Natural Dyes

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Lecture No. # 21

So far we have been talking about dyeing and its procedure, the basics of dyeing, the typical natural dyeing recipes and so on and so forth. Today's lecture is dedicated to the preparation for dyeing, preparation of the cloth, how the cloth should be prepared before it is taken for dyeing. We know that there are the simplest way of preparing the cloth is to wash it, but there are certain very specific procedures that need to be followed when dyeing has to be done. Is it dyeing with synthetic dyes or be it dyeing with natural dyes, one needs to prepare the cloth very effectively for a better dye uptake.

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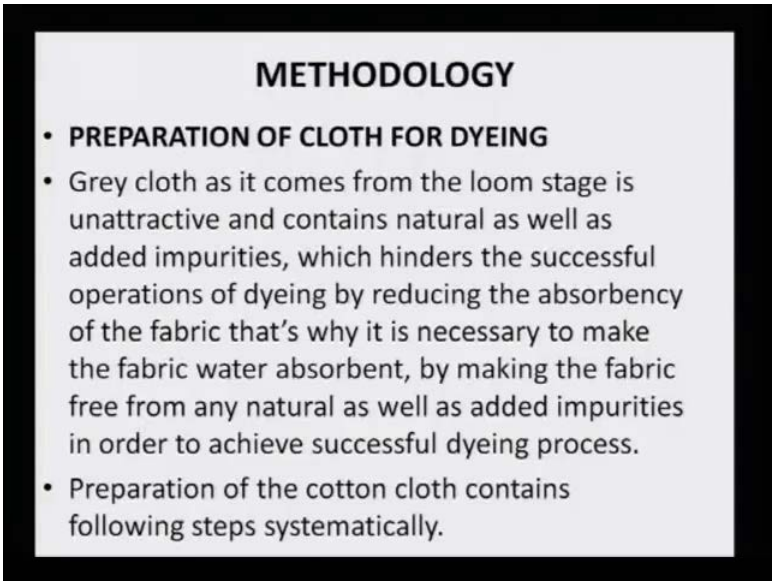

Now, the methodology of preparation of cloth is the following: Grey cloth as it comes from the loom stage is unattractive and contains natural as well as added impurities, which hinders the successful operations of dyeing by reducing the absorbency of the fabric that is why it is necessary to make the fabric water absorbent, by making the fabric free from any natural as well as added impurities in order to achieve successful dyeing process. So, one thing should be very, very clear that when the grey cloth is coming after

the viewing of the cloth, it is to be remembered that it needs to be purified. And this purification is in terms of its washing and because that will this washing of the waxes of the oils of the impurities will enhance the absorbency of the fabric.

We know that if the water absorbency enhances the dye uptake automatically enhances in the case of cellulosic fiber as well as in the case of proteinaceous fiber. So, whether it is cotton or whether it is wool or silk - the first thing that one needs to do with the grey cloth. Grey cloth is the raw and washed and bleached cloth is called grey cloth; it contains lot of natural impurities and some of them are even added impurities. So, this should be removed before it is prepared for dyeing.

Preparation of cotton cloth contains following steps systematically. In order to you know prepare cotton which is toughest to dye. We have to take lot of precautions, because unless and until the cotton is washed properly; it will not ah have good absorbency, and if it does not have good absorbency because of the waxes and the oils on the cotton surface it is going to be even tuff to dye it.

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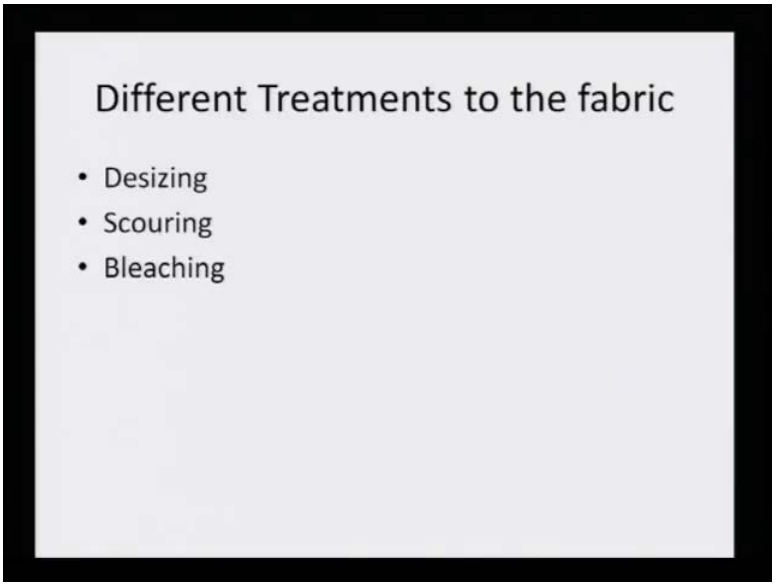

So, let us try to look at the procedure. Different treatments to the cotton fabric are it needs to be desized; it needs to be covered and it needs to be bleached finally. So, there are three main steps that cotton needs to undergo - one is desizing; the other one is scouring; and the third one is bleaching.

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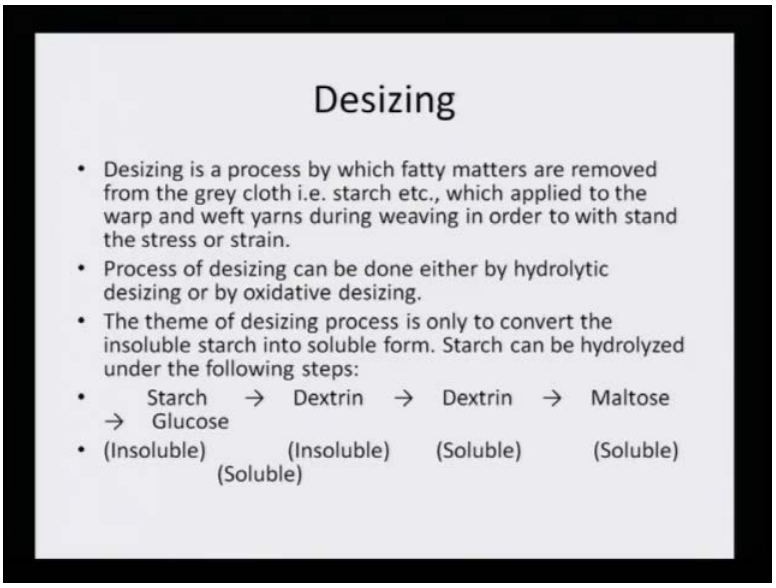

Desizing: Let us try to understand what exactly is meant by desizing. Desizing is a process by which fatty matters are removed from the grey cloth such as starch which applied to the warp and weft yarns during weaving in order to withstand the stress or strain. What happens? Cotton is very tender. So, in order to you know draw it in to yawns and then the yawns being you know oven in the warp and the wept, what happens is that this starch has to be added. If starch is not added, cotton is very soft and the yawn would break during the process of weaving. Now in order to facilitate weaving starch is particularly added to the yawn.

