Natural Dyes

Prof. Padma Vankar

Department of Chemistry

Indian Institute of Technology, Kanpur

Lecture No. # 14

Continuing with the chapter of mordant and the use of mordant, the definition of mordant, we now have to understand this particular aspect of natural dyeing very well. Why because it is one of the most important chemical moiety that participates in natural dyeing.

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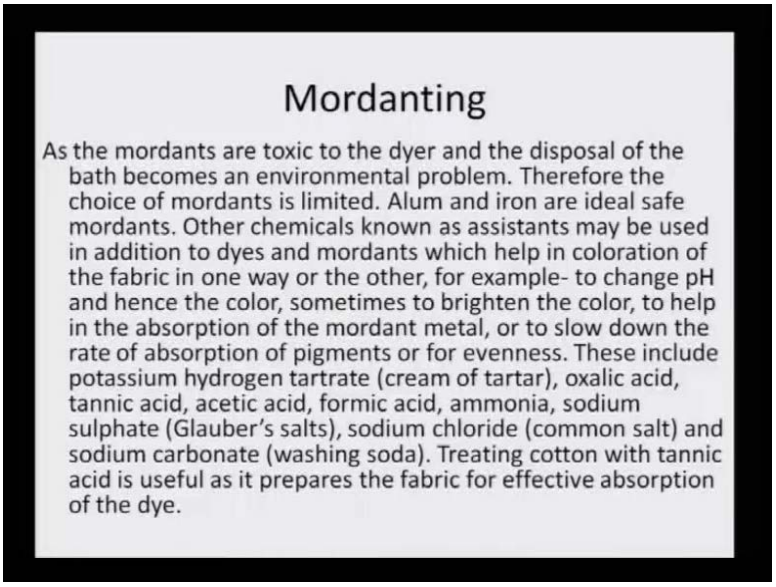

Other chemicals known as assistants may be used in addition to dyes and mordants which help in coloration of the fabric in one way or the other, for example, to change p H and hence the color, sometimes to brighten the color, to help in the absorption of the mordant metal, or to slow down the rate of adsorption of pigments or for evenness. There are many other chemicals that are used during the natural dyeing processes. But the role of mordant is undoubtedly the most important. These include potassium hydrogen tartrate or it is commonly call as cream of tartar or oxalic acid, tannic acid, acetic acid, formic acid, ammonia, sodium sulphate or Glauber's salts, sodium chloride, common salt and sodium carbonate which is the washing soda, vinegar, etcetera.

Treating cotton with tannic acid is useful as it prepares the fabric for effective absorption of the dye. See what happens is that cellulosic fibers do not have free OH group. As a result, the chelation with the metal when we learn more details of mordanting as we go along in this lecture, you will appreciate that they need to be activated on a coating or a dip in the tannic acid bath always enhances the presence of these OH groups on the cotton fabric which are free now to attach to the metal, and the metal is attached to the dye. So, that brings it (( )) it is like a bridging head. They are like bridging head and here this side is the dye and this side is the fabric. So, that is the kind of role of the mordants and tannic acid enhances this role by offering more attaching surfaces on the surface of the fiber.

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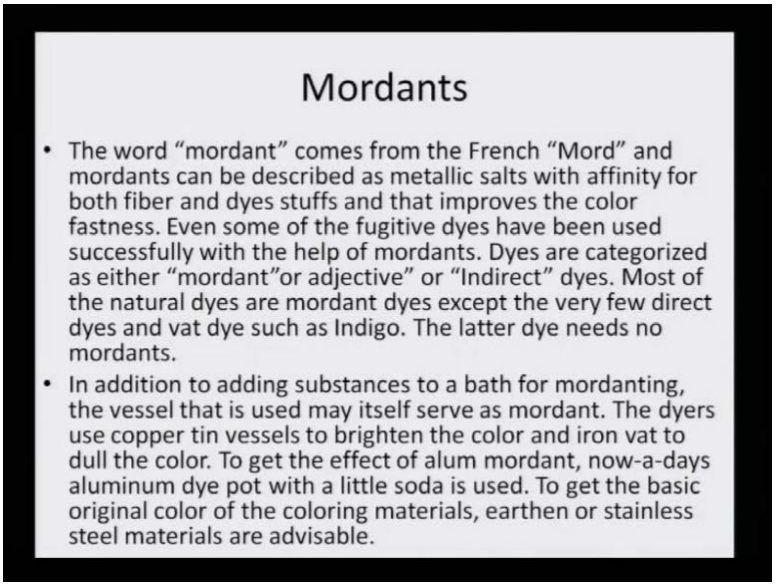

The word mordant comes from the French word mord and mordants can be described as metallic salts with affinity for both fiber and dyes stuffs and that improves the color fastness. Even some of the fugitive dyes have been used successfully with the help of mordants. Dyes are categorized as either mordant or adjective or indirect dyes. Most of the natural dyes are mordant dyes expect for a few direct dyes and vat dye like indigo. The latter dye needs no mordants and that is why I said sometimes you know the excess of the dye runs off or leaves off, because mordant holds up these dye molecules. And therefore, they are called as adjective dyes or indirect dyes which use the mordants. Other dyes which do not use which are dyed with without the use of mordant are called direct dye.

In addition to adding substances to a bath for mordanting, the vessel that is used may itself serve as mordant. Yesterday we saw that you know using a tin pot or an iron pot could change the extract color. And so the same thing is now to be understood more specifically that this metal vessel will also start contributing its color, because some of it will leach into the dye extract. So, the dyers use copper vessel - copper tin vessel to brighten the color and iron vat to dull the color. To get the effect of alum mordant, now-a-days aluminum dye pot with a little soda is used. To get the basic original color of the coloring materials, earthen or stainless steel materials are advisable. Why because they will not leach any metal into the dye extract.

So, the original dye color will come on to the fabric. But if it is a tin pot or if it is an iron pot or if it is a aluminum pot they some amount of leaching under that p H condition form the vessel will take place and that will alter the dye color. So, one needs to keep in mind that stainless steel utensils should be used while using natural dyeing process.

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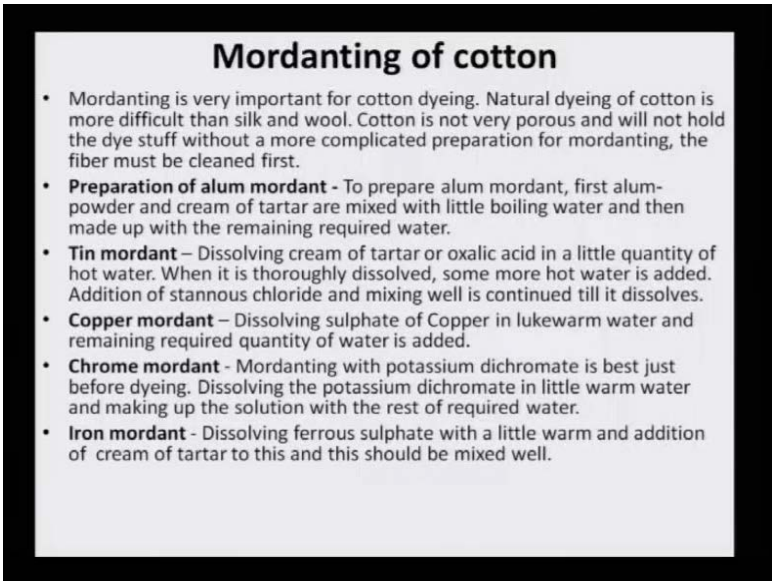

Mordanting of cotton: Now that is most important, why because cotton is one of the toughest to dye and it is extra you know in a time and energy and effort has to be made for preparing the cotton for natural dyeing. Mordanting is very important for cotton dyeing. Natural dyeing of cotton is more difficult than silk and wool as what I said a while ago. Cotton is not is not very porous and will not hold the dye stuff without a more complicated preparation for mordanting, the fiber must be cleaned first. So, the first

thing is that all the grease and the other material waxes of the cotton must be removed by scavering and it is not a very porous material. Therefore, you know special preparation of the cotton needs to be done. I told a while ago that cotton needs a tannic acid treatment. So, what happens when the cotton fabric is scavered or washed with mild alkali or alkaline soap solution. The second step is the pretreatment with tannic acid and the third treatment is with the mordant.

