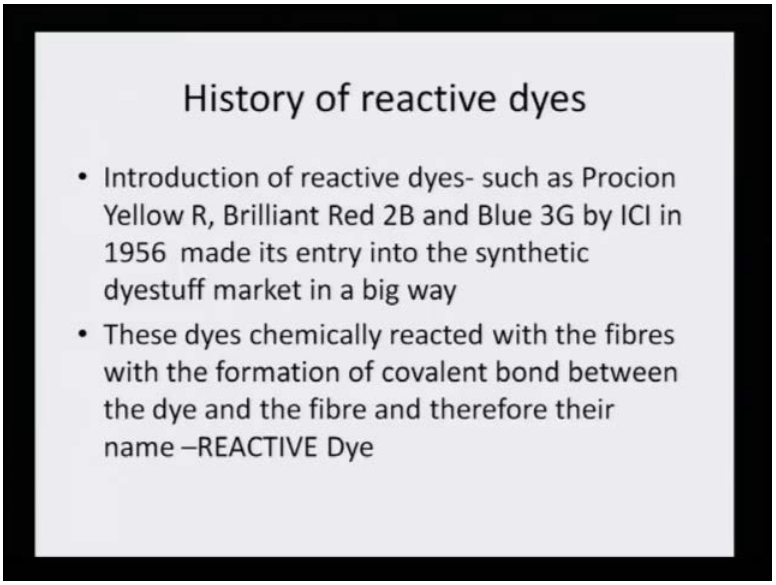

Looking at the history of the reactive dyes; introduction of reactive dyes such as procion yellow R, brilliant red 2B, and blue 3G by ICI in 1956 made its entry into the synthetic dyestuff market in a big way. These dyes chemically reacted with the fibers, with the formation of covalent bond between the dye and the fiber and therefore, their name reactive dye. You have seen in many cases, we saw that how, when we were learning about the dyeing or of the fiber, it was only the electro static attraction; the Vander wall

forces the hydrogen bonding. Whereas, in the case of reactive gas, reactive dyes they form distinct covalent bond with the fiber

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So, that is why they are called reactive. Reactive dyes must have the following qualities, if they have to be used. Should be in powder or liquid forms, should have excellent stability, should have good solubility, low to medium substantivity, good compatibility good diffusion, and leveling properties, rapid fixation, high degree of fixation, and excellent washing fastness. We have talked about fastness time and again. No dye will be considered as a good dye, whether it is synthetic dye or whether it is natural dye unless and until, the dye fixes when and the fabric has good fastness property.

All other above properties may or may not be present. To be able to be certified as a good category dye; fastness and fixation are the two things which are of prime importance. So, but in the case of reactive dyes, it is important that they should be in powder or liquid form should be stable at temperatures up to 100 degree Celsius, should have good solubility, because all this is done in aqueous medium. And they should have low to medium substantivity; that means, they should not you know, remain they should get transferred, get exhausted and should have good compatibility with the fabric. Again the word compatibility means, because everything is related to the chemistry- the chemistry of the fiber and the chemistry of the reactive dyes. If they are matching only then, the reactive dyes can used with the fabric.

So, it is immaterial whether we use reactive dyes with natural fiber or synthetic fibers, but the compatibility factor is very good is very important. Secondly, good diffusion and leveling properties should be present in reactive dyes, because unless the dye diffuses into the interior of the fiber, there would not be leveling, there would not be evenness, and there will be patches of dyes here, and there and that will not be considered has a good dyeing material.

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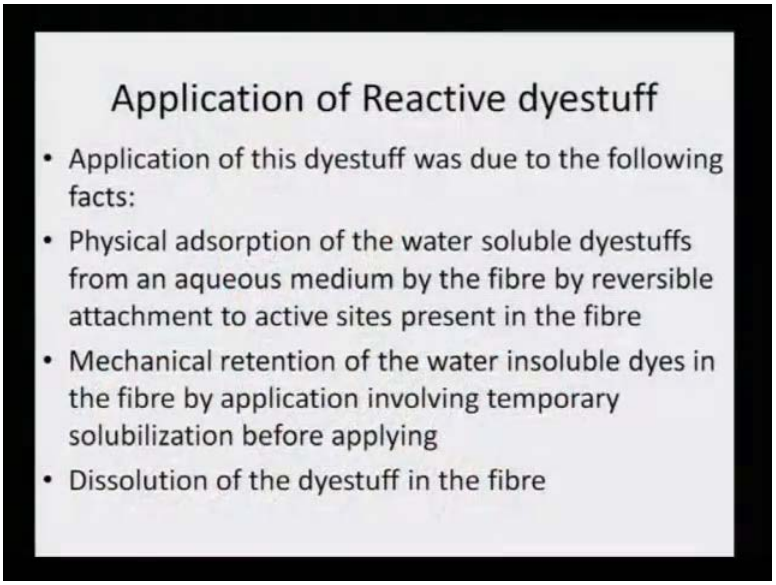

Application of reactive dye stuff: application of dye stuff was due to the following facts. Physical adsorption of water soluble dyestuffs from an aqueous medium by the fiber by reversible attachment to active sites, present in the fiber; mechanical retention of the water, insoluble dyes in the fiber by application involving temporary solubilization before applying; dissolution of the dyestuff in the fiber.

So, when the dye is used; if it is water soluble form, it is a physical, simple physical adsorption. And the dye is simply coming, and adsorbing on to the fiber. And slowly then impregnates, but if the dye is not water soluble or insoluble then, there is only a mechanical retention. It is just sitting on that. And therefore, slowly it is you know some kind of temporary solubalization has to be applied, because the dye must dissolve, in order to get into the core of the fiber.