The process of desizing can be done either by hydrolytic desizing or by oxidative desizing. So, desizing or removal of such starchy impurities is done by two methods - one is the hydrolytic method and the other one is the oxidative method. Either of them are used, it is not that both the processes are used. The theme of desizing process is only to convert insoluble starch into soluble form. So, because this insolubility will further create a non absorbency of dye solution at the later stage of dyeing that is why it is important to remove starch. What if the starch is not removed? If starch is not removed from the fabric, it will only create more dye aggregates to settle in one place and it will affect the dye absorbency.

I told you if you recall that by capillary action between the mesh, there are pores you know when the warp and the wept these are two-dimensional threads that view the cloth

when they are oven; there are small pores now it is through this pores by the capillary action the dye enters the fabric and that is what we call dye uptake. Now dye uptake will be hindered if starch is present because starch is in the insoluble form. So, this insoluble starch needs to be converted in to the soluble form and that is the dextrin, and the dextrin is further converted in to maltose and maltose is converted in to glucose. So, from one form to the other the whole idea of this conversion from starch to glucose by the hydrolytic process or by the oxidative process is to convert insoluble to soluble form.

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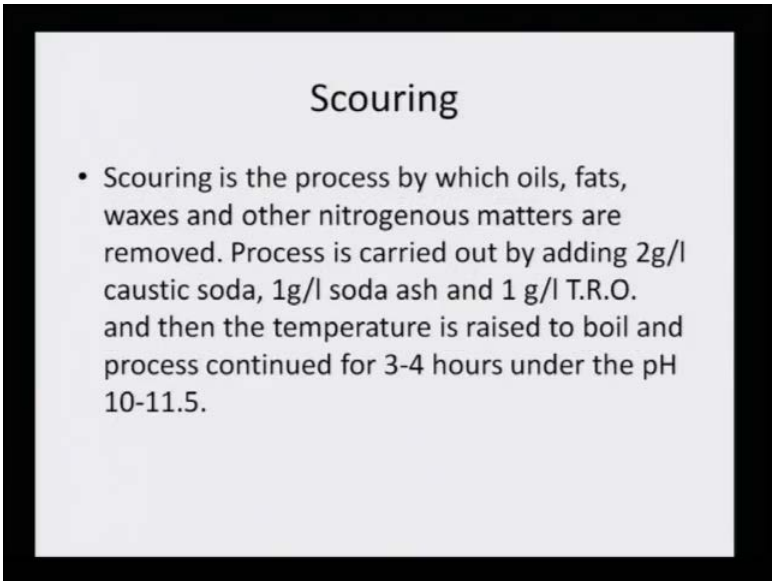

Now, similarly the next step that is done to the fabric cotton fabric particularly, but this is also true for silk and wool is the scouring step. So, only desizing is done in the case of cotton, but scouring is common to cotton and silk and wool all. Scouring is a process by which oils, fats, waxes and other nitrogenous matters are removed. The process is carried out by adding two grams per liter caustic soda or one gram per liter soda ash or one gram per liter T.R.O. That is the terpene oil and then the temperature is raised to boiling and the process continued for three to four hours under the pH of 10 to 11.5; that means, under alkaline condition the whole substance fabric be it cotton, be it silk, be it wool are washed in order to remove the oils and fats and waxes. Now T.R.O is a solvent and therefore, it is like petroleum oil, it is derived from petroleum ether, and so it solubilizes the oils and the fats and the waxes and thus it even washes away these and the caustic soda acts like a washing powder to remove these, but this is a very harsh scouring

method. There are milder scouring methods with milder soaps also possible particularly for silk and wool

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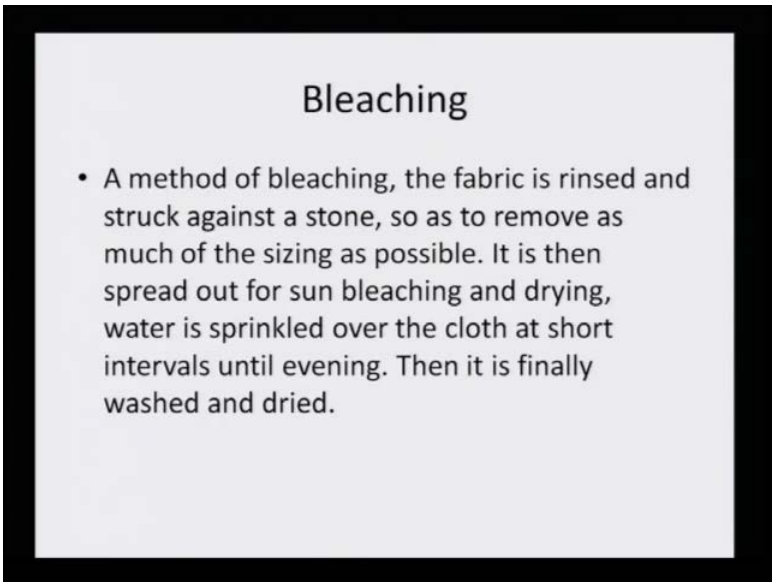

Now bleaching is very essential when we are dyeing; we are about to dye cotton bleaching is a must. A method of bleaching, the fabric is rinsed stuck against a stone, so as to remove as much of the sizing as possible. It is then spread out for sun bleaching and drying, water is sprinkled over the cloth at short intervals until evening. This is finally, washed and dried. So, this is like sun bleaching, but there are now chlorine bleaches; there are hydrogen peroxide bleaching and so on and so forth. But the traditional method of bleaching is by washing it and putting it in the sun. The UV rays of sun actually act like a bleaching agent, and remove any kind of light colored substance which may be causing any coloration to the fabric. So, the fabric then becomes quite white and ready to be use for dyeing.