Preparation of alum mordant - To prepare alum mordant, first alum powder and cream of tartar are mixed with little boiling water and then made up to the remaining water solution. So, alum mordant is prepared with cream and cream of tartar as a modifier and alum sodium potassium alum or sodium potassium sulphate, aluminum sulphate these are various combinations of different types of alums are available in the market they can be used. Tin mordant - Dissolving cream of tartar or oxalic acid in little quantity of hot water, and then to that addition of stannous chloride and mixing it can make a tin mordant. Copper mordant - Dissolves copper sulphate in lukewarm water and then you know just make it up with more quantity of water. Chrome mordant - Mordanting with potassium dichromate is best just before dyeing. Dissolving the potassium dichromate in little warm water and making up the solution is how this mordant is prepared and used.

Iron mordant - Dissolving ferrous sulphate with the little warm water and adding a little bit of cream of tartar mixed at a good combination for the mordanting process. So, for alum mordant, tin mordant and iron mordant along with the mordant that is the ferrous sulphate, alum sulphate, the there is an additional add addition of cream of tartar. Whereas in the case of copper mordant and chrome mordant the salts are directly use in the aqueous solution and used as mordant.

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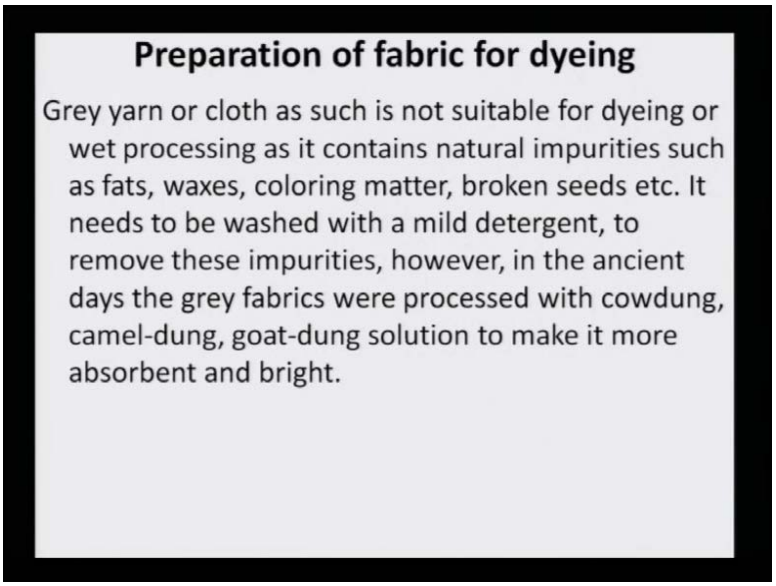

Preparation for the fabric for dyeing: Grey yarn or cloth as such is not suitable for dyeing or wet processing as it contains natural impurities like fats, waxes, coloring matter, broken seeds etcetera. It needs to be washed with the mild detergent, to remove these impurities. However, in the ancient days the grey fabrics were processed with cow-dung camel-dung, goat-dung solution to make it more absorbent and bright. That is because you know they were using accidently these cow-dung, camel-dung can cow urine and such things, because they thought they were rich in ammoniacal solutions. And they thought that you know giving a pretreatment with these will make the color brighter. But there is a lot of chemistry and chemical reaction behind this usage which of course, they did not understand well. But nevertheless the grey yarn and cloth must be washed which is called the scavering process with the help of a mild detergent.

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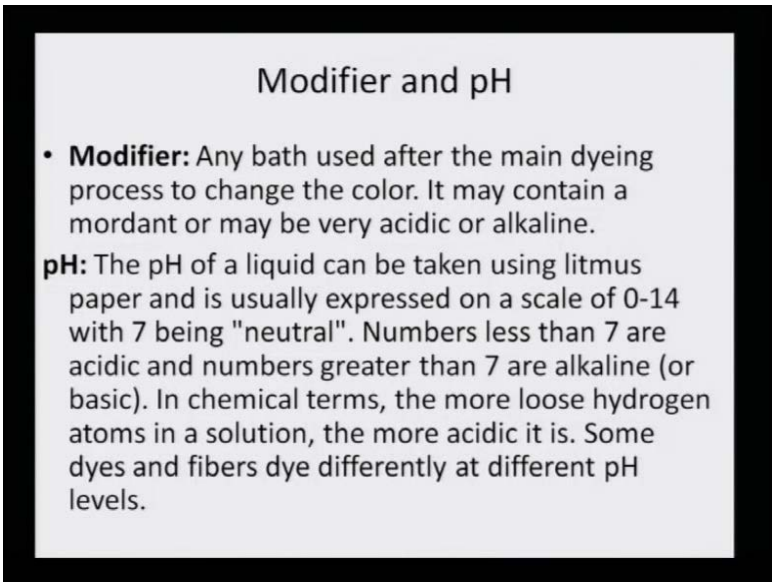

Modifiers and p H: Modifier - any bath used after main dyeing process to change the color. It may contain a mordant or may be even very acidic or alkaline. So, sometimes some chemicals you know have to be added additionally like the case of cream of tartar or oxalic acid or vinegar or washing soda these are like modifiers. p H of course, plays a very, very vital role and time in again I have been emphasizing. The p H of the liquid can be taken using litmus paper and is usually expressed on a scale of 0 to 14 which 7 being 7 being neutral. Numbers less than 7 are acidic and numbers greater than 7 are alkaline or basic.

In chemical terms, the more loose hydrogen atoms in the solution, the more acidic it is. Some dyes and fibers dye differently at different p H levels. I give you an example of anthocyanins, you see they are very reddish when they are in acidic p H and they are very purplish and blue when they are in alkaline p H. So obviously, if the p H or kept differently the same dye will show different color on the fabric.

