Natural Dyes

Prof. Padma Vankar

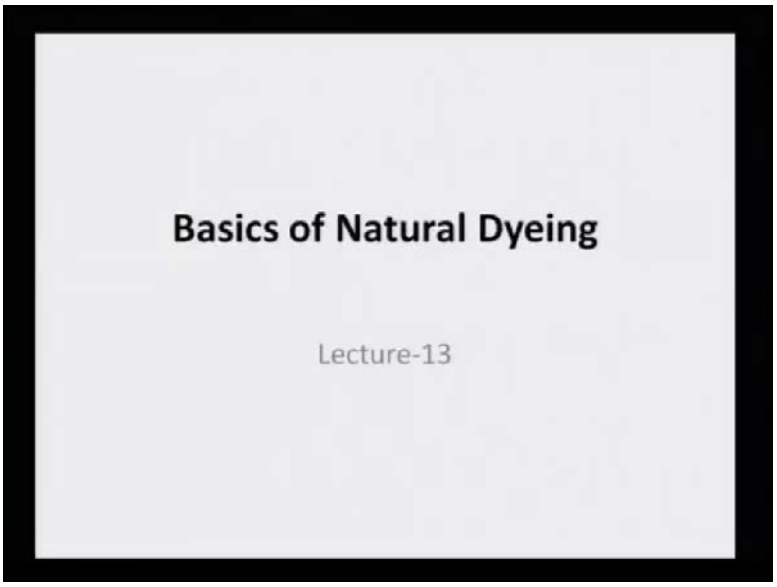
Department of Chemistry

Indian Institute of Technology, Kanpur

Lecture No. # 13

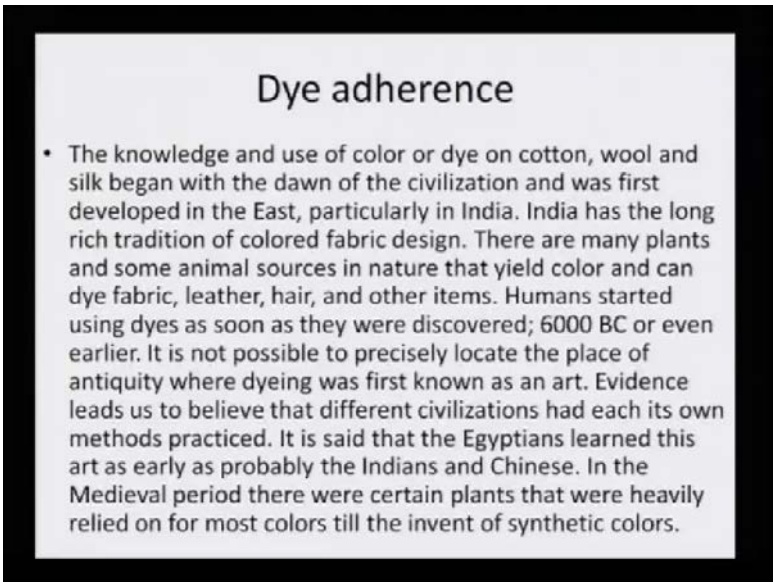
Having learnt about the structure, the constitution, the medicinal properties of natural dyes. We will now start moving towards how natural dyeing is done even that is a little tricky situation and it is to be learnt properly in order to get proper results; it is simple, but it still has its own procedural details which need to be understood.

(Refer Slide Time: 00:54)



So, now in this lecture we have mainly basics of natural dyeing and we will go long and learn about the natural dyeing process.

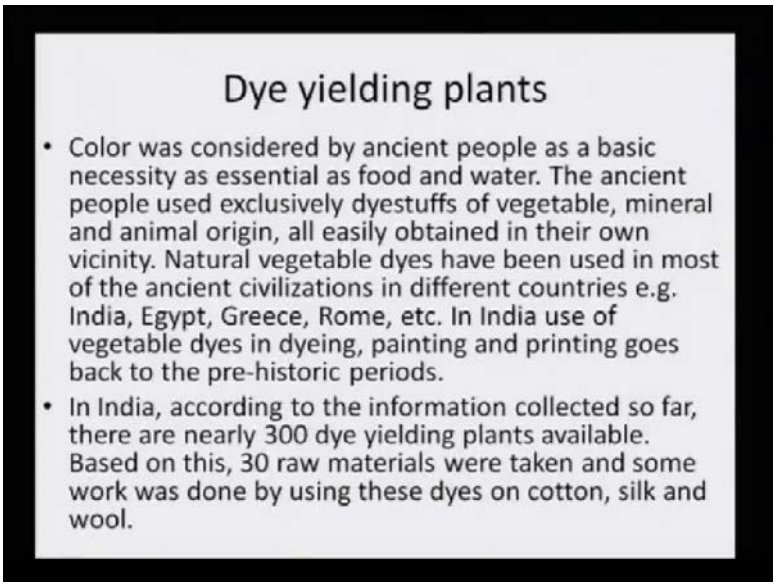
(Refer Slide Time: 01:05)



The knowledge and use of color or dye on cotton wool and silk began with the dawn of the civilization and was first developed in the east, particularly in India. India has the long rich long rich tradition of colored fabric design. There are many plants and some animal sources in nature that yield color and can dye fabric, leather, hair and other items. Humans started using dyes as soon as they were discovered; 6000 B C or even earlier. It is not possible to precisely locate the place of antiquity where dyeing was first known as an art. Evidence leads us to believe that different civilizations had each its own methods to be practiced. It is said that the Egyptians learned this art as early as probably the Indiana and the Chinese. In the medieval period there were certain plants that were heavily relied on for most colors till the invent of the synthetic colors.

So, from this we clearly understand that we whether for runners in the art of natural dyeing. The other civilizations or other cultures that used were Egyptian and Chinese. So, at least that much is confirmed that we started or we were one of the first ones to use natural dyes or natural dyeing.

(Refer Slide Time: 03:09)



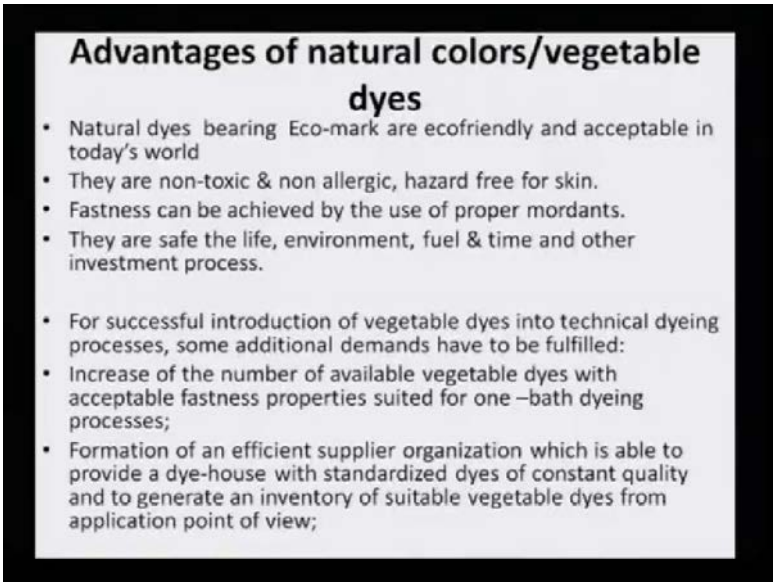
Dye yielding plants: Color was considered by ancient people as a basic necessity as essential as food and water. The ancient people used exclusively dyestuffs of vegetable, mineral and animal origin, all easily obtained in their own vicinity. Natural vegetable dyes have been used in most of the ancient civilization in different countries that is India, Egypt, Greece, Rome, etcetera. In India use a vegetable dyes in dyeing, painting, printing goes back to pre-historic periods.

So, we are just learned and when we are learning the history of dyestuff that time also we learnt mostly the history of the natural dyes, because the synthetic dyes have come in to the market very recently after the advent of the synthetic dyes in 1856 and so on. So, before that it was only natural dyes and there were people who were collecting dye yielding plants from their vicinity, because procuring such plants was easy. It was not that somebody who was staying down south was trying to get a plantation from the northeast - that was not possible; that was not feasible.

People were relaying on three main sources - one was the vegetative force source that is from the plants; the second was the animal source - very few dyes have been extracted from animal source we have seen lack dye and cochineal are two such examples and sometimes some minerals were used which were colored and they were colored because of the transition metal that were present. So, basically they were metal salts or metal oxides of transition metals.

In India according to their information collected so far, there are nearly 300 dye yielding plants available. Based on this, 30 raw materials were taken and some work was done by using these dyes on cotton, silk and wool. And today, of course, in our laboratory cell we have worked on more than 60 plants. So, it is every day new research is happening and every time there is a new dye yielding plant which is I identified or screened. It is evaluated for its dyeing property for on cottons, silk and wool - some are very good with silk and wool, because of their pretentious nature, but others are good on the cellulosic fiber. So, therefore, these dye plants may have different adherability, but they basically meant for dyeing. If we isolate go on isolate many, many, many plants it is of no use unless they are used in application of dyeing.

(Refer Slide Time: 07:19)



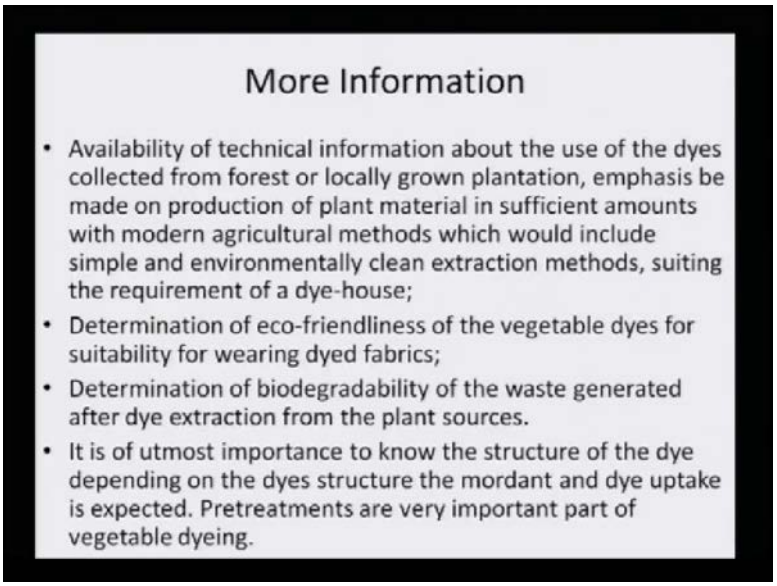
Advantages of natural colors - let us just go on to revise because why is natural dyeing having a revival, what is the reason for its resurgence is because there are certain very marked advantages with these natural colors. Natural dyes varying eco-mark or ecofriendly and acceptable in today's world; they are non-toxic, non allergic, hazard free for skin. Fastness can be achieved by the use of proper mordants; they are safe for the life, environment, fuel, and time, another investment process. So, it it is found that they certainly have more advantageous situation than their counter parts synthetic dyes. They are very safe to handle and for the environment. They less amount of fuel and time is required for this, and therefore the total investment for a natural dyer is much less.

For successful introduction a vegetable dyes into technical dyeing processes, some additional demands have to be fulfilled. Increase of number of available vegetable dyes with acceptable fastness properties suited for one-bath dyeing processes, which means that if the vegetable dyes has to come into the market there are certain modification and acceptability that needs to be honored, otherwise it will not be able to reach the common consumer market.

And the main criteria for that is that the number of dye yielding plants should increase, but these dye yielding plants must have good fastness properties. It is not that we accumulate, you know five hundred plants and we list them we screen them, but the dye content is poor or the dyeing ability is very poor or the dye adherence is very poor or their wash fastness is very poor or their life fastness is very poor in that case these dyes are not be considered. Formation of an efficient supplier organization which is able to provide a dye-house with standardized dyes of constant quality and to generate an inventory of suitable vegetable dyes from application point of view - so it is very important.

Screening is of course, one research activity where newer and newer plants, newer and newer sources must be screened. But after screening, there is another very important exercise that needs to be done and that is that each dye should go through a very rigorous testing procedure of finding out the optical density or finding out how is the dye adherence to which fabric does it really suite, whether it is suitable for cotton or silk or wool these things have to be taken into serious account. And then an inventory should be made that they these are the color gametes which can be obtained from these dyes, and therefore these dyes are worth bringing into the commercial market unless and until this practice is done. It will not be of much utilization.

(Refer Slide Time: 09:56)



More information about the basic dyeing process is that availability of technical information about the use of dyes collected from forest or locally grown plantation, emphasis be made on production of plant material in sufficient amounts with model agricultural methods which would include simple and environmentally clean extraction methods, suiting the requirements of the dye-house. So by now, you at least understand, what are the different methods of extraction of natural dye or vegetable dye, and therefore, these things have to be taken into account. It is not that you know any plant that can be grown locally can be taken for a dye yielding plant – no, with modern agricultural methods the forming has to be improved. So that, that part of the plant - see if we are the trying to extract dye from flowers, the plant must be flowering in huge quantity. So, those parameters have to be set where the floral aspect can be enhanced.

If suppose the fruit has the dye content then the fruiting how fast the ripening of the fruiting can be done; how much in quantity that fruiting can be enhanced by adding some plant hormones. So that, the total yield of this organized forming for the from the point of view from dye yielding plant material should be enhanced.

Determination of eco-friendliness of vegetable dyes for suitability for wearing dyed fabrics. Now, it is very important since we have already learnt about the toxicity of dyes and particularly the toxicity of a synthetic dye. We need to testify this very fact that all the new dyes that have been screened for from the array of natural dye yielding plants

must also be eco-friendly. And for doing that we will dedicate one full lecture for testing the eco-friendliness, but for doing that let me just briefly tell you that it is important to a certain 4, 5 chemicals surely in the dye powder as well as in the fabric. And they are the first is the presence of azo dye which actually releases amines and 22 banned amines we already known have been listed which are derivates of azo dyes.

The second chemical is that when thus cotton is grown pesticide is sprayed on it for a preventing it from various attacks of pests and insecticides and herby sides and all those things are used. Now these chemicals are come as residues on the cotton and when this cotton is then drawn into yarn and then the yarn is drawn into fabric, what happens is that the pesticides residue continues. Now because of that the there is residues of a pesticides in the material and when it is dyed it is it is still persisting in that. So one needs to test these dyed fabrics for the pesticide residues then there are heavy metals because during the process of natural dyeing metals also are used as bridging heads we will spend some time in this also.

In the next lecture, probably we will be talking about the mordants and these material mordants which may remain on the surface of the fabric, and may be hazardous for this skin contact. Therefore, they should be tested for the eco-friendliness. Similarly, when the fabric is processed there is a lot of use of formaldehyde. So, how much of formaldehyde is still remaining in the process fabric also needs to be evaluated, because formaldehyde is also a skin irritant. So, therefore, all these 4, 5 notorious chemicals, the toxic heavy metals, the banned amines, the pesticide residues and the formaldehyde need to be tested.

Determination of biodegradability of ways generated after dye extraction from the plant sources. That is well assured and an ascertained because these plant material after the extraction of the dye or divide of the dye, but has lot of pulp in that. The biotic material is either left for composting which can be used in the agricultural forming processes or they can be burnt in the furnaces where heat needs to be generated. But for burning furnaces, they need to be dried up first and then only these biotic materials can be used. There are two uses, but they are completely biodegradable there is no problem about their biodegradability.

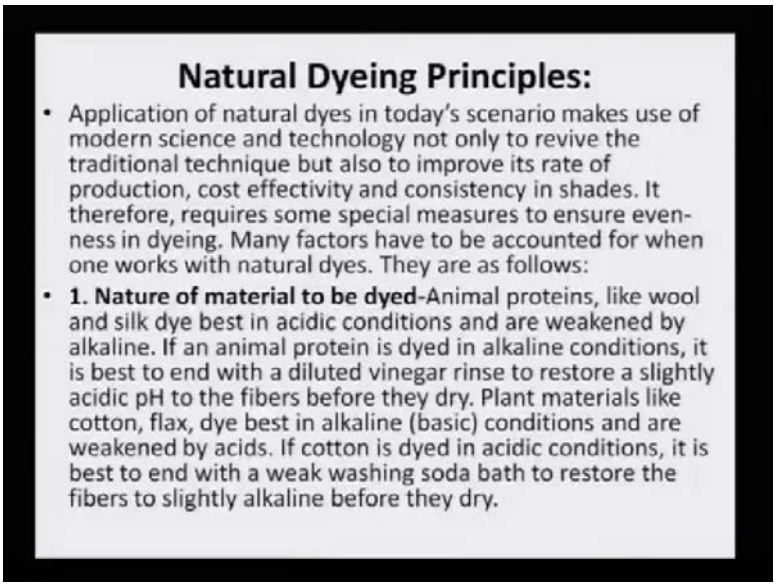
So, therefore, it is important to understand that there is the whole life cycle of the plant is fully complete. The dye is the plant is grown; the dye is taken to the dye factory, and the remaining extractant from or the the extractant is actually used for the dye. And the concentration of that gives us the dye powder or dye paste or whichever way we want to store it. And the biotic material is actually then sent for composting or for burning purposes. It is of utmost importance to know the structure of the dye depending on the dye structure mordant and dye update is expected. Pretreatments are very important part of vegetable dye.

Now there is one very major drawback with the natural dyes that they are not structurally, so modified that they can adhere to the fabric very nicely, in order for this nice reaction to occur. These mordants play a very vital role or some kind of a fabric pretreatment is required. Now these fabric treatments could be a various type use of a metal mordants, use of bio mordants, use of all kind of tannins, and use of enzymes, use of P E G - all this is possible. And all this is done mainly to enhance the dye adherence of dye ability, because otherwise the fabric and the dye are not very compatible. In order to make them come together adhere and stick together, it is needed to have these kind of mordanting methods or pretreatment methods.

If suppose pretreatment is not carried out, the dye will not adhere, and I took the example of curcument in several times, and I will again repeat that because curcument a does not have those oxochromes enough oxochromes to attach to the metal or to attach to the fabric, therefore it is fugitive. Similarly, we find indigo. You will see that indigo also runs of very easily in the first few washing and that is because they you have seen the indigo molecule, the indigo tin it does not have too many oxochromes.

So, as a result there if there is a lack of oxochromes the metals will not attach to it and then the metals do not attach to it the chelation to the fabric will not occur very readily. So, there is a lot of chemistry around this art that one needs to understand the basic structure of the dye. If the dye you must have. So, remembered that the synthetic dyes which I mentioned and gave a comparative idea about the structures had lots of oxochromes and not only hydroxy groups they have sulphonic acid group and there was sodium salt of sulphonic acid and so on and so forth. So, that made a very good conjugation that made very good oxochromic contribution to these chelation process or adherence process natural dyeing principles.

(Refer Slide Time: 19:53)



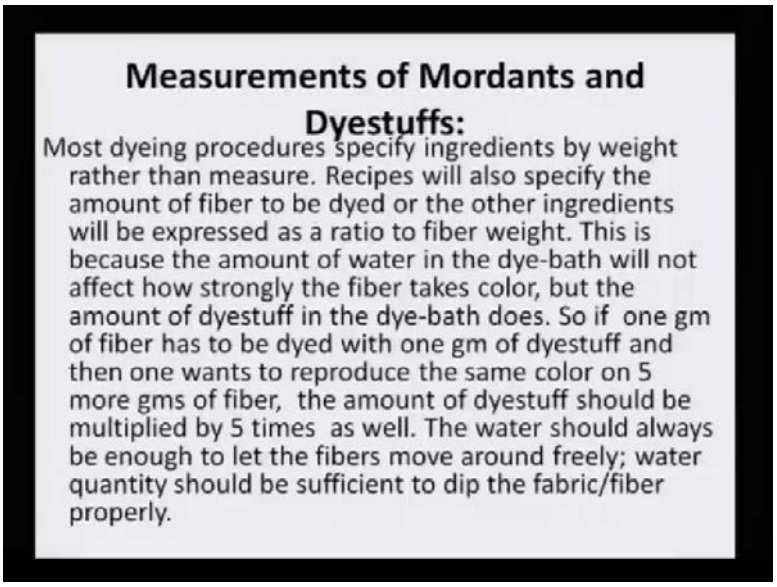
Application of natural dyes in today's scenario makes use of modern science and technology not only to revive the traditional technique, but also to improve its rate of production, cost of effective, cost is effectively and consistency in shades. It therefore, requires special measures to ensure evenness in dyeing. Many factors have to be accounted for when one works with natural dyes, and they are as follows.

So, when we are trying to learn about natural dyeing, we have to keep in mind a few factors; the first factor is nature of material to be dyed. Animal proteins, like wool and silk dye best in acidic condition and are weakened by alkaline. If an animal protein is dyed in alkaline conditions, it is best to end with the a diluted vinegar rinse to restore a slightly acidic pH to the fibers before they dry. Plant materials like cotton, flax, dye best in alkaline or basic condition and are weakened by acids. If cotton is dyed in acidic conditions, it is best to end with the weak washings soda bath to restore the fibers to slightly alkaline before they dry.

So, you see that if we are looking at the material what is a basic nature of material;. if it an animal protein like wool and silk it is best to dry under acidic conditions. And if it is and if the dye solution is not even acidic final rinse vinegar always adds one edge over the dyeing and the color concert very brightly. Similarly, the cotton flax it is best is dye under alkaline conditions, but when the alkali or the pH is you know maintained at a

particular pH of final rinse with acid A. So, washing soda definitely helps in restoring the color of the required shade.

(Refer Slide Time: 22:29)



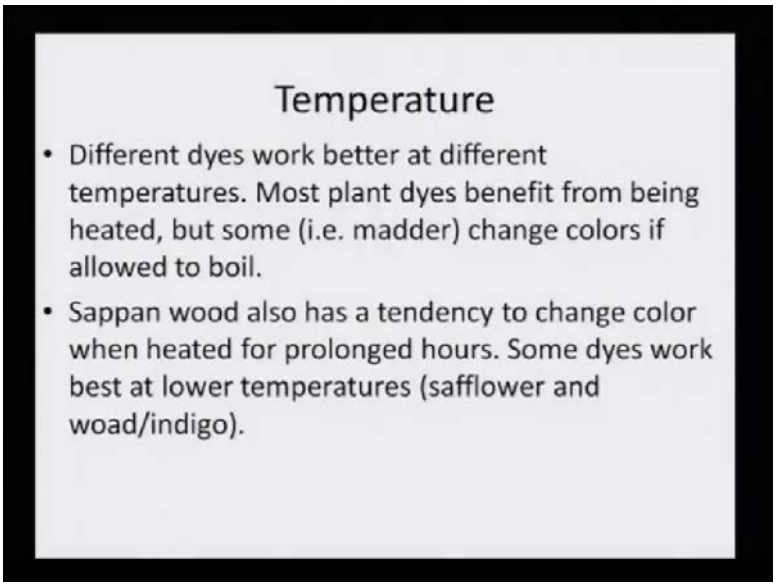
Measurements of mordant and dyestuff: What should be the recipe, how much of mordant should be used with how much of fabric. Because as I mentioned a in my last lecture that these measurements have to be very accurate in order to have shade reducibility one cannot just take any amount and add to an any amount and get the same result. It is not like that just the way when we cook in our kitchen. We have a certain measurement idea and that idea is also followed here. So, most dyeing procedures specify ingredients by weight rather than measure.

Recipes will also specify the amount of fiber to be dyed or the other ingredients will be expressed as a ratio to fiber weight. This is because the amount of water in the dye-bath will not affect how strongly the fiber takes color, but the amount of dyestuff in the dye-bath does. So, it is very important that the water is to fabric, the dye is to water; all these ratios are already fixed. So, that the dye-bath has a definite concentration of the dye powder.

So, if one gram of fiber has to be dyed with one gram of dyestuff and then one wants reproduce the same color on 5 more grams of fiber, the amount of dyestuff should be multiplied by 5 times as well. The water should always be enough to let the move around freely; water quantity should be sufficient to dip the fiber or the fabric properly. Because

if all these parameters are not taken into consideration there what will happen that the evenness of dyeing will not occur. Somewhere the dyes dye powder will show aggregate and the other places will remain faded. So, it will have a very patchy look and any fabric which is dyed in a patchy manner cannot be considered as a good dyed material.

(Refer Slide Time: 25:06)

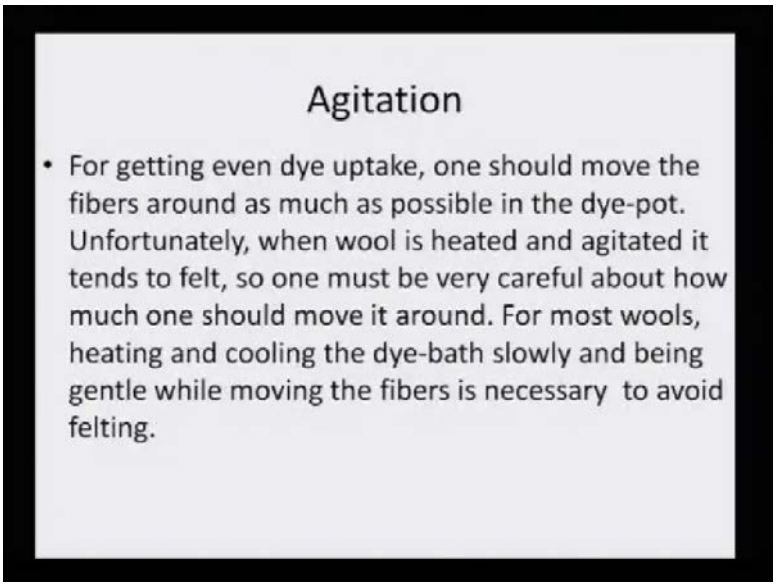


Temperature is another factor which is to be considered, because when we are considering different parameters of basics of natural dyeing, temperature is a must to be considered.

Different dyes work better at different temperatures. Most dye plant dye is benefit from being heated, but some like madder change color if allowed to boil. Now, Sappan wood I gave you an example also has a tendency to change color when heated for prolonged hours. Some dyes work best at lower temperatures that is safflower and wood or indigo. So, you see that cannot have one hard and fast rule that all heating should be done at 100 degrees water boiling, because within that when the water is boiling that is the best temperature for a dyeing that is not true because some of the natural dyes are very heat sensitive. And the examples that were now shown to you are Madder and Sappan wood and they change to very undesirable color and this process of change from good color to bad color is irreversible. So, once it changes to that bad color it is not that cooling the dye solution will bring it back to its original color. So, a result to avoid deterioration of

the dye it is important to keep a check on the temperature. Similarly a check on temperature is required for safflower and indigo as well.

(Refer Slide Time: 26:43)



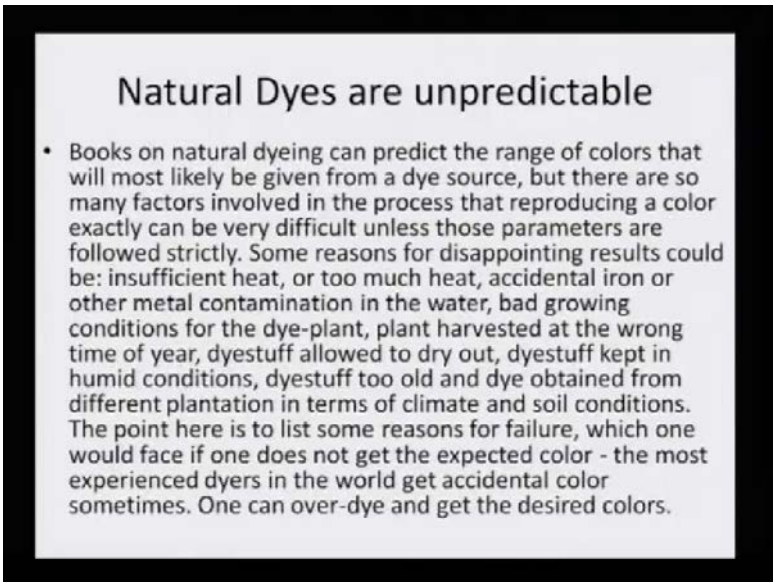
Then it is also important that the rate of circulation of this dye solution should also be maintained which we called as agitation. Agitation means shaking or swirling or mixing for getting even dye uptake one should move the fiber around as much as possible in the dye-pot. Why? Because otherwise dye aggregates will sit on one place and that will cause patchiness, but if the fabric is continuously moved then the patchiness can be avoided, and therefore it is important to understand that agitation like temperature place a very important role in natural dyeing.

Unfortunately, when wool is heated and agitated it tends to felt, so one must be very careful about how much one should move it around. For most wools, heating and cooling the dye-bath slowly and being gentle while moving fiber is necessary to avoid felting. See, what is felting, it is it is like some striations from the wool will come out. Now if one is swirling the wool too hard because it is kind of a tender fiber. So, tender fibers need to be addressed in a little softer manner gentler manner, but cotton and all can be stirred varies or agitated at a high speed.

And you will see that as we go long, I will show you a machine of jigger I will show you a machine on which silk is dyed, and these machines winch machines, jigger machine do

hold the fabric for at a very fast speed but that speed optimization in case of wool is extremely important.

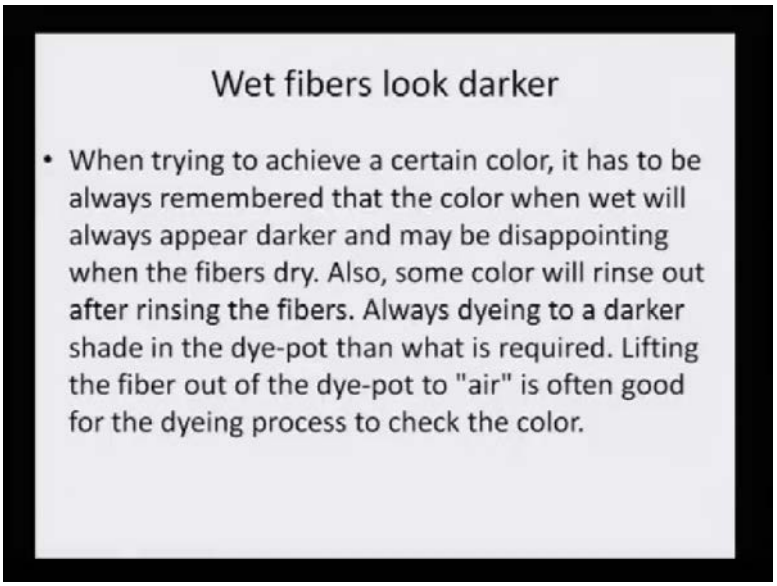
(Refer Slide Time: 28:58)



Natural dyes are said to be unpredictable well that is not surely so any more, but initially books are natural dyes can predict the range of colors, but will most likely be given from a dye source, but there are so many factors involved in the process that reproducing a color exactly can be very difficult unless those parameters are strict followed strictly. Some reasons for disappointing results could be: insufficient heat, or too much of heat, accidental iron or other metal contamination in the water, bad growing condition of the dye-plant, plant harvested at the wrong time of the year, dyestuff allowed to dry out, dyestuff kept in humid condition, dyestuff too old or dye obtained from the different plantation in terms of climate and soil conditions. So, the point here is to list some of the reasons for failure which one would face if one does not get the expected color - the most experienced dyers in the world get accidental colors sometimes. One can over-dye and get the desired color

So, the idea of telling you all this is that, that when that color cannot be reproduced or if it is not reproducible there are so many factors which are listed here one or all can be responsible for this unevenness or unlikeliness or and desirable result. So, in such a case if one keeps all these factors in mind, and tries to eliminate all the mistakes, all the possible mistakes then one can definitely achieve good and correct result.

(Refer Slide Time: 30:54)



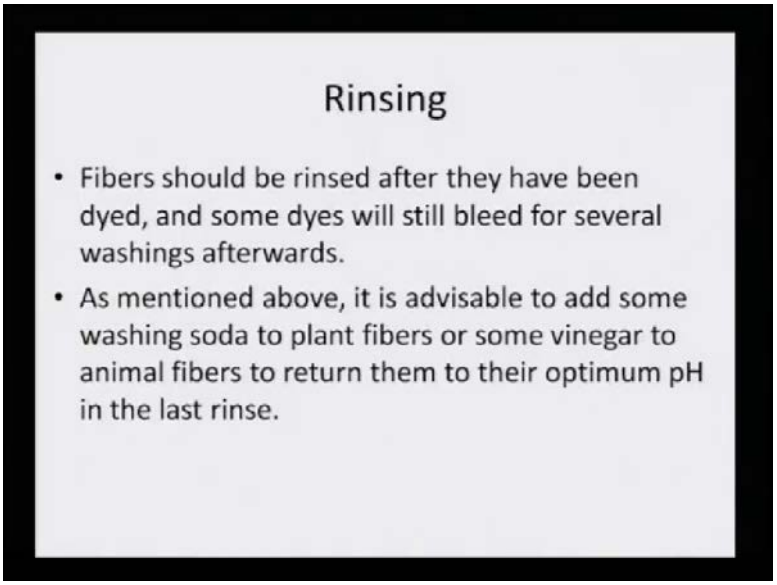
Wet fibers always look darker. When trying to achieve a certain color, it has to be always remembered that the color when wet will always appear darker and may be disappointing when the fibers dry. Also, some color will rinse out after rinsing the fibers. Always dyeing to a darker shade in the dye-pot than what is required. Lifting the fiber out of the dye-pot to air is often good for dyeing process to check the color. See, what happens if we are trying to match the shape, and we try to see that this shade is dark and the wet cloth is a almost matching, but when it dries it become lightering color. So, in such a situation there will be a discrepancy.

Now, in order to avoid that discrepancy, it is fast; it is always advisable that the shade should be darker when it is wet. So, then only when it dries, it may come to the same shade but if it does, if this is not kept in mind, and if a dry cloth and a wet cloth are matched after drying that wet cloth will become lighter in shade and there will be change in shade quality. So, it is important to point out these little, little points because many a times natural dyers tend to make mistakes. So, the temperature, agitation and you know wet fiber being originally a little darker than the dry fiber should be kept in mind.

Now, I also told that over dyeing is possible. Over dyeing is possible, because you see in natural dye if the desired shade is not obtained we can again put back the fabric into the dye bath, and let it agitate at the required temperature for another 1 hour. Some more dye will be taken up. Let me tell you that dye is not taken up one at a time, it is always taken

in substantial quantity at you know at different instances that is there is a why agitation is required. That is the reason why temperature is required, and therefore, if over dyeing is a necessary to get the required shade even that is possible in the case of natural dyes.

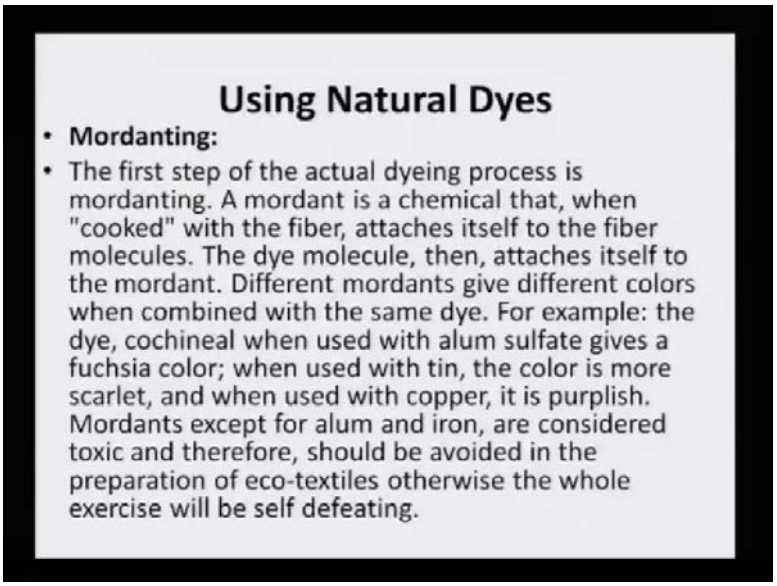
(Refer Slide Time: 33:41)



Rinsing: Fiber should be rinse after they have dyed, and some dyes will still bleed for several washings afterwards. You may have noticed that colors like magenta, peacock blue always run into the water or we say in terms of dyers language bleed. Now, this bleeding can cause that this color will run into another cloth is the there are washed together. So, that that is the reason that all the surface dye must be washed off by this rinsing process, otherwise, if there would be a tendency to bleed. As mentioned above, it is advisable to add some washing soda to plant fiber or some vinegar to animal fiber to return them to their optimum pH in the last rinse.

We just learnt a little while ago that if we are dyeing animal fiber, we must finally give it a final rinse with vinegar; if we are dyeing cellulosic fiber, we should give a final rinse with washing soda - that is precisely why because the dye should adhere to the fabric and there the color should not get run off in the rinsing process.

(Refer Slide Time: 35:08)