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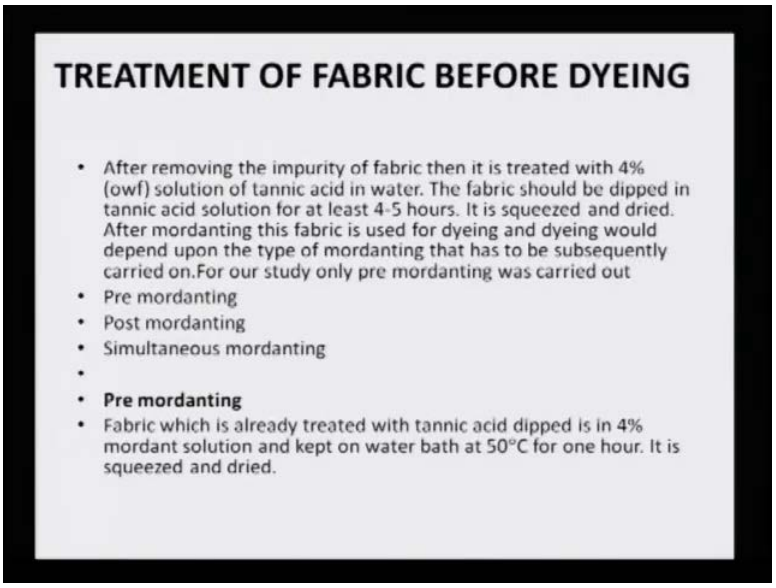

Treatment of fabric before dyeing: Now as we know that in the case of cotton, we also did a treatment of tannic acid time and again I am repeating this word because of this sentence, because tannic acid treatment is only associated with cotton. And right now we are trying to see how cotton fabric is prepared, and as we are going along I am also giving you an insight in to the preparation of silk and wool. So, fleetingly I am also mentioning what is necessary for preparation of silk and wool, but primarily we are focusing on the preparation of cotton fabric for dyeing. So, after removing the impurities of fabric, it is then treated with 4 percent weight of the fabric solution of tannic acid in water. The fabric should be dipped in tannic acid solution for at least four to five hours; it is squeezed and dried. After mordanting, this fabric is used for dyeing and dyeing would depend upon the type of mordanting that has to be subsequently carried on. For our study only pre mordanting was carried out, but of course, it is possible to do post mordanting and simultaneous mordanting as well. So, before we go on to the mordanting let us spend a little time on the pre treatment of cotton with tannic acid.

This tannic acid could view from the bio sources like one can use myrobalan or one can use ha terminalia, chebula which is myrobalan or one can use quercus infectoria which is gall nut, and these two are natural tanning tannic acid containing bio treatments, whereas one can even treat the cotton fabric with tannic acid which has been synthesized in laboratories. So, whether we use synthetic tannic acid or whether we use isolated tannic

acid or whether we use crude gall nut powder or myrobalan powder all give the tannic acid, and tannic acid treatment must be done just before the mordanting.

Because it is not advisable to keep the tannic acid treated fabric; it wills in due course of time due to air oxidation, it creates a greenish sting on the fabric. So, the prime reason for using tannic acid is to facilitate the dye uptake for cotton, and the second reason for using tannic acid is that it adds adding surfaces on to the fabric which lacks due to desizing and bleaching and all that we the three processes that we just saw. That has actually remove the attaching groups from the surfaces of the fabric, and therefore, tannic acid treatment provides you know bonding edges for the dye to come and attach.

So, that is how the tannic acid plays a very important role, and after tannic acid, of course, then we have the process of mordanting. We have the choice of mordanting by three different methods pre mordanting, post mordanting or simultaneous mordanting, and we have studied this time and again I have been telling about mordanting. Pre-mordanting fabric which is ready treated with tannic acid is now dipped into 4 percent weight of the mordant solution not necessarily always 4 percent, we have seen that in the case of copper and chromium mordant, even one to two percent is sufficient to provide the desired shape. And therefore, we should not dose too much metal mordant on to the fabric only that much percentage should be used which is required for the fabric for the adheration of the dye.

So, after that it is then squeezed and it is dried. You will see that after tannic acid treatment or after mordant treatment, the fabric is never ever washed; it is simply squeezed and dried. So, what happens, the excess of the tannic acid solution or the excess of the mordant solution just runs off and whatever is adhering to the fabric is what is required, on both the sides fabric will have the mordant and the tannic acid and that is what is the requisite amount that should be present on the fabric - no excess is required.

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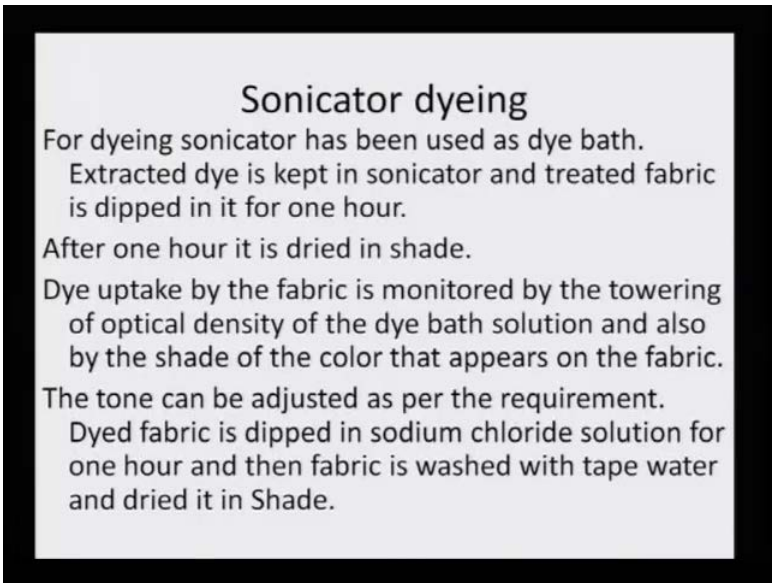

Now one very important innovation that we did in the laboratory was use of sonicator. So, I am just trying to take you through the important features of dyeing. We know conventional dyeing has been practiced for years, but has it made any impact by you know improving the process, has the industry being benefited? No, because conventional dyeings' do have their own disadvantages; there are dyes where you know the dye gets deteriorated or discolored or there are problems of doing it faster because of the production size and so on and so forth.

So, we have developed a process of sonicator dyeing with natural dyes, for dyeing in sonicator has been you know very popularized technique now lot of industry is interested, and there are collaborations happening where we are suggesting the use of big dye baths which has transducers fitted at the bottom, and which can be used for sonicator dyeing.

Extracted dye is kept in sonicator, and treated fabric is dipped in for one hour maximum to maximum an hour is required. After one hour, it is dried in shape. Dye uptake of the fabric is monitored by the towering by the lowering of the optical density of the dye bath solution and also by the shade of the color that appears on the fabric. Now you can make out that what is meant by the shade of the color, the depth of the color, because yesterday we did that that due because of this color matching machine, we are able to ascertain the L A B values, the K by S values, so this is what it means and the UV visible

spectrophotometer helps us to find how the color depth in the dye bath solution, because it is simple phenomena.

See, if we make a dye bath of certain concentration - say x concentration, and after dyeing the dye bath will never have x concentration it will always have x minus y concentration. Now, this x minus y is what as actually gone on to the fabric, because the dye cannot disappear anywhere; it has to be either in the dye bath or on the fabric that was dipped. So, these particular phenomena can be analyzed on UV visible spectrophotometer, and the color depth, and it is you know reflectance and transmittance and all that can be found out with the help of K by S which is measured by the color scanning machine.