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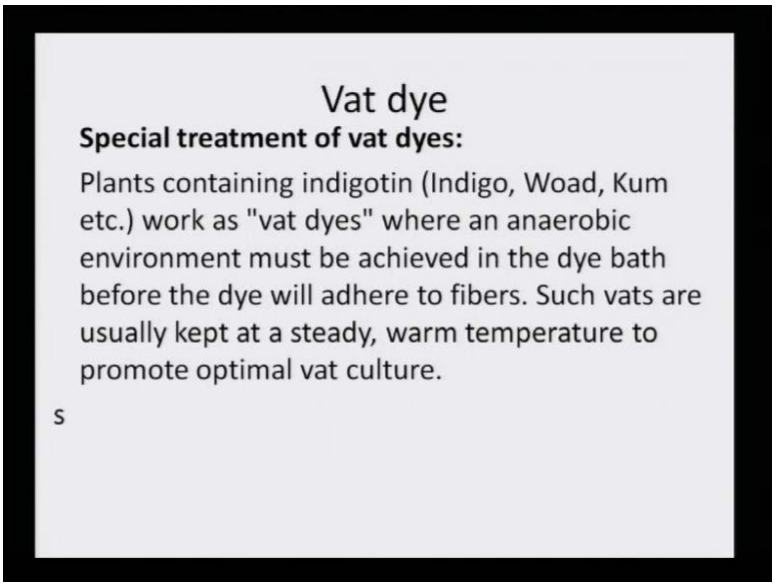

Where dye needs some special kind of attention and mention? Special treatment of vat dye: The vat dye example is indigo. Whether it is from any source of the indigo there are several sources of indigo not only the indigo leaves, but woad, kum, you know various verities, species which yield indigo tin. Plants containing indigo tin work as vat dyes where an where an anaerobic environment must be achieved in the dye bath before the dye will adhere to the fibers. Such vats are usually kept at a steady, warm temperature to promote optimum vat culture.

So, what happens is that the dye is actually in the leuco form that is the colorless form when this indigo tin solution is added to the fabric. But with the help of air oxidation and moisture the leuco or the colorless turns into the blue color and these process requires keeping the dye under you know study warm condition, so that the vatting process can take place. So, this is a very, very typical process of indigo dye where no mordant is used. But yet the color adheres very well to any of the fiber whether it is proteinaceous fiber or whether it is the cellulosic fiber that is cotton or in the earlier case wool or silk it will dye very evenly in all the cases.

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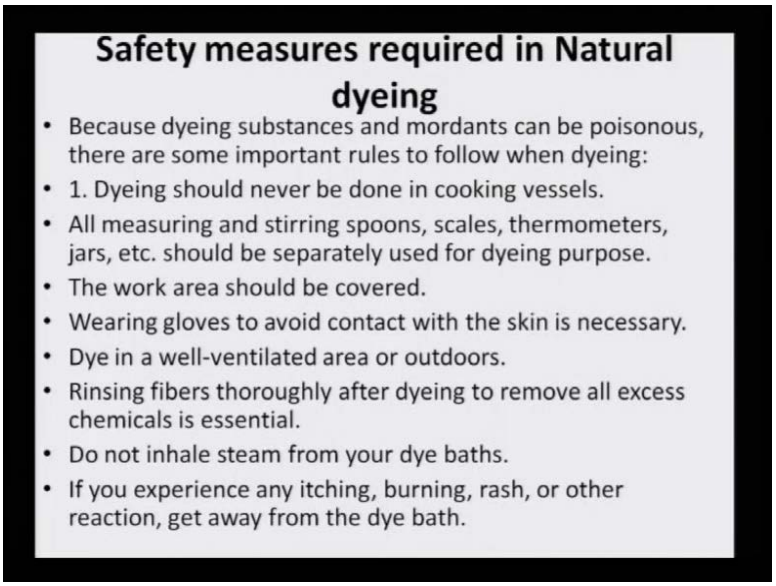

Safety measurements are required in natural dyeing: Because dyeing substances and mordants can be poisonous, there are some important rules that need to be remembered and kept in mind. Dyeing should never be done in cooking vessels. All measuring and stirring spoons, scales, thermometers, jars, etcetera should be separately used for dyeing purposes. The work area should be covered. Wearing gloves to avoid contact with the skin is necessary. Dye is a well-ventilated area or dye in a well-ventilated area or outdoors. Rinsing fibers thoroughly after dyeing to remove all excess chemical is essential. Do not inhale steam from dye baths. If you experience any itching, burning, rash, or other reaction, get away from the dye bath. So, these are certain safety measures which also need to be absorbed and understood very carefully otherwise accidents can happen anywhere.

So, one needs to remember that mordants are like metal salts, some of them are toxic. So, they have to be handled very carefully wearing glows and all the measuring devices likes spoons, scales, thermometer, jar, which are used for dyeing purpose must be kept aside. So, these are some of the safety measurements.

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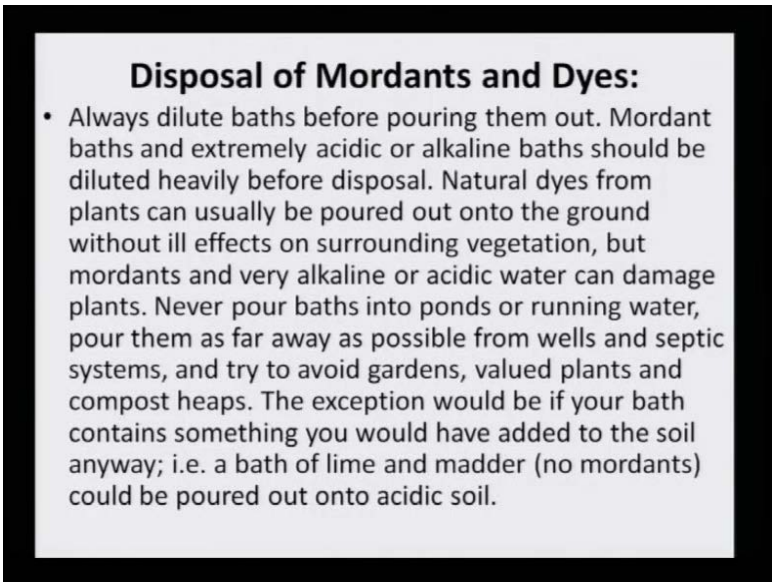

Disposal of the dyes and mordants also must be taken care. It is not that use it and just through it anywhere, because then your contaminating the environment and on one hand we are saying natural dyes are good, because they are eco friendly and on the other hand the use of mordant and then improper disposal of the mordants can create environmental problem.

Always dilute baths before pouring them out. Mordant baths and are extremely acidic or alkaline baths should be diluted heavily before disposal. Natural dyes from the plants can usually be poured out into ground without ill effects on surrounding vegetation, but mordants and very alkaline or acidic water can damage plants. Never pour baths into ponds or running water, pour them as far away as possible from wells and septic systems, and try to avoid gardens, valued plants and compost heaps. The exception would be if you bath if your bath contains something you would have added to the soil anyway; a bath of lime and madder no mordants could be poured out into acidic soil. So, one has to keep the chemical content in mind before the disposal of these dyes.