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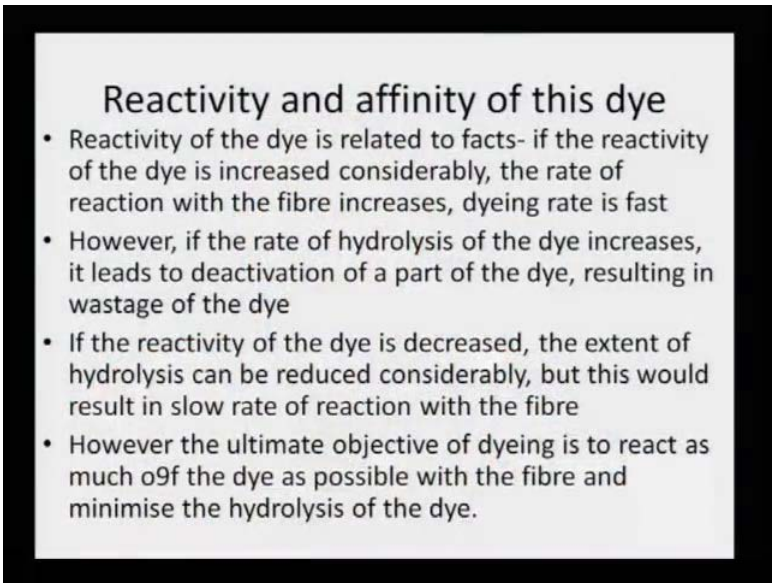

Reactivity and affinity of this reactive dye, because you see it is important that the as the name suggest, it is the reactive dye; it should have affinity, liking for the fiber. Otherwise it will not impregnate, it will not pierce, it will not penetrate into the fiber. So, this factor is so important, that when we choose a reactive dye, for any kind of fiber it is to be kept in mind that the reactive dye, and its affinity for that particular fiber must be very high.

Reactivity of the dye is related to facts, that if the reactivity of the dye is increased considerably. The rate of reaction with the fiber increases, and the dyeing rate is fast, Which is understandable. However, if the rate of hydrolysis of the dye increases, it leads to deactivation of a part of dye, resulting in wastage of dye; if the reactivity of the dye is decreased, the extent of hydrolysis can be reduced considerably, but this would result in slow rate of reaction with the fiber. So, you know, there are three situations. There is you know, if the reactivity is good, it will go into the dye, into the fiber and the rate dyeing will be very fast, but at the same time the rate of hydrolysis will also increase.

So, a part of the dye will get deactivated, but if the rate is slow of you know dyeing, then the rate of hydrolysis is also considerably slowed down, but this would mean that you know not much dye has actually penetrated into the fiber. So, therefore, you know one has to strike a balance. However, the ultimate objective of dyeing is to react as much of the dye as possible with the fiber, and minimize the hydrolysis. Because if hydrolysis out ways, then the dye is wasted. So, we have to take in mind or keep in mind that most of it

must be used for dyeing, rather than the dye getting hydrolyzed in the dye bath; so, how to optimize that the rate of the dying should be much higher as compared to the rate of the hydrolysis.

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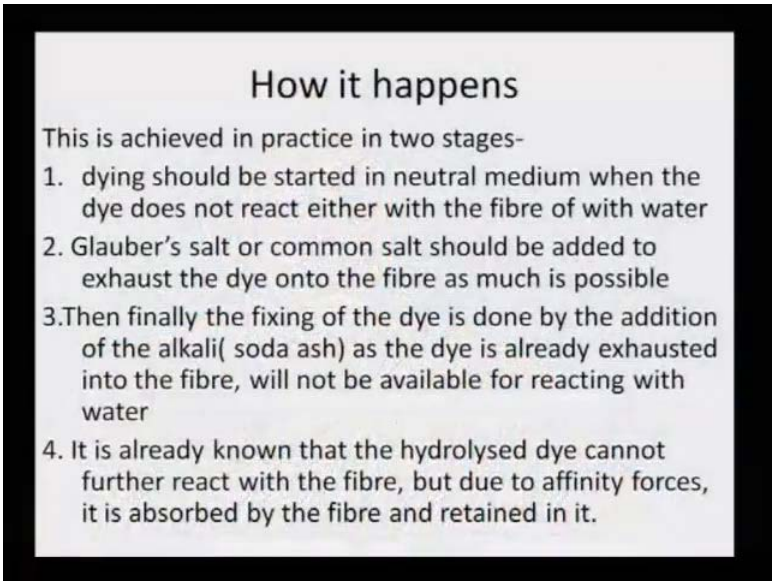

How it happens. This is achieved in practice in two stages; dyeing should be started in neutral medium when the dye does not react either with the fiber or with the water. Glauber's salt or common salt should be added to exhaust the dye onto the fiber as much as possible. Then finally, the fixing of the dye is done by the addition of the alkali that is soda ash, as the dye is already exhausted into the fiber and will not be available for reacting with water.

It is already known, that the hydrolyzed dye cannot further react with the fiber, but due to affinity forces, it is absorbed by the fiber and retained in it. So, what happens is that, you know this dyeing procedure is very very different; from the dyeing procedures you have learnt so far. One has to see that there are two competitive reactions occurring. One is the dyeing of the fabric by forming covalent bonds, and the other one is the hydrolysis of the dye per se in the dye bath, but the hydrolyzed dye has no color contribution to be made

Therefore, glauber's salt or common salt. Glauber's salt is sodium sulphate or sodium chloride should be added so, that the dye completely exhausts on to the fiber as much as possible. And then finally, this dye must be fixed with the help of an alkali, and

preferably, it is soda ash. That dye is already exhausted on to the fiber and will not be available for reacting with water. So, hydrolysis will be kind of controlled.