Now another thing that was absorbed that when we do mordanting, it is step wise process; that means, first tannic acid treatment then the fabric is dried then mordanting treatment - fabric is dried and then finally, dyeing. So, it involves three steps; even if we take silk and wool it is two steps. And naturally when there is multi step procedure offered to the industry, it is always very you know cumbersome - it is TDS. Because any extra step in the dyeing process can actually create waste of money, waste of time, waste of energy. So, if there is a possibility to kind of merge one or two steps there would be saving of time, saving of cost, saving of energy. So, you see that it is going to be advantageous.

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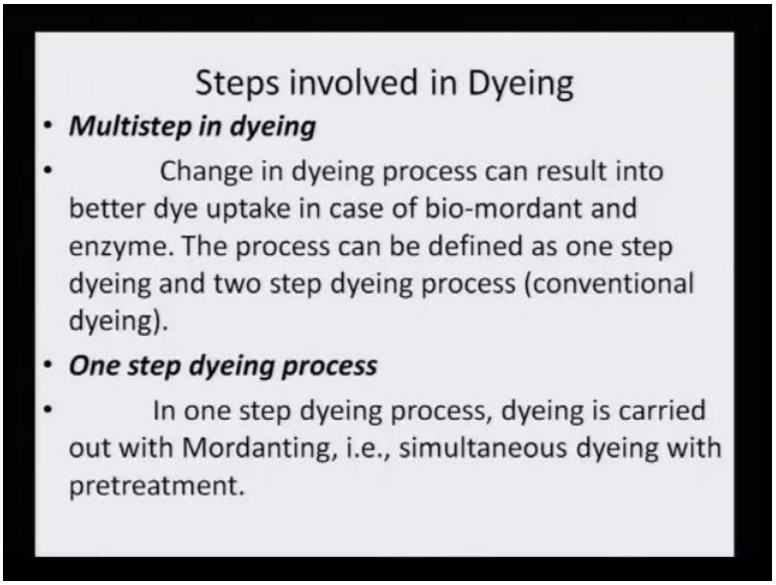

So, multi step dyeing which was popularly the conventional method of dyeing. By going step wise: tannic acid step, mordanting step, dyeing step change in dyeing process can result into better dye uptake in case of bio-mordants and enzyme; this was absorbed. So, can we now do some alteration with the metal mordant by replacing it with bio-mordant or enzyme, can we merge these processes for the betterment or for the ease for the industry people to follow it? Yes, the answer is that one step dyeing process can be introduced and has been introduced. In one step dyeing process, dyeing is carried out with mordanting - that is simultaneous dyeing with the pretreatment, so pretreated cloth because tannic acid cannot be added into it. So, therefore, after the pretreatment of the tannic acid, the cloth can be simply put in to a bath where the mordant and the dye both are present. So, that would reduce the step and from a multi step dyeing process it can be brought down to one step dyeing.

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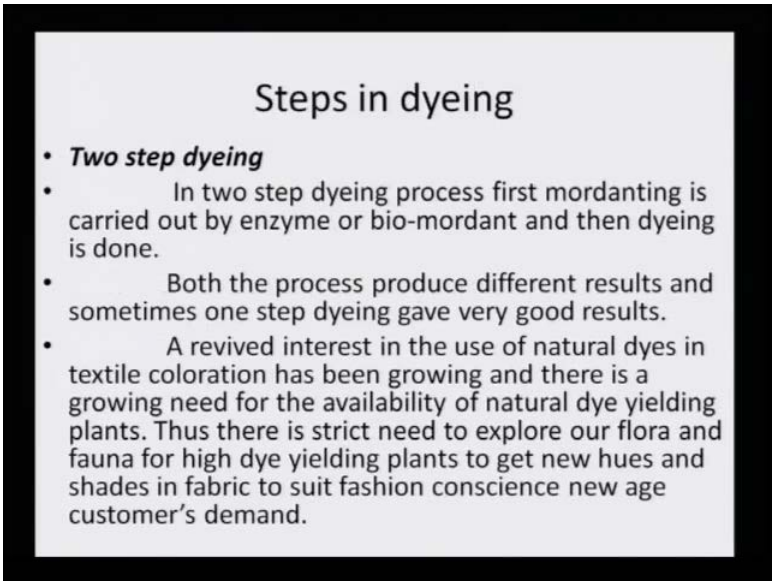

Steps in dyeing: Then there are two step dyeing also that two step dyeing process was mordanting is carried out by enzyme or bio-mordant or mordant and then dyeing is done. Both the processes produces different results and sometimes one step dyeing gave very good results. Now revived interest in the use of natural dyes in the textile coloration has been growing, and there is a growing need for the availability of the natural dye yielding plants. Thus there is strict need to explore our flora and fauna for high dye yielding plants to get new hues and shades in fabric to suite fashion conscience new age customer's demand.

So, if we try to look at the whole dyeing process from the industry point of view, always it is a welcoming change that any innovation in the process. If it can reduce three things, that is the cost, the energy consumption, and the time; then it is a welcoming change and such innovations are most whole heartedly accepted by the industry.

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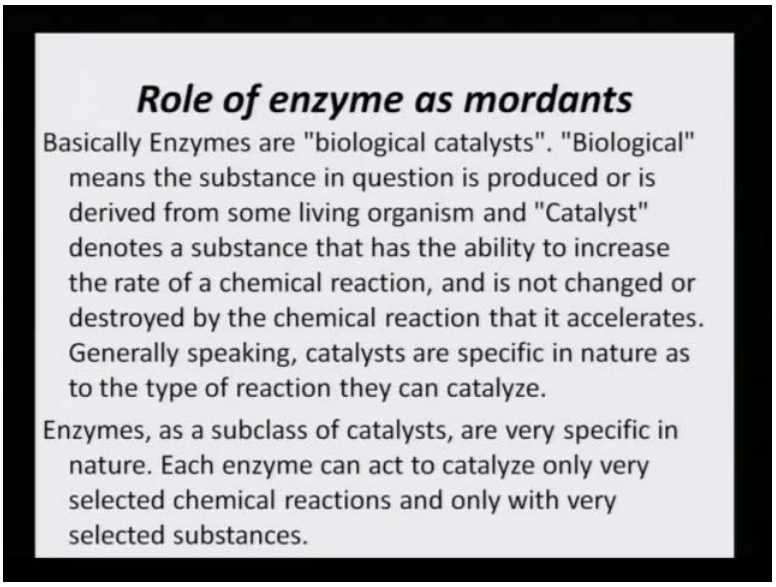

Now let us try to see why was it necessary to replace metal mordants. We know that all along we have been talking about the eco friendliness of natural dye. Now because of dosing or the using a usage of metal mordants, particularly the copper and the chromium metal mordants which are under the category of toxic heavy metals, we had a limitation there. And because the effluent still has about 2 to 4 percent of these metal salts after the mordanting of the fabric, and it is run out into the river streams or water bodies or even into the agricultural land, it has its own ecological impact on these effluent not being able to recover these metal mordants. But at the same time, we know that natural dyeing cannot be used without the help of these metal mordants. So, is there a method that we can somehow reduce the quantity of the metal or use a bio-mordant which can be a source of metal, but at the same time it has so little the metal component just optimum for the reaction or the dyeing to be sufficient with this metal mordant present in the bio-mordant.