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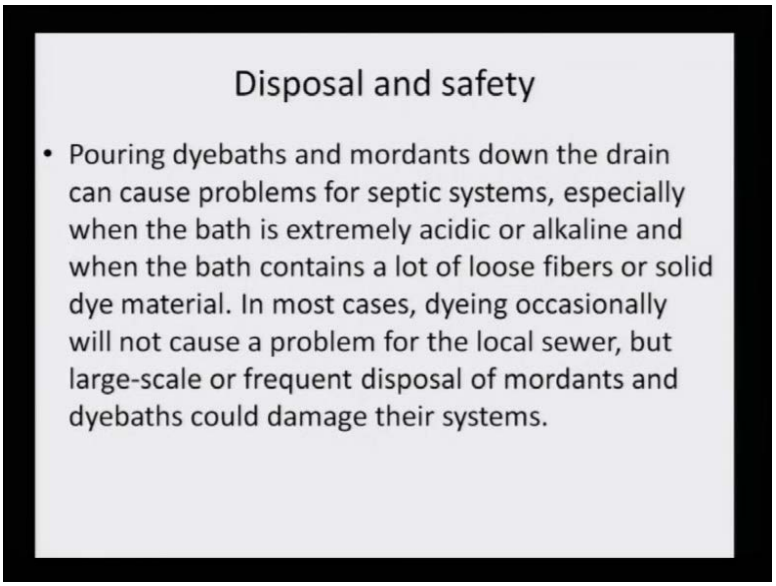

Disposal and safety: Pouring dye baths and mordants down the drain can cause problems for septic systems, especially when the bath is extremely acidic or alkaline and when the bath contains a lot loose fibers or solid dye material then also it may create a choking. In most cases, dyeing occasionally will not cause a problem for the local sewer, but large-scale or frequent disposal of mordants and dye baths can damage their systems. So, all this must be taken into come into account, because of using in large scale the disposal is a big criteria to be kept in mind.

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Overdyeing as I said was possible with natural dyeing and it is an odd that one can bring the shape of the required color by overdyeing if it has not come to that state by the first process. Overdyeing is the process of taking already dyed in one dye bath and dyeing it with something else. It can often produce much better color than dyeing with one dyestuff alone. For instance, dyeing a fiber yellow and then overdyeing with blue can achieve beautiful greens.

Historically, over dyeing was often used commercially to take advantage of two dyestuffs in the same color range with different properties like brazilwood produces a really bright red that fades, and madder produces a very long lasting red, but madder red is not always as bright. So, the two were often used together. So, overdyeing could be with the same dye with different dyes and therefore, it can be utilized again and again, and maximum amount of dye can be up taken on the fabric. So, with these we have come to an end of this chapter of understanding the basics of dyeing.

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Now, we will try to look at the word mordant and the mordanting of textile why and how they are important. I will now skip a few things here, because it would be otherwise repetitive, but nevertheless the term mordant is used for chemicals which usually have a metal with a valence of at least two or more, they can also be other types of compounds as well. Natural dyes as also referred as mordant dyes; do not readily adhere to cotton. So, mordants are used to make them adhere. Mordants are needed to set the color when

using natural dyes. Different mordants will give different hue color with the same dye. We just talked about it. So, we are just trying to recapitulate, a mordant is thus a chemical agent which allows a reaction to occur between the dye and the fabric. In textiles, mordants are used to fix the color in dyeing or fabric printing, especially for fabrics of plant origin and when that is use with cotton. So, in order to make the dye adhere to the fabric - cotton fabric mordanting is a must.

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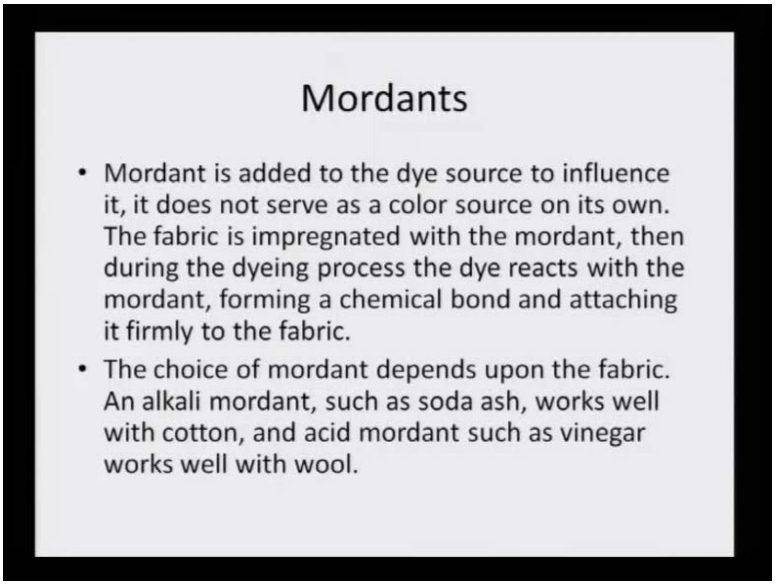

Mordants is added to the dye source to influence it, it does not serve as a color source on its own. The fabric is impregnated with the mordant, then during the dyeing process the dye reacts with the mordant, forming a chemical bond and attaching it firmly to the fabric. So, it is not dye a source that should be clearly understood. It is a compound which is at dye attaching agent. The choice of mordant depends upon the fabric. An alkali mordant, such as soda ash, works well with cotton, and acid mordant such as vinegar works well with wool and silk.

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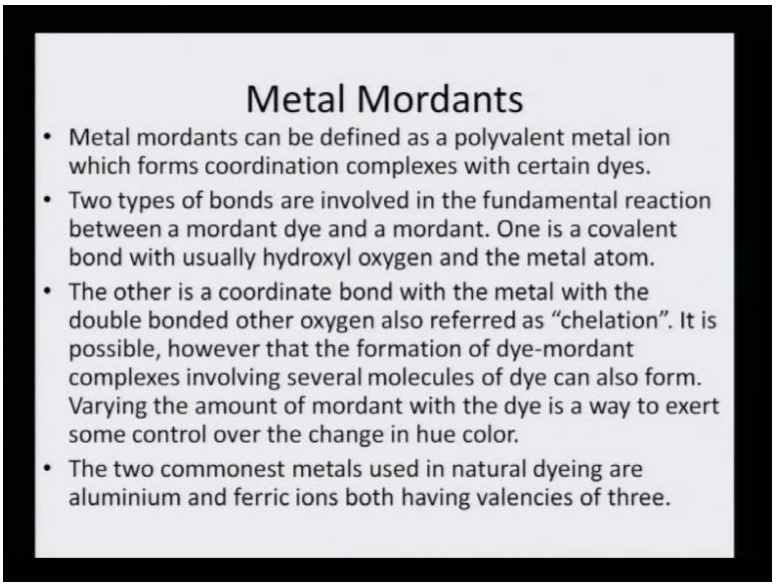

Metal mordants can be defined as polyvalent metal ion which forms coordination complexes with certain dyes. Now, we are trying to get into the chemistry. A metal transition metal as you would recall has many oxidation state and therefore, it is called polyvalent metal ion and it has the capacity to coordinate with several positions of the dye. Two types of bonds are involved in the fundamental reaction between a mordant dye and a mordant. One is a covalent bond with usually occurs with the hydroxyl oxygen and the metal atom. And the other is a coordinate bond with the metal with the double bonded oxygen also referred as chelation. It is possible, however that the formation of the dye-mordant complexes involving several molecules of dye can also form. So, you see that it is a nice arrangement.

Oxygens of the dye will participate with the metal of the mordant in covalent bonding and some of the carbonyl groups of the dye which have C double bond O will have lone pair on the oxygen and these lone pair will have a coordinate bond. So, there is a combination of coordinate bond and covalent bond when these mordants are attaching to the fabric and the dye. However, the formation of the dye mordant complexes involving several molecules of the dye can also occur. Varying the amount of mordant with the dye is a in a way exert some control over the change in hue color; hue color is a shade color. The two commonest metal used in natural dyeing are aluminum and ferric ion both having valences of three.