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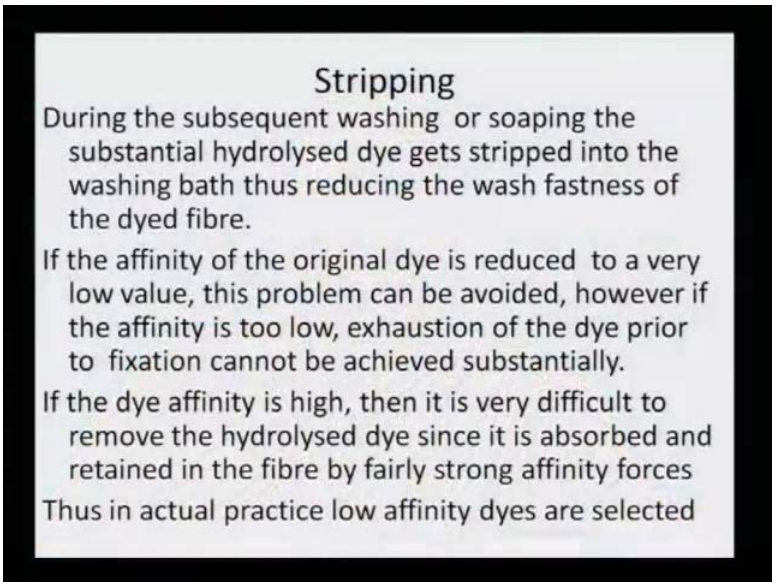

Stripping, during the subsequent washing or soaping; the substantial hydrolyzed dye gets stripped into to the washing bath, thus reducing the washed fastness of the dyed fiber. So, what happens? Actually this hydrolyzed dye is also going and sitting in on the fiber. So, when it is washed all this extra hydrolyzed dye is striped off or washed off, and it causes poor washing fastness. So, therefore, if the affinity of the original dye is reduced very low value, this problem can be avoided. However, if the affinity is too low, exhaustion of the dye prior to fixation cannot be achieved substantially. So, you see there are two things happening at the same time; if we try to stop the hydrolyses of the dye, then the rate of the dyeing decreases and vice versa.

So, how to optimize that dyeing should be good, hydrolysis should be less, and the stripping should be even minimal. If the dye affinity is high, then it is very difficult to remove the hydrolyzed dye; since, it is observed and retained in the fiber by fairly strong affinity forces. Thus in actual practice, low affinity dyes are selected; so, the ideal situation is that, low affinity dyes should be selected, in order to avoid this hydrolysis, and rate of dyeing; you know confusion, because hydrolysis has to be minimized. So, that more and more dye is available for penetration into the fiber.

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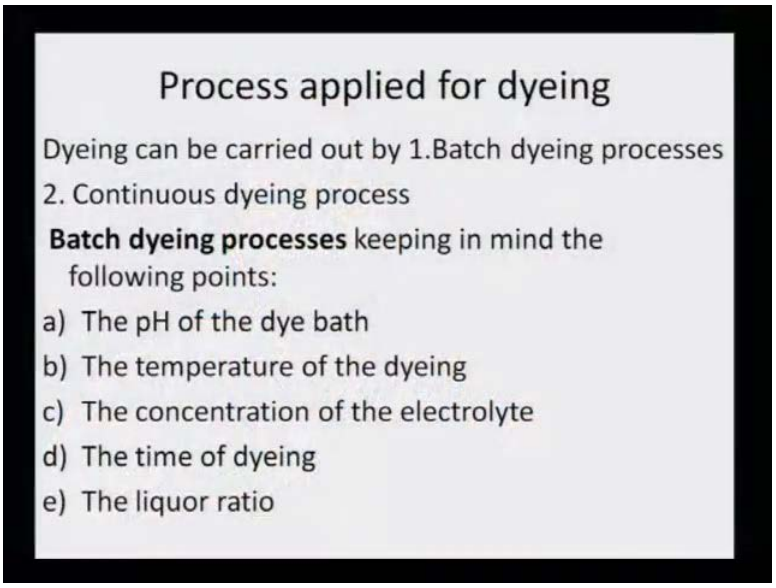

Processes applied for dyeing. When we are using reactive dyes - what are the possible processes that are used in commercial scale. Dyeing can be carried out by batch dyeing process or by continuous dyeing process as the name suggests. That means, there is one batch, second batch, third batch that kind of dyeing. And other one is a continuous process; that means, one after the other, the fabric is stitched and it is dyed one after the other. Batch dyeing processes keeping in mind the following points, because when we are trying to use reactive dyes in batch dyeing processes; what are the points that need to be kept in mind.

The pH of the dye bath, the temperature of dyeing, the concentration of the electrolyte that is the glauber's salt and common salt whichever we are using sodium sulphate or sodium chloride; the time of dyeing and the liquor ratio, because, it is very important as you saw that reactive dyes are again very pH sensitive. So, the pH of the dye bath will decide, whether it is going to hydrolysis or or whether it is going for dyeing. The temperature also, because some of these reactive dyes are cannot with stand very high temperature. So, the temperature of the dyeing also has to be maintained.