Basically even enzymes of course, have a different role to play. But enzymes somehow participate in a manner which is different from the metal mordants or the bio-mordants

which are having metal contents, but they offer sides of attachment, and because they offers sides of attachments of the dyes when they are applied on the fabric; they offer the dyes to come and sit on that. So, basically enzymes are biological catalyst, the biological means the substances in questions is produced or is derived from living organisms and catalyst denotes a substance that has the ability to increase the rate of chemical reactions, and it is not changed or destroyed by the chemical reactions that it accelerates. Generally speaking, catalysts are specific in nature as to the type of reaction they can catalyze. So, this is the kind of general enhanceation of the enzyme.

General you know how it is considered, but enzymes has a sub class of catalysts, are very specific in nature. Each enzyme can act to catalyze only very selected chemical reactions and only with very selected substance. So, the only drawback with enzymes is that they are very selective, and they act more like a catalyst and since they are from the biological origin; there reactivity is kind of just like a lock and key arrangement; not every key can open every lock. Similarly, not every enzyme is compatible with every dye. So, one has to make a study where dye is shown to have a lock and key arrangements with the enzymes; only then that enzyme will be effective on that particular dye. So, this kind of, you know matching has to be made about the compatibility of the dye and the enzyme when we are using enzymes as bio-mordants.

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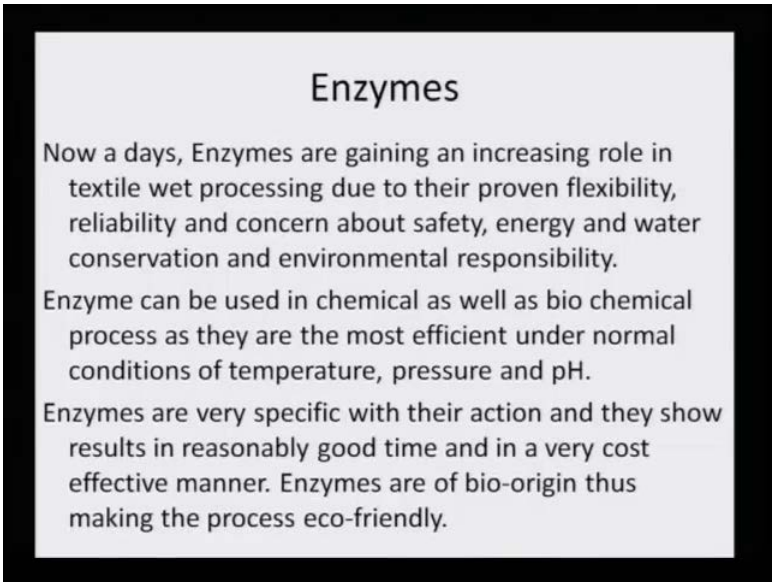

Enzymes: Now a days, are gaining an increasing role in textile wet processing due to their proven flexibility, reliability and concern about safety, energy and water conservation and environmental responsibility. Enzyme can be used in chemical as well as bio chemical processes as they are the most efficient under normal conditions of temperature, pressure and pH. Enzymes are very specific with their actions and they show results in reasonably good time and in a very cost effective manner. Enzymes are of bio-origin thus making the process eco friendly. Why enzymes were accepted, because they are from the biological origin. So, they are like bio catalyst and therefore, they can be degraded and therefore, they are eco friendly.

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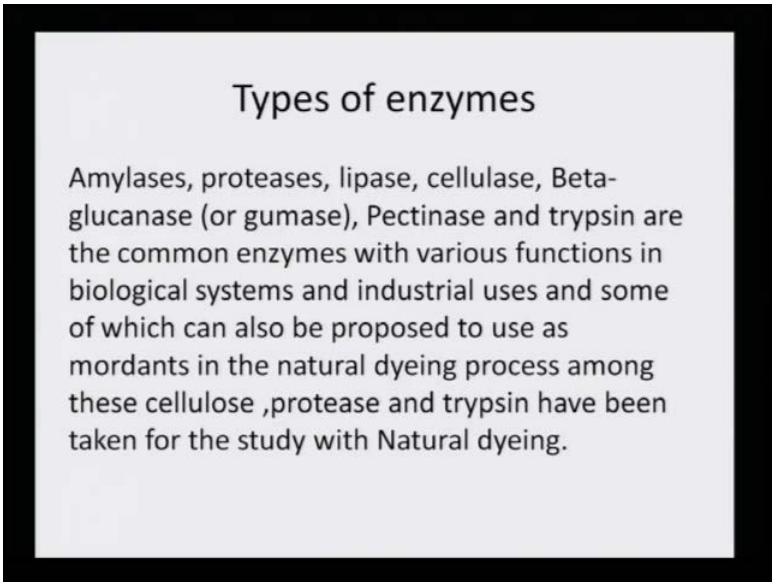

Types of enzymes that are used in the textile industry - amylases, proteases, lipase, cellulase, beta-glucanase or gumase, pectinase, trypsin are the common enzymes with various functions in biological systems and industrial uses and some of which can also proposed to use as mordants in the natural dyeing process among these cellulose, protease and trypsin have been taken into study by us and we have shown that this really work very well with the natural dyeing and the natural dyes.