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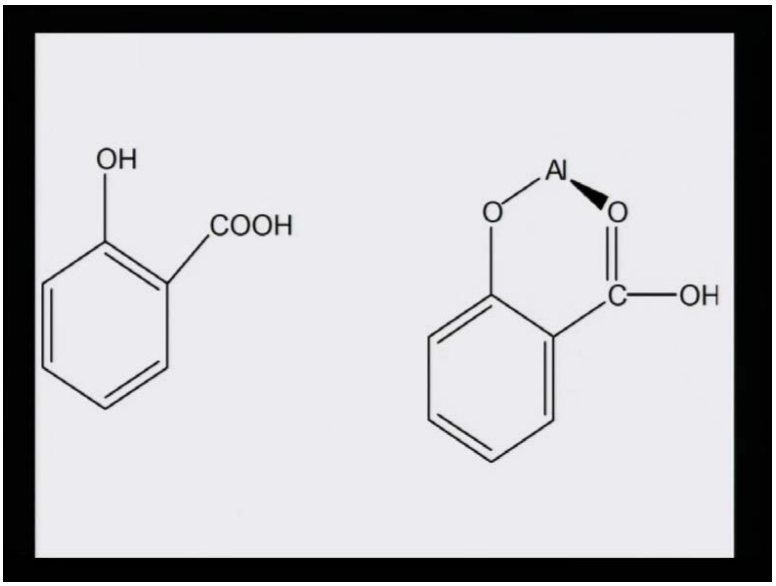

So, you see if we have a simple you know carboxylic hydroxyl carboxylic acid and if aluminum is attached, these is how the l Al O and the Al O. This is a coordinate bond and this is a covalent bond that occurs in the molecule.

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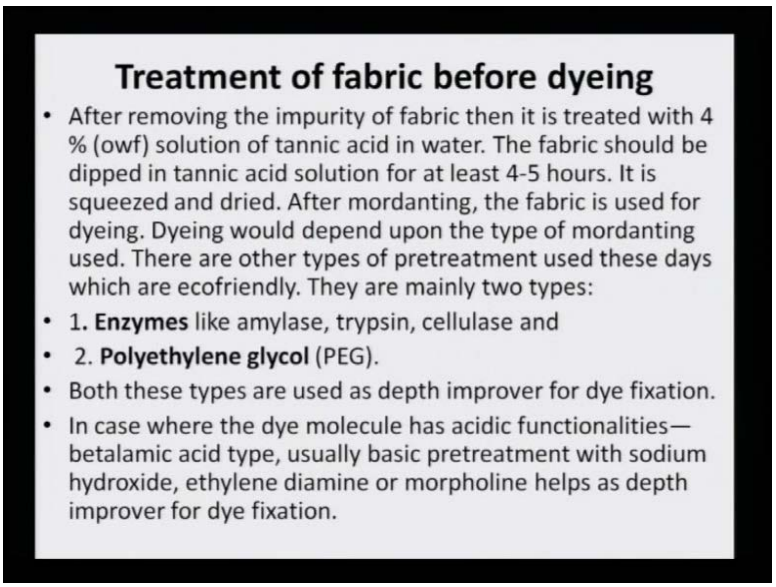

Treatment of fabric before dyeing: After removing the impurities of fabric then it is treated with 4 percent weight of the fabric solution of tannic acid in water. The fabric should be dipped in tannic acid this is for cotton dyeing when we are preparing for free treatment for cotton. Tannic acid is only and only used when cotton dyeing is carried out.

The fabric should be dipped in tannic acid solution for at least 4 to 5 hours. It is squeezed and dried. After mordanting, the fabric is used for dyeing. Dyeing would depend upon the type of mordanting used. There are other types of pretreatments used in these days which are also eco friendly. They are mainly two types; one is the enzyme and the second one is polyethylene glycol or PEG. I mention these two a little while ago. Both these types are used as depth improver for dye fixation.

So, they help in the dye up take or in other words they improve the color depth. In case where the dye molecule has acidic functionalities that is betalamic acid type, usually basic pretreatment with sodium hydroxide or ethylene diamine or morpholine helps as depth improver for dye fixation. So, you see here also we have this acid base kind of combination to improve the color to improve the depth of the color and therefore, they are called as depth or depth improver or dye fixer.

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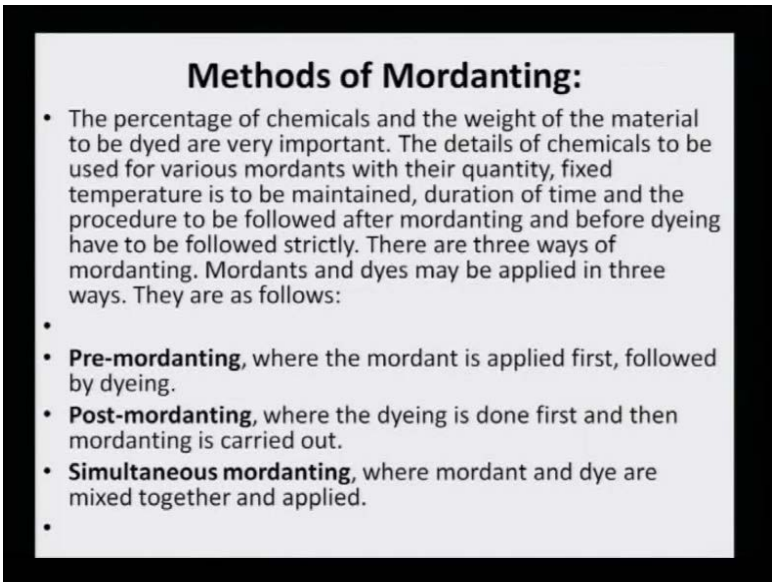

Methods of mordanting: Now, mordant ideally is should be used with the dye that we have understood, but whether to use it before dyeing as a pretreatment or whether it should be used together with the dyeing that is simultaneously or whether the mordanting should be done after dyeing that is post-mordanting or various other options that can be considered when one is trying to play around with different shades of dyeing.

The percentage of chemical and the weight of the material to be died are very important. I told you that all measurements have to be done very specifically. The details of

chemicals to be used for various mordants with their quantity fixed, temperature is to be maintained, duration of time and the procedure to be followed after mordanting and before dyeing have to be followed strictly. There are three ways of mordanting. Mordants and dyes may be applied in three ways. They are pre-mordanting, where the mordant is applied first, followed by dyeing. Post-mordanting, where the dyeing is done first and then mordanting is carried out and the third one is the simultaneous mordanting, where mordant and dye are mixed together and applied. So, you see that three different processers where one can use the combination of dye and mordant are post pre-mordanting, post-mordanting and simultaneous mordanting.