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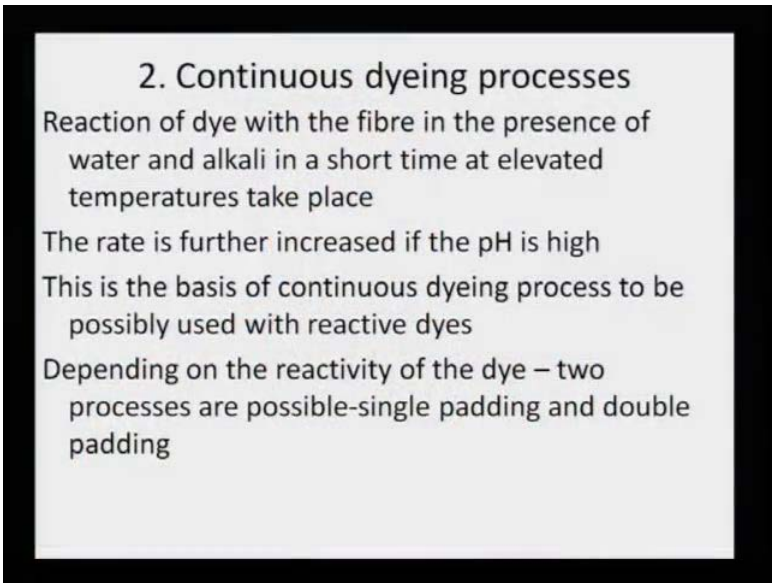

Then how much of the glauber salt is to be added or common salt has to be added, because that will control the rate of hydrolysis of the dye. In the continuous processes, reaction of the dye with the fiber, in the presence of water alkali in a short time at a elevated temperature takes place. So, in the continuous process, there is this water, alkali everything and the temperature is high; the rate is further increase if the pH is high. This is the basis of continuous dyeing process to be possibly used with reactive dyes. And so, it is more popular to use continuous dyeing process for reactive dyes rather than batch.

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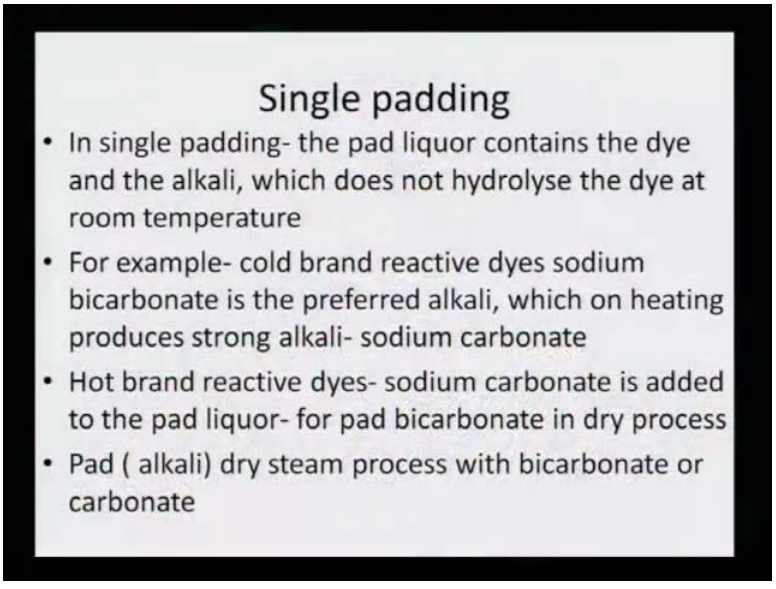

But batch can also can be used for smaller volumes of fabric. Depending on the reactivity of the dye, two processes are possible. One is single padding, and the other is double padding. In the continuous dyeing processes also there could be just one single padding; that means, one time it is taken or there could be double padding process. Let us try to understand what does the word single padding continuous process mean. In single padding the pad liquor contains the dye, and the alkali which does not hydrolyze the dye at room temperature.

So, first it is kept at room temperature and at that temperature that alkali does not hydrolyze the dye. For example, cold brand reactive dyes, sodium bicarbonate is the preferred alkali, which on heating produces strong alkali that is sodium carbonate. So, slowly when the temperature is raised, the alkali becomes from sodium bicarbonate to sodium carbonate, and its strength also becomes very high.

Hot brand reactive dyes would requires sodium carbonate is added to the pad liquor; for pad bicarbonate in dry process then pad alkali for dry steam process with bicarbonate or carbonate.

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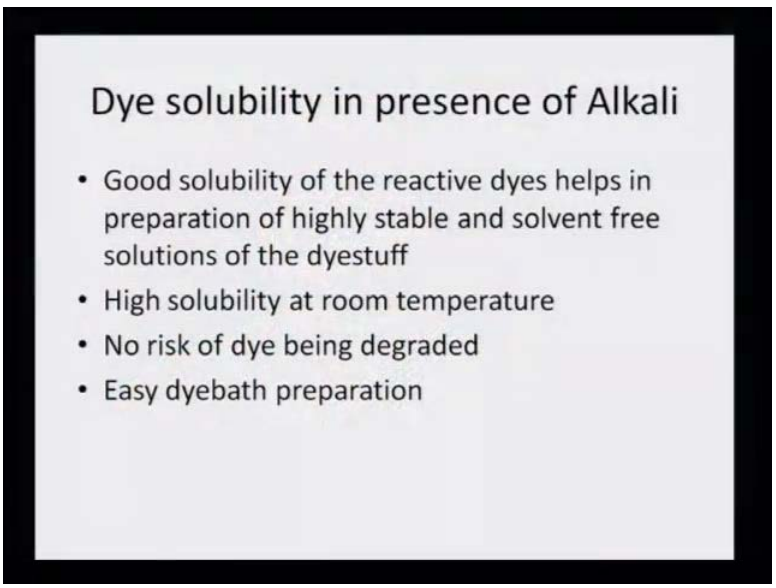

So, there are various options which can be followed for single padding. Dye solubility in presence of alkali. Good solubility of the reactive dye helps in the preparation of highly stable and solvent free solutions of the dyestuff. Because as one of the main points we had seen, that solubility of the dye is very important. And unless and until the dye is soluble in aqueous medium, it will not penetrate into any kind of fiber; high solubility at room temperature, no risk of dye being degraded and easy dye bath preparation, these are some of the things that must be kept in mind.

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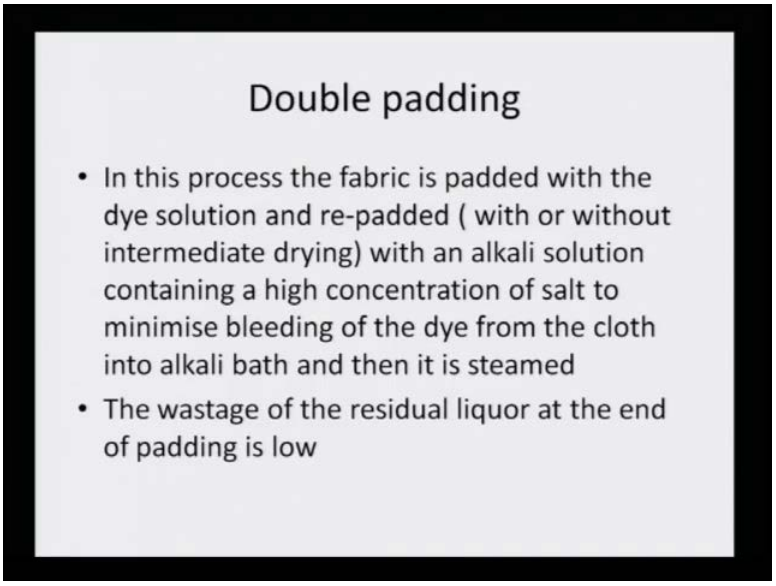

In the double padding process, in this process the fabric is padded with dye solution and re-padded with or without intermediate dying. So, twice it is done. So, double padding has the name suggest.

It may be necessary to dry in between or it without even drying in in the intermediate step it can be re-dyed or re-padded; with an alkali solution containing a high concentration of salt, to minimize bleeding of the dye from the cloth into alkali bath. And then it is steamed. So, finally, if the dye is fixed with the help of steaming process that is the treatment with steam. The wastage of the residual liquor at the end of padding is low; in this case, because you know it has been reused pursing and the alkali was added at the second stage, not in the beginning.

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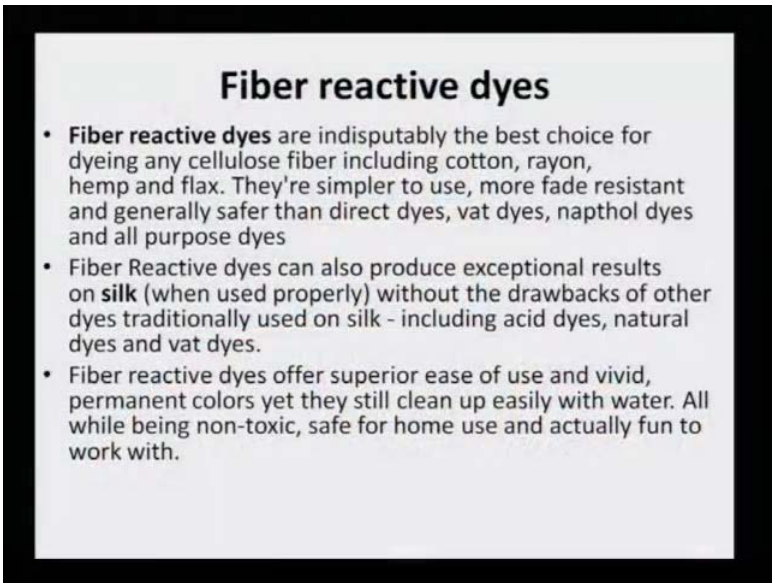

So, hydrolysis also minimized. Some fiber reactive dyes are also available. Now, as the name suggests; they are indisputably the best choice for dyeing any cellulosic fiber, including cotton, rayon, hemp, and flex. They are simpler to use more fade resistant, and generally say for than direct dyes, vat dyes, naphtha dyes and all purpose dyes. So, you see that, fiber reactive dyes are very good for cellulosic fiber and not only cotton, it is rayon hemp and flux which have components of cotton, they are suited for that those kind of fibers as well.

Fiber reactive dyes can also produce exceptional results on silks, when used properly without the draw backs of other dyes traditionally used on silk; including acid dyes, natural dyes and vat dyes. Fiber reactive dyes offer superior ease of use, and vivid permanent colors, yet they still clean up easily with water; all while being non toxic safe for home use and actually fun to work with. So, you see that, this kind of fiber reactive dyes are good for cotton, and all kind of other cellulosic fibers and as well as for silk.

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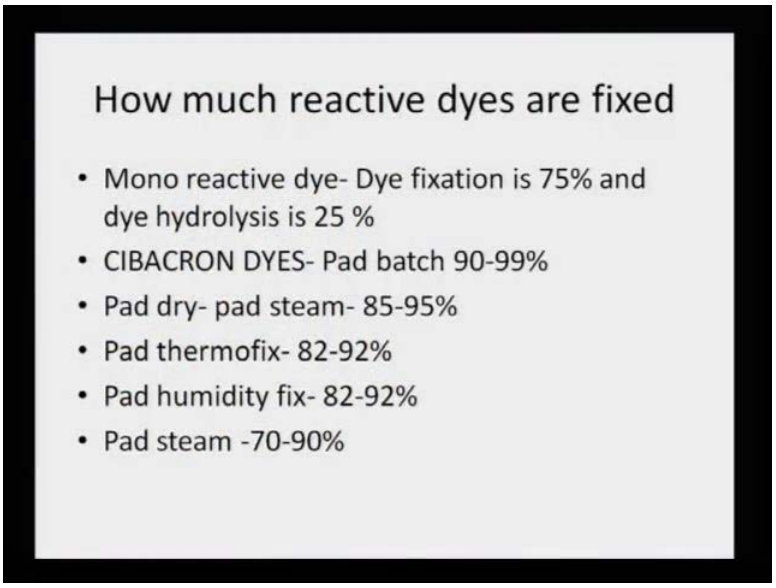