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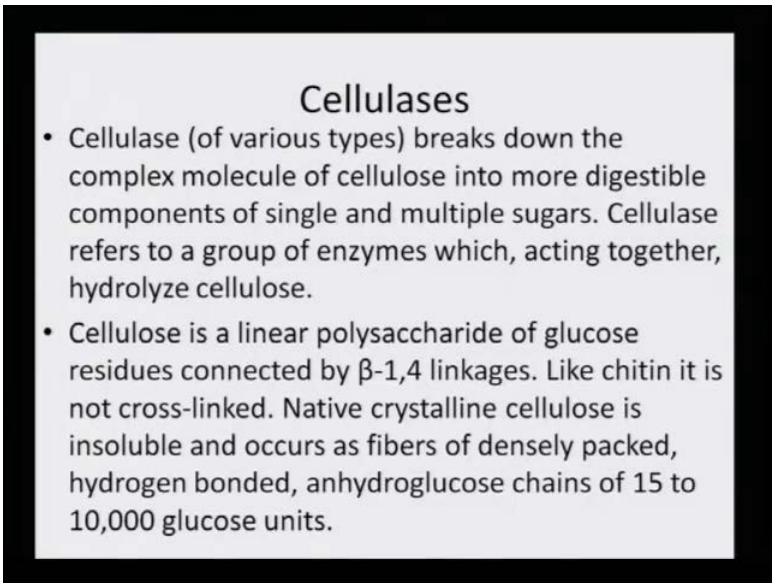

For example, if you try to take example of cellulases; cellulase of various types breaks down the complex molecule of cellulose into more digestible components of single and multi sugars. Cellulase refers to a group of enzymes which, acting together, hydrolyze cellulose.

Cellulose is a linear polysaccharide of glucose residues connected by beta- 1,4 linkages. Like chitin it is not cross-linked. Native crystalline cellulose is insoluble and occurs as fibers of densely packed, hydrogen bonded, anhydroglucose chains of 15 to 10,000 glucose units. So, celluloses, cellulases work on cellulose, as the name suggests. So, if you remember that much and the structure of cellulose is that it has 1, 4 linkage of the beta type of various glucose rings which are attached to one another.

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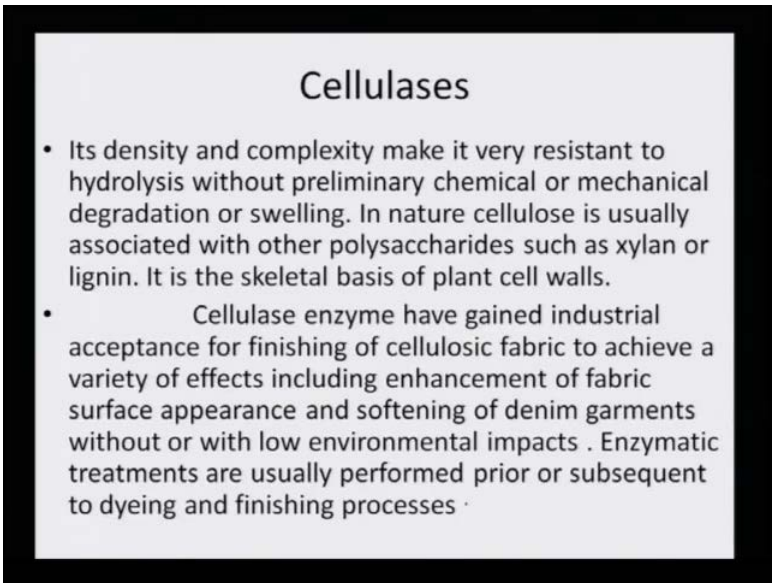

Its density and complexity make it very resistant to hydrolysis without preliminary chemical or mechanical degradation or swelling. In nature cellulose is usually associated with other polysaccharides such as xylan or lignin. It is the skeletal basis of plant cells walls.

Cellulose enzyme have gained industrial acceptance for finishing of the cellulosic fiber or fabric to achieve a variety of effects including enhancement of fabric surface appearance and softening of denim garments without or with low environment impacts. Enzymatic treatments are usually performed prior or subsequent to dyeing and finishing processes. So, enzymes and the use of enzymes and the use of cellulose particularly has already been there in the textile industry, but for using it for natural dyeing, it has been used for the first time by us because it is compatible with cotton. And so, if one has to enhance the cotton dyeing property, use of cellulose really, really helps us and it helps the dye uptake.

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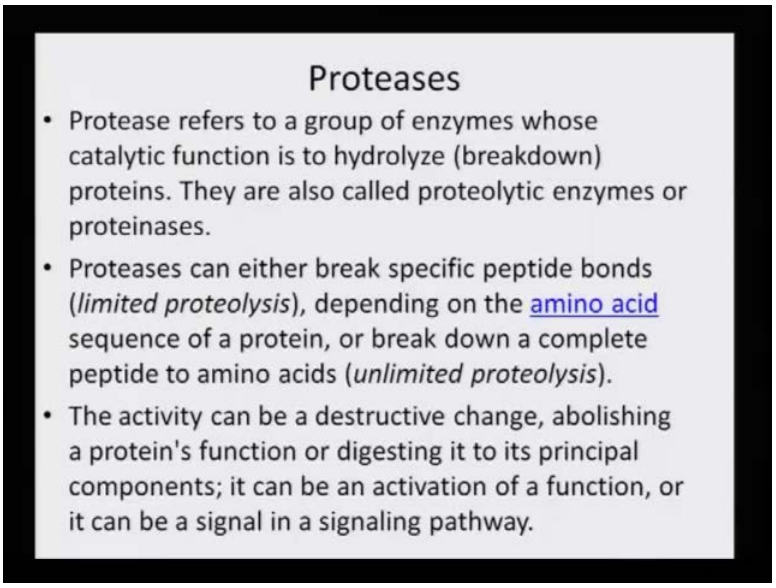

Similarly, proteases or a class of enzymes referred to an enzyme whose catalytic function is to hydrolyze or breakdown proteins as the name suggest - proteases, so prote. They are also called proteolytic enzymes or proteinases.

Proteases can either break specific peptide bonds or depending on the amino acids sequence of a protein, or breakdown a complete peptide to amino acids - that is unlimited or limited proteolysis can take place. It can breakdown to peptide bonds only or it can breakdown to its most smallest unit that is the amino acid. The activity can be destructive change abolishing a protein’s function or digesting it to its principal components; it can be an activation of a function, or it can be a signal in a signaling pathway.