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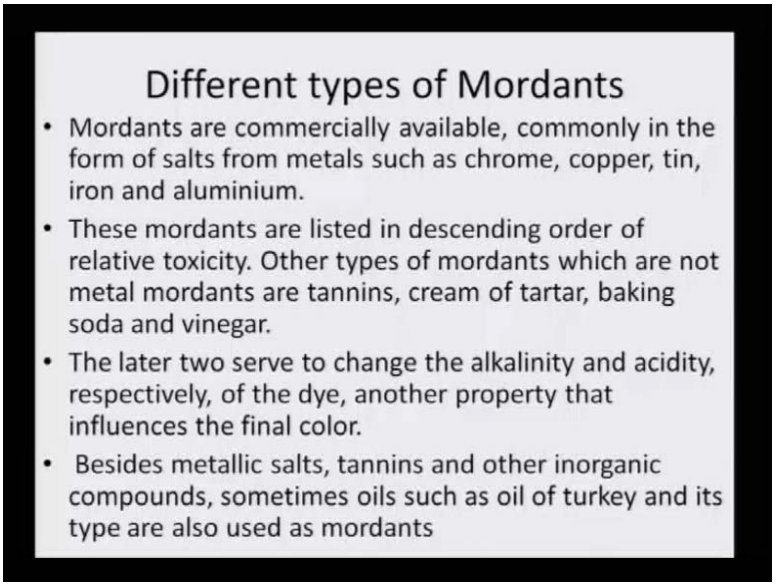

Different types of mordants: Mordants are commercially available, commonly in the form of salts of metals such as chrome, copper, tin, iron and aluminium. These are the common five mordants that are used with natural dyes. These mordants are listed in descending order of relative toxicity. Other types of mordants which are not metal mordants like tannins, cream of tartar, baking soda, vinegar are also like pre-treatments. The later two serve to change the alkalinity and acidity, respectively of the dye, another property that influences the final color.

So, we know that p H plays of very, very vital role and when small changes in p H have to be brought about we cannot use hydrochloric acid and sodium hydroxide, but instead very mild like cream of tartar is a tartaric acid salt, baking soda is mild is sodium

bicarbonate or vinegar which is of dilute form of acetic acid must be added. Besides metallic salts, tannin and other inorganic compounds, sometimes oils such as oil of turkey and its type are also used as mordants, but that is very, very rare in today's world of natural dyeing, but never the less I thought I should mention that there are some other oil based chemicals also which are used as mordants in the mordanting of natural dyes.

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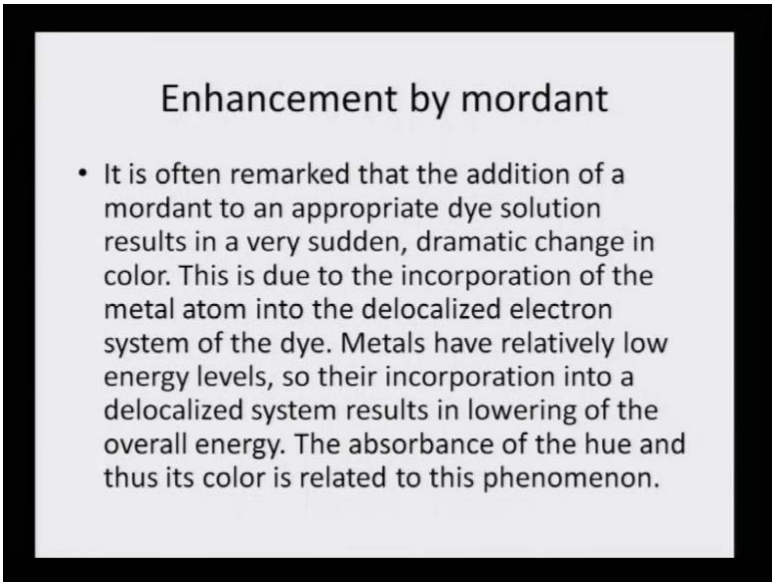

Enhancement by mordants: It is often remarked that the addition of a mordant to an appropriate dye solution resulting in very sudden, dramatic change in color. This is due to the incorporation of the metal atom into the delocalized electron system of the dye. Metals have relatively low energy levels, so, their incorporation into the delocalized system results in lowering of the overall energy. The absorbance of the hue and thus its color is related to this phenomenon. So now, we get down to more understanding of the absorption, and the UV and the optical intensity what happens when the metal comes, the metal is at a low energy and it enters the delocalized electron system and therefore, the hue color improves.

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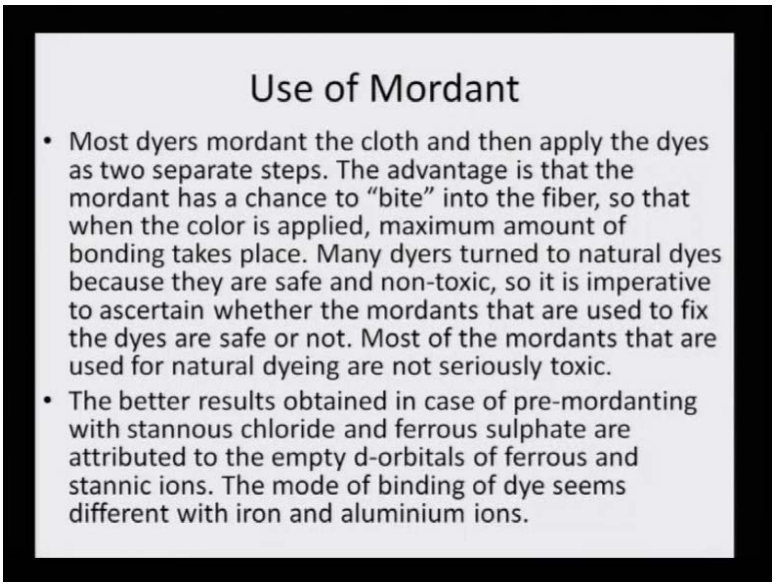

Most dyers mordant the cloth and then apply the dyes as two separate steps. The advantage is that the mordant has a chance to bite into the fiber, so that when the color is applied, maximum amount of bonding takes place. Many dyers turned to natural dyes because they are safe and non-toxic. So, it is imperative to ascertain whether the mordant that are used to fix the dyes are safe or not. I told you a while ago that it should not be that on one hand we are talking about eco friendliness of natural dyes and on the other hand, we are trying to contaminate the you know the environment with the help of all these different chemicals. Then it will not strike a good balance and therefore, one should keep in mind the safety point of view. Most of the mordants that are used for natural dyeing are not seriously toxic. If when can avoid use of chrome mordant or copper mordant it is better.

The better results obtained in the case of pre-mordanting with stannous chloride and ferrous sulphate are attributed to the empty d-orbitals of the ferrous and that stannic ions. The mode of binding of dye seems different with iron and aluminum. If you try to now look at the chemistry, we will see that the empty d-orbitals also participate. So, it is the covalent bond, the coordination bond, and the coordination bond comes from the participation of the d-orbitals. So, we trying to understand what exactly is the main chemical role of a mordant.

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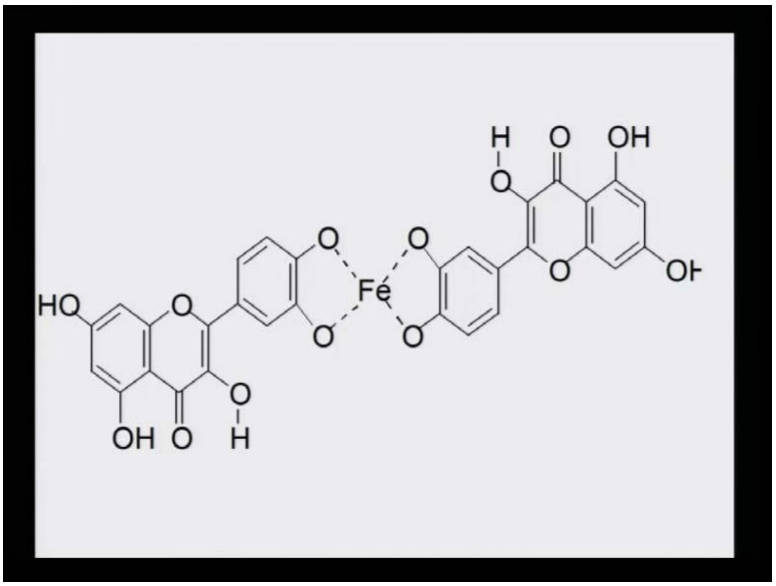

If we try to look at this structure, you see in the middle is the iron and it is connected to four oxygen to two of them it forms the coordinate bond and with the other two it forms coordinate bond, yes.