How much reactive dyes are fixed. We have to take a look, because we know there is a parallel hydrolysis process, we have been talking about it. So, if we try to look at some of the statistics; we can find out that mono you know, mono reactive dyes.The dye fixation is only 75 percent; even though the dye taken is 100 percent and the dye hydrolysis is 25 percent. Similarly, for cabochon dyes which are dyed by pad process one finds that 90 to 95 percent can be actually fixed. So, the wastage is only 10 to 9 to 10 percent or pad dry 1 to 10 percent.

Pad dry, pad steam process; that means, once it is dried and it is put into that, then second time it is steamed, these are all double padding process. There the dye fix was found to be 85 to 95 percent, and the hydrolysis was the rest. Similarly, there is another process called pad thermo fix will be learn about it has we go along, that was able to fix that dye almost to 82 to 92 percent, and pad humidity fix, also another process of padding could fix dye between 82 to 92 percent similar as pad thermo fix. And pad steam could fix dye from 70 to 90 percent. So, you see that this is the kind of wastage that one can expect, because of the hydrolysis factor.

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How important is the affinity factor. Therefore, if the affinity forces are you know good strong, then the dye will adhere, and the rate of dyeing will be much faster and more and more dye will be taken up; if if the reactive dye chosen has low or medium affinity, it will show the following. Good penetration and leveling excellent wash off, and wet fastness properties, and low risk of tailing. So, you see these are some of the properties, because if the affinity has to be kept low, otherwise if too much as it goes their, then it sits and gets hydrolyzed. So, that is not good, because it is getting hydrolyzed inside and then finally, it will be stripped off.

So, what appears that the dye has gone very readily into the fiber actually gets hydrolyzed within the fiber. So, that should not happen. So, low affinity, but good affinity forces will create good penetration, and leveling that is even dyeing excellent washing, and wet fastness properties. And therefore, will be good a factor. And an important factor when we are considering dyeing with reactive dyes. Now, if we have to you know in general, compare the various processes their merits, and demerits.

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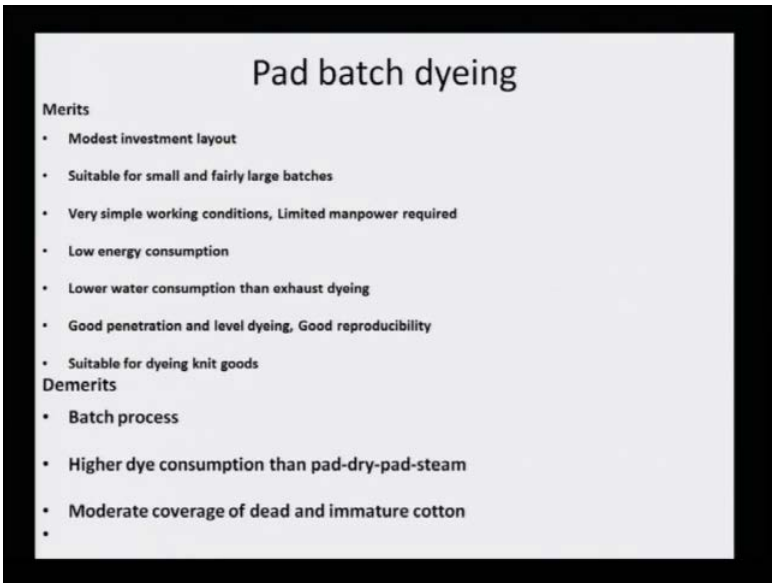

One can see that in pad batch dyeing which showed almost like dye up take off 70 to 90 percent; the merits are it is, it has a modest investment layout suitable for small and fairly large batches, very simple working conditions, limited manpower required, low energy consumption, low water consumption than exhaust dyeing. Good penetration and leveling dyeing, good reproducibility and suitable for dyeing knit goods. So, you see pad dyeing can be, when we are talking about reactive dyes.

These are the merits of the pad dyeing process, but the demerits are the batch process are you know very difficult, in the demerits the high dye consumption than pad dry, pad steam process, moderate coverage of the dead and immature, cotton. So, you see there are for every process, whichever dyeing process we take there will be merits and demerits.

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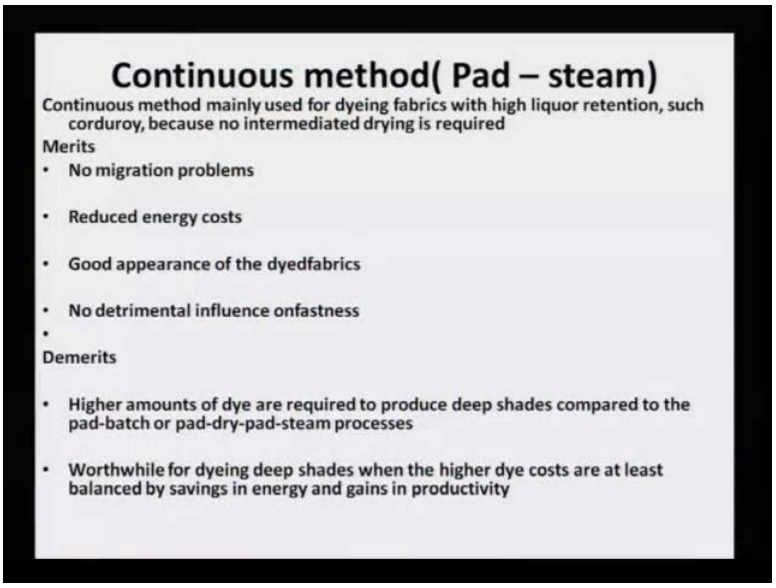

Now, if the merits out way the demerits, we did not worry; even in the continuous pad steam process, there are merits that no migration process problem takes place, reduced energy costs, good appearance of the dyed fabric, no detrimental influence on fastness; these are some of the you know merits of the continuous pad steam process, and it is very suitable for dyeing fabrics which require high liquor retentions such as, corduroy. Because no intermediated drying is required. So, it is possible to do pad steam, and there are you know this good number of merits.