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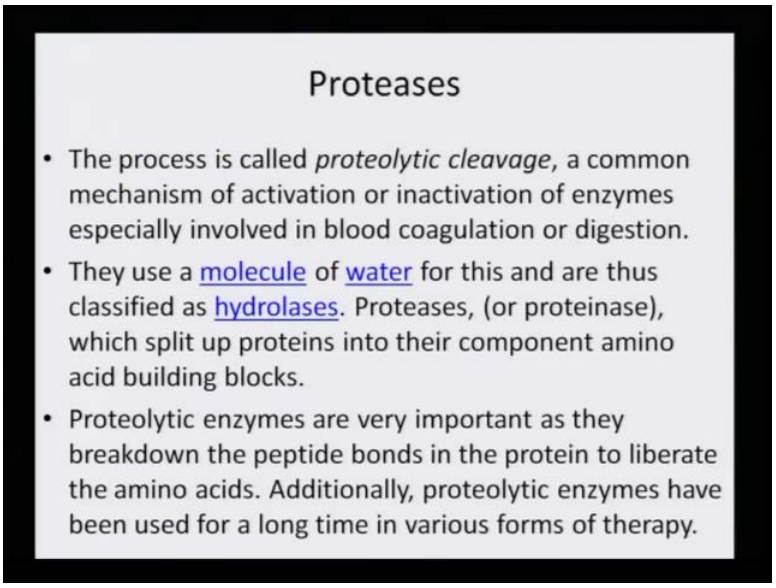

However, we are concerned with proteases how they can work in the dyeing system. The process is called proteolytic cleavage, a common mechanism of activation or inactivation of enzymes especially involved in blood coagulation and digestion. These are where the proteases is used, but when it comes to you know they use a molecule of water and thus they are also classified as hydrolases. Proteases or, which split up proteins into component of amino acid building blocks. Proteolytic enzymes are very important as they breakdown the peptide bonds in the protein to liberate the amino acids. Additionally, proteolytic enzymes have been used for a long time in various forms of therapy. So, there are hundreds and hundreds of uses of proteases, but what we are concerned or what we are interested in is the use of proteases in the hydrolases or in the activation or in the bio-mordanting of wool and silk.

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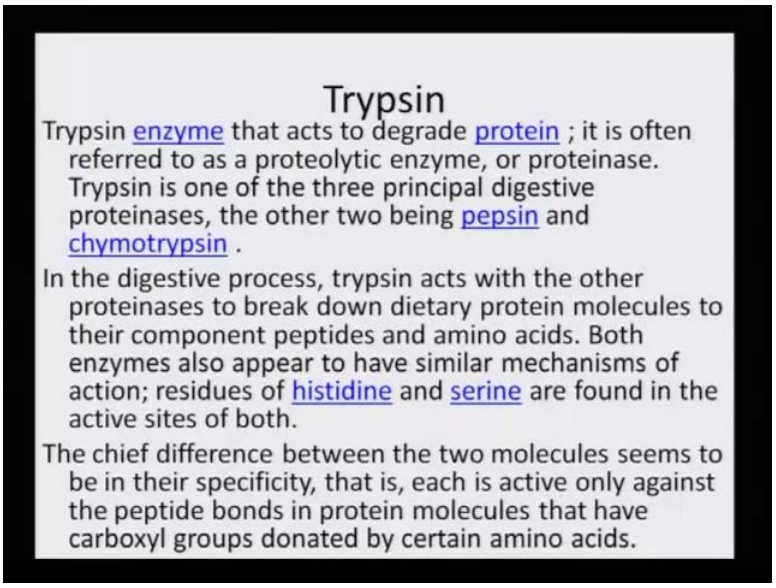

Similarly, there is another dye sorry another enzyme called trypsin. Trypsin enzyme that acts to degrade protein; it is often referred to as a proteolytic enzymes - it is one of the proteases or proteinases. Trypsin is one of the three principal digestive proteinases, and other two being pepsin and chymotrypsin, but we are not concern mainly with the digestive action of the trypsin.

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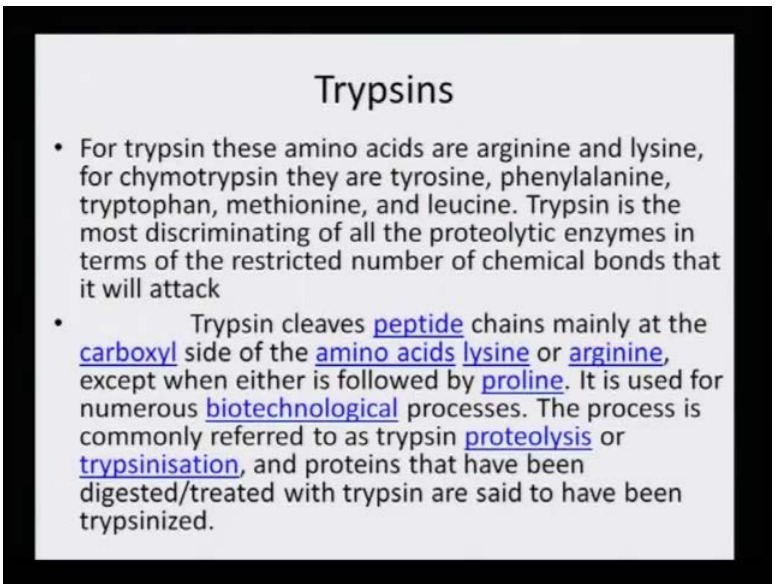

What we are interested that how trypsin cleaves the peptide chains mainly at the carboxyl side of the amino acid and therefore, can it help us in the dyeing process, can it act as a bio-mordant and that is what is of prime concern.

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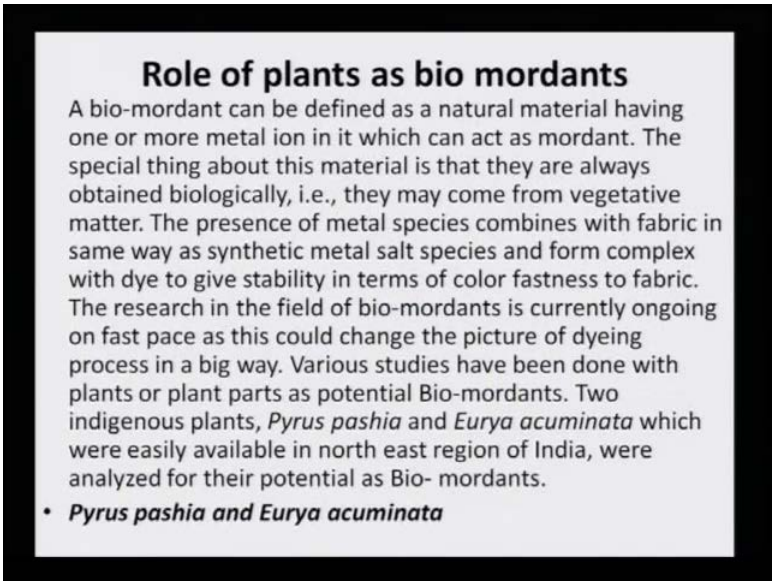

Role of plants as bio mordants: A bio-mordant can be defined as a natural material having one or more metal ion in it which can act as mordant. So, either we use metal mordant solve directly or use a bio-mordant source which has metal salt, but in a very small, but requisite amount. The special thing about this material is that they are always obtained biologically, that is they may come from vegetative matter. The presence of metal species combines with fabric in the same way as the synthetic metal salt species would do and from the complex with dye to give stability in terms of color fastness to fabric. The research in the field of bio-mordant is currently going on on fast pace as this could change the picture of dying process in a big way. If we are able to use bio-mordants then the lot of problem that is created by the metal mordants can be overcome.