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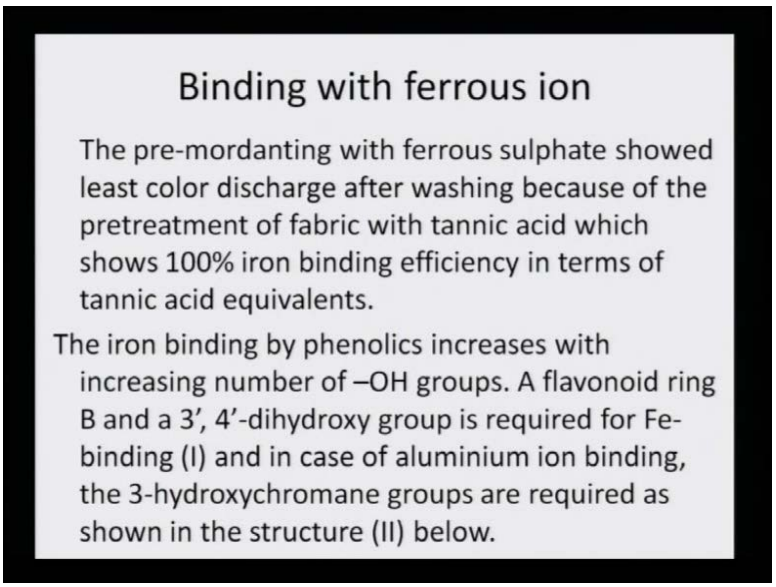

Binding with ferrous ion: The pre-mordanting with ferrous sulphate showed least color discharge after washing because of the pretreatment of the fabric with tannic acid which shows 100 percent iron binding efficiency in terms of tannic acid equivalents. The iron binding by phenolic increases with increasing number of OH. A flavonoid ring B and a 3

prime, 4 prime-dihydroxy group is required for iron binding one and in the case of aluminum iron binding, the 3-hydroxychromane group are required as shown in the next structure. So, we just go back to these structure and see that the two you know alpha hydroxy group or the once which are required for such iron iron attachment.

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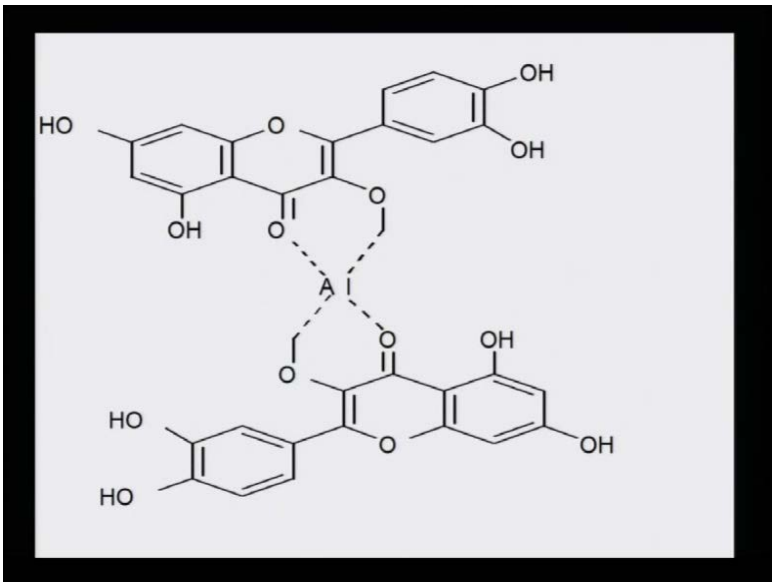

Similarly, if you go the next slide we will see that the carbonyl and the hydroxy that is the chromane part takes part with the attachment. So, you see now you understand that for iron, hydroxy for hydroxy were enough for chelation, but in the case of aluminum it is carbonyl and oxygen, and it is carbonyl and oxygen on the other molecule which brings them together. So, this kind of difference in combining with the metal and the hydroxy of the carbonyl group is very, very typical of aluminum. Whereas for iron only the presence of hydroxy group itself can act as a good chelating agent.

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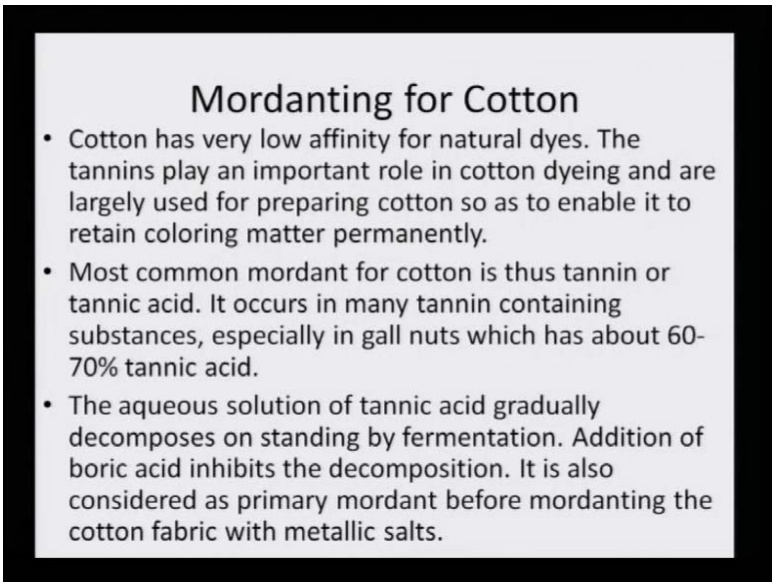

Mordanting of cotton: Because cotton is the most tough to dye and therefore, again and again I am mentioning these because I want you to understand and appreciate that cotton dyeing is the toughest and so many measures have to be taken. A tannic acid pretreatment, a mordant you know pre-mordanting or post-mordanting or simultaneous mordanting is a must. Cotton has very low affinity for natural dyes. The tannins play an important role in cotton dyeing and are largely used for preparing cotton so as to enable it to retain color matter permanently. Most common mordants for cotton is thus tannin or tannic acid. It occurs in many tannin containing substances, especially in gall nuts which has about 60 to 70 percent tannic acid either we can use natural tannins or we can use you know isolated tannic acid.

The aqueous solution of tannic acid gradually decomposes on standing by fermentation. Addition of boric acid inhibits the decomposition. It is also considered as primary mordant before mordanting the fabric cotton fabric with metallic salts. So, tannics first thing that you should understand is that you know tannic acid a biotic material. So, if it is kept for long hours it will detoriate, but sometime addition of boric acid can help in restoring the properties of tannic acid, but if tannic acid solutions are made freshly and the cotton is dipped at that particular time that is the best way do it and it is like a pretreatment before doing the mordanting.