Demerits are that higher amounts of dye are required to produce deep shades, compared to the pad batch or pad dry pad steam processes. So, among the various process, you know this process is more suited for thicker fabric like corduroy, and denims, and so on and so forth. Because more dye penetration is required. Worthwhile for dyeing deep shades when the higher dye costs are at least balanced by saving in energy, and gains in productivity. So, if we are trying to look at the industrial process, we have to keep in mind the cost affectivity also. And definitely pad steam process is very cost effective.

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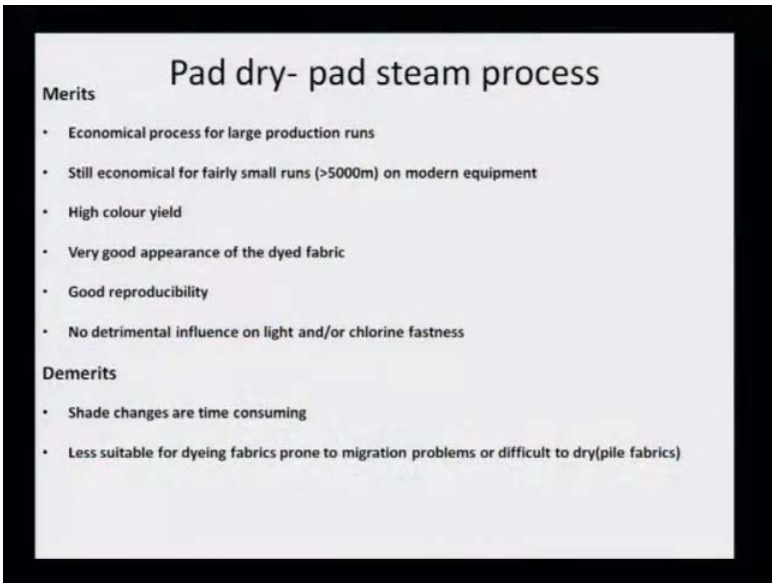

Again if we have to look at the merits of the pad dry and pad steam process, it is economical for large production, still economical for fairly small runs on moderate modern equipment, high color yield very good appearance of the dyed fabric, good reproducibility, no detrimental influence on light or chlorine fastness. You see that these points are so important, when one tries to look at the industrial dyeing process. So, if one has to use reactive dyes which continues process must be used, whether single padding, even among double padding what is the kind of pad dry pad steam or various other options, that we just spoke about which one is the best process for for a particular reactive dye needs to be asserted.

But as every process as as I said, have merits and demerits; we have to even look at the demerits. Shade changes are time changes or time consuming less suitable for dyeing fabrics, prone to migration problems, problems are difficult to dry in between. So, you see there are some times you know, if the shade matching has to be done; re-padding has to be done. Then there is a problem, because these pad dry, pad steam cannot be used.

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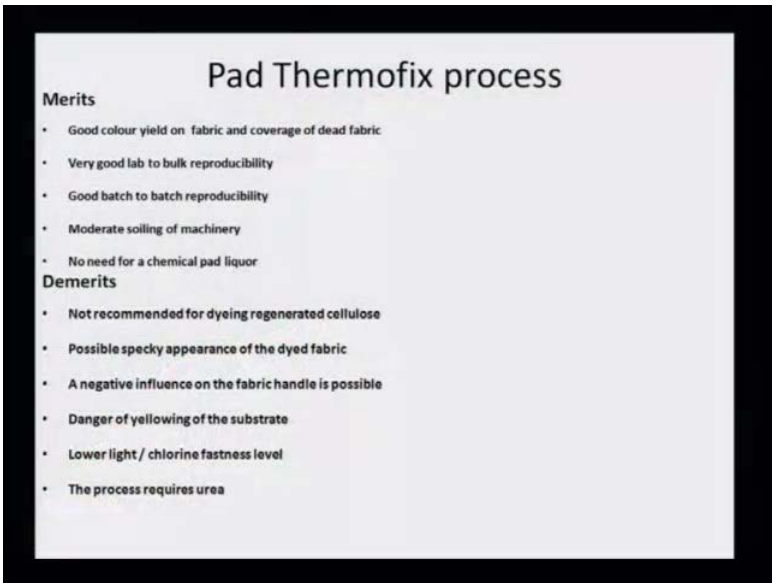

As what I was talking about that pad thermo fix process which gives almost like 82 to 92 percent of the dye fixation, and very only you know 8 to 18 percent hydrolyzed dye is wasted; the merits are good color yield on fabric and coverage of dead fabric, good very good lab to bulk reproducibility, good batch to batch reproducibility, moderate soiling of machinery, no need for chemical pad liquor. So, because the name as the name suggests it is a thermo fix, it is fixed at a higher temperature. So, therefore, the color yield of the fabric is very very good.

And it can be reproduced again and again for the same shape. That is what is an added advantage of this particular method. The demerits are not recommended for dyeing, regenerated cellulose possible specking appearance of the dyed fabric and negative influence on fabric handle is possible danger of yellowing the substrate, lower light and chlorine fastness level, the process requires urea. So, now, there are several draw backs in this process. So, one has to very very carefully see, whether it is really worth, because color good color reproducibility verses many other demerits. So, what is required by the industry needs to be readout, but the pad thermo fix process is also one of the padding methods, and therefore, I thought that I should discuss the merits and the demerits with you.

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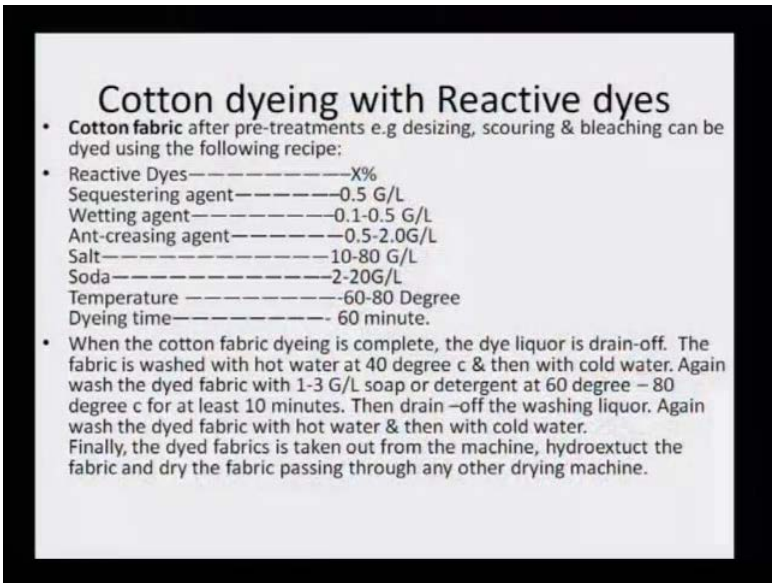

If we have to take a ideal cotton dyeing then with a reactive dyes; then the cotton fabrics after pre treatments that is desizing, scouring and bleaching; can be dyed by the following recipe. I am giving you an example, by showing you time and again that you see be its synthetic fabric or be it natural fabric; be it synthetic dye, be it natural dye. There is a recipe in every case. And what is an ideal recipe has been worked out mainly and primarily keeping in mind that the dye uptake should be maximum, dye should not be wasted, dye should not be hydrolyzed, instead dye should go into the fabric.

And good dye affinity of the fabric and the dye should be there, the compatibility will only prove that the washing fastness, the light fastness, the dye adherence and all that will be matching. So, let us try to take any x percentage of the reactive dye, sequestering agent is taken as 0.5, wetting agent has 0.1 to 0.5, anti creasing agent 0.5 to 2 gram per liter all are in gram per liter, salt is taken 10 to 80 gram per liter, soda ash is taken to 20 gram per liter, and the temperature that is maintained is 60 to 80 degrees and the dyeing time is just one hour that is 60 minutes.

When the cotton fabric dyeing is complete; the dye liquor is drain off. The fabric is washed with hot water at 40 degrees, and then with cold water. Again wash the dyed fabric with 1 to 3 gram per liter soap or detergent at 60 degrees to 80 degree for at least t 10 minutes. Then drain off the washing liquor, again wash the dyed fabric with hot water and then with cold water. Finally, the dyed fabrics is taken out from the machine

hydroextuct, the fabric and dry the fabric passing through any other drying machine. So, you see that dyeing procedure is very simple. It is not a very elaborate procedure, but one has to add all these agents that is (( )) to keep a balance, wetting agent to wet the fabric, and anti crease agent you know, because there is possibility of the fabric coming together. So, it should remain in the creaseless form.

Salt is added as a you know leveling agent, and soda is added as a retardant, because see otherwise more and more this has to be done under the alkaline condition, but the alkali should not be too strong. So, therefore, the alkali should either the sodium bicarbonate or carbonate which does not make the pH adversely high. And the temperature is kept at 60 to 80 degrees and the time taken is only 60 minutes or one hour. In this cotton fabric dyeing is done, and the liquor is drained off the fabric is washed with hot water, because washing is very important. All the hydrolyzed dye that is sitting within the fiber, must need to be washed off with the hot water, and then with cold water.

And then, the fabric should be you know, washed with a mild detergent again; first with plain water, then with mild water and that to at elevated temperature. So, both water washing and soap washing - mild soap washing must be done between 60 to 80 degrees for 10 to 15 minutes. In order to strip of the hydrolyze dye. So, that is a very important and a kind of a separate type of a step that is required when we are dyeing with reactive dyes; we did not face this kind of a situation when we were learning about natural dyes. There was no stripping or no hydrolyses or no such you know, affectivities that we have to take care of, but with these dyes although they have are very very substantive.

They are they have good exhaustion, but at the same time they have their own draw backs at there is a possibility, because of the structural details and the alkali being present there, that they get hydrolyzed. So, such precautionary measures have to be taken to avoid the hydrolysis of the dye. So, that the dye pursue can actually participate in the dying process, and form covalent bonds with the fiber, because otherwise the whole exercise will be very few type.

So, now you have seen that dyeing with the reactive dye is so very important, and so different from the earlier process that you have learn; that this thus sound that it is a very unique, and a different kind of process that happens, you learnt about new techniques of dyeing that is the single padding, and the double padding; and among the double padding

also the pad dry and the pad steam process, the pad thermo fix process, the there were so many other pad humidity process and so on and so forth, because these are various variation where somehow the hydrolyses of the dye, reactive dye is curved and more more dye is make to penetrate in to the fabric. So, the ultimate goal is to have a good dyeing process for using reactive dyes.