Various studies have been done with plants or plants parts as potential bio-mordants. Two indigenous plants - that is Pyrus pashia and Eurya acuminata which were easily available in the north east region of India, were analyzed for their potential as bio-mordants. So, two plants have been already identified by us - that is Pyrus pashia and Eurya acuminate, and they have been found to have excellent bio-mordanting capability.

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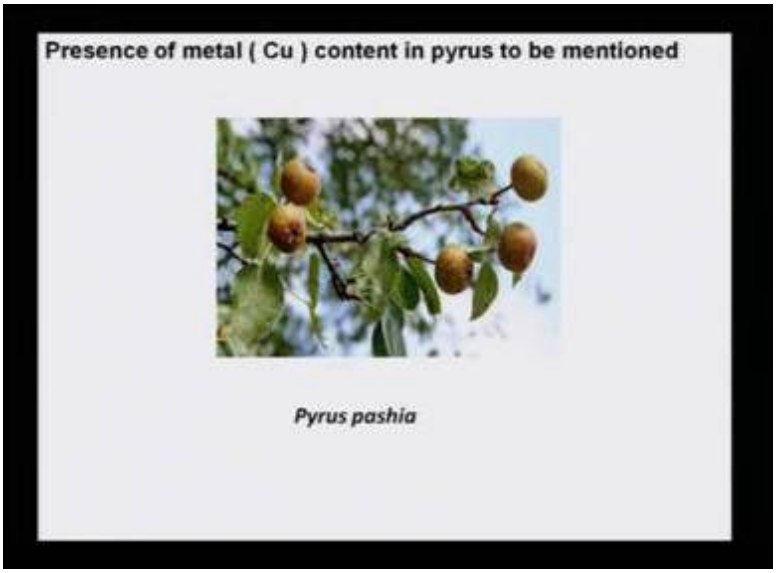

Now, this is the picture of Pyrus pashia and by the analysis of the fruit of this Pyrus pashia which is more like, you know berry's; the it was found that copper metal was present and it was analyzed on atomic absorption spectrometer.

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Similarly, this is the picture of Eurya acuminate; the leaves of Eurya acuminata have the presence of aluminum, and this aluminum also was analyzed through atomic absorption spectroscopic. So, you see that these two plants already have and there may be many more such plants which have metal salts in their fruit or flower or bark or leaves and

those plants can be used as bio-mordants, and completely the metal mordanting step can be eliminated.

Now another advantage of using bio-mordant is, that when the dye is been extracted from the plant part of the dye yielding plant at that point of time only, these bio-mordant yielding plants also can be co-heated together; that means, they can be boiled together and thus the mordanting and the dye extraction, rather the extraction of the mordant and the dye extraction can be done simultaneously. Now this extract already has the mordant now, in the form of bio-mordant. So, if the extract is simply concentrated and dyeing is carried out, one full step will be avoided in the dyeing process.

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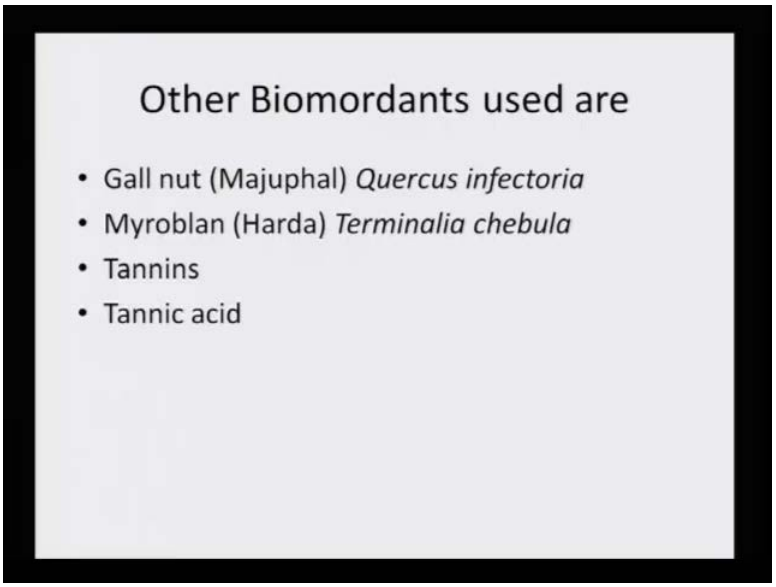

Other bio-mordants as I said are Gall nut - that is Majuphal, Quercus infectoria or Myroblan which is Harda which is also called botanically as Terminalia chebula; it also can be used in place. So, these are Myroblan and Gall nut have been used from time and again, but nobody actually knows whether they have any metal content or not, but they definitely have tannin content. So, may be the tannin is contributing. So, they can be also classified as bio-mordants, and of course, we have tannin from various barks of the plants and therefore, it is possible to actually use these tannins very easily for the purpose of dyeing. Now tannic acid also synthetic tannic acid can be also used at the same time.

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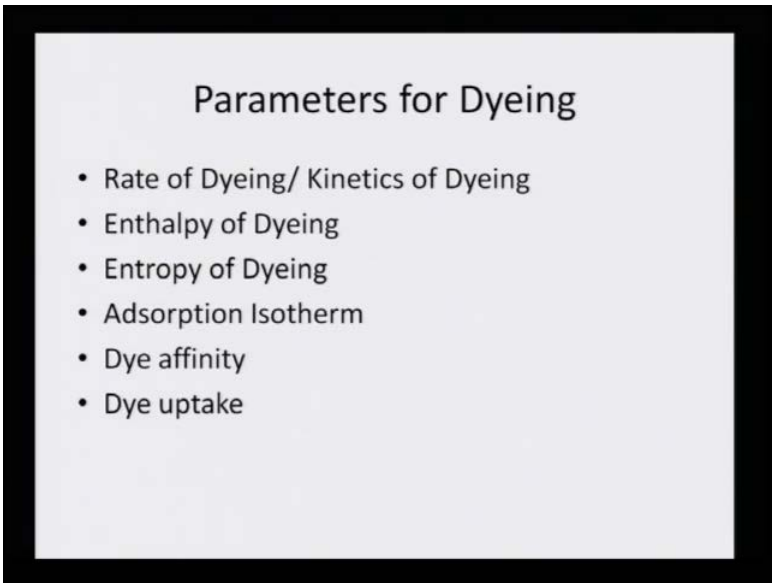

So, therefore, if we have to then look at various other parameters of dyeing - rate of dyeing, kinetic of dyeing, enthalpy of dyeing, entropy of dyeing, adsorption isotherm, dye affinity, dye uptake; all these can be ascertain. There are procedures available, but it is more from the scientific point of view that these parameters are tested for dyeing.