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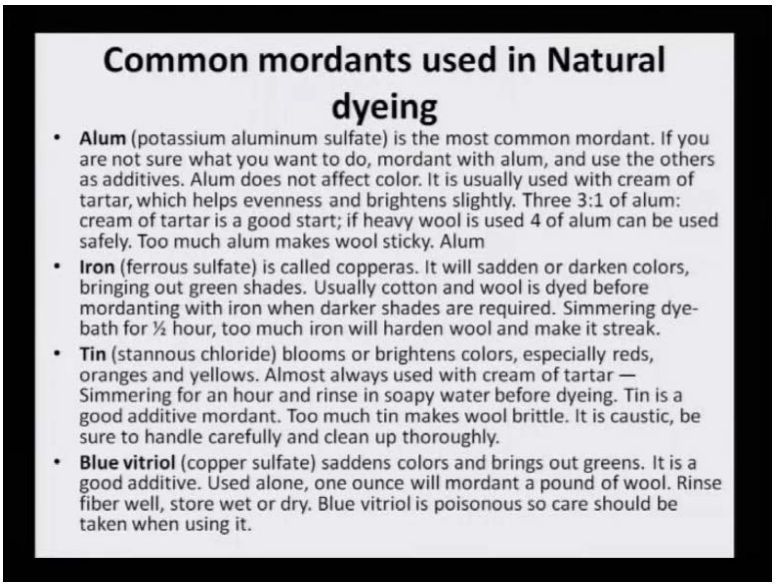

Common mordants: We have already discussed about the alum which is nothing but potassium aluminum sulfate, we have discussed about ferrous sulfate which is also you know it always creates a dark and dull color for the dyes. If suppose a dye is used and deeper shades are required on the darker side then iron mordant should be used. If the color that is to of the dye should be restored on the fabric then alum mordant which is potassium aluminum sulfate should be used. Similarly, stannous chloride also brightens the color and especially it is ideal for red, oranges and yellow. Blue vitriol or copper sulfate also makes the color a little on the dull side. So, one should make the choice what is the shade that is needed to be attain and accordingly the mordent should be chosen from the five common mordents that are normally used and they are alum, iron, tin, blue vitriol and potassium dichromate.

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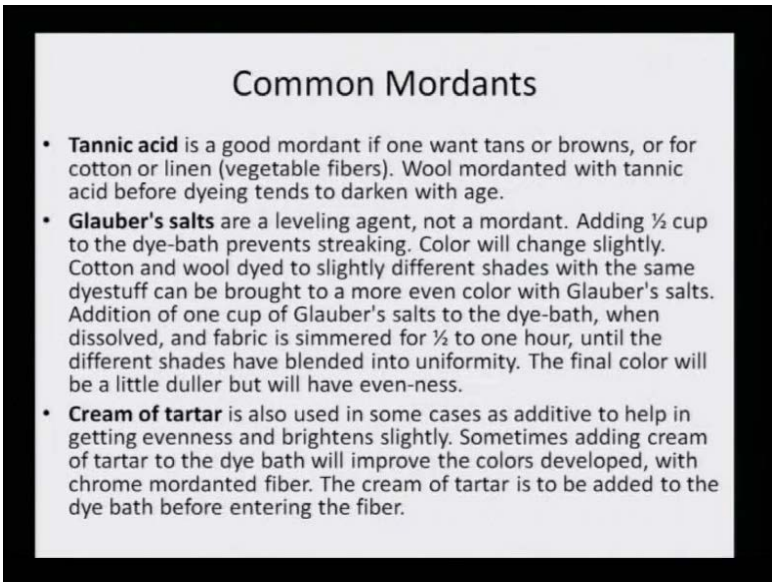

Some other common mordents are tannic acid we have already talked about it, Glauber's salt is like a leveling agent because it is sodium sulfate it makes the dye distribute on the fabric very evenly, cream of tartar is used in some cases as additive to help to get the evenness and bright brighten slightly. So, we have seen that mordents were prepared with the cream of tartar. So, definitely it plays a role both brightening up and making evenness in the dyeing.

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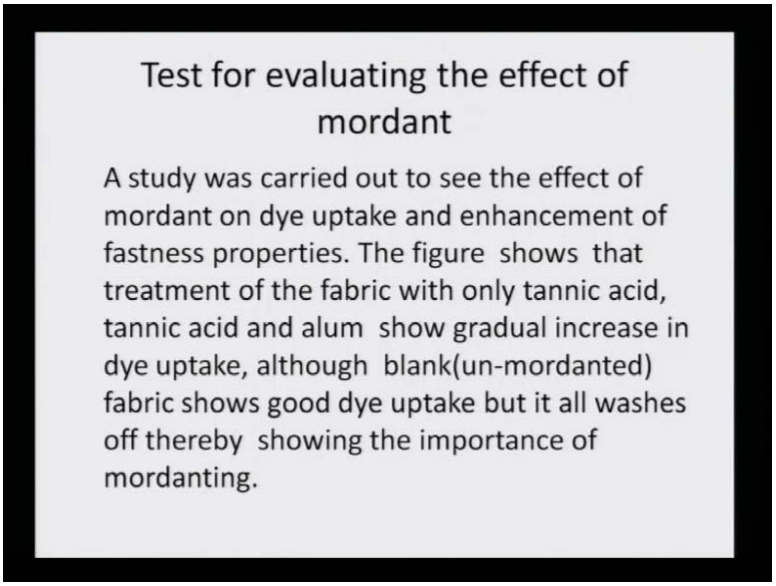

Test for evaluating the effect of mordanting: Now,`whether a mordent is truly participating or not can be only understood by testing their effect of mordenting. A study was carried out to see the effect of mordent on dye uptake and enhancement of the fastness property. The figure in the next shows that you know when the dye was taken a blank tannic acid treatment and tannic acid alum treatment the dye uptake increased.

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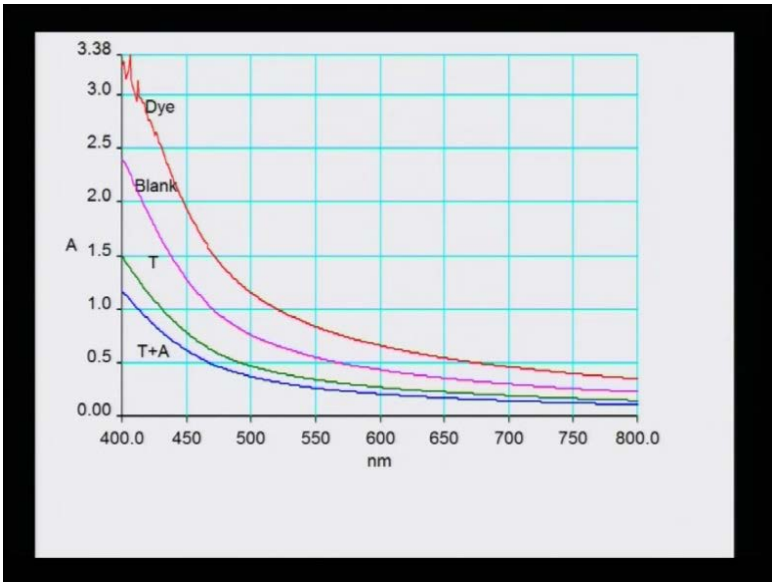

So, the optical density shows that the dye which was initially 3.38 as now reduced in the case, because all the dye has got transferred to the fabric. So, this is the kind of contribution the tannic acid make an mordants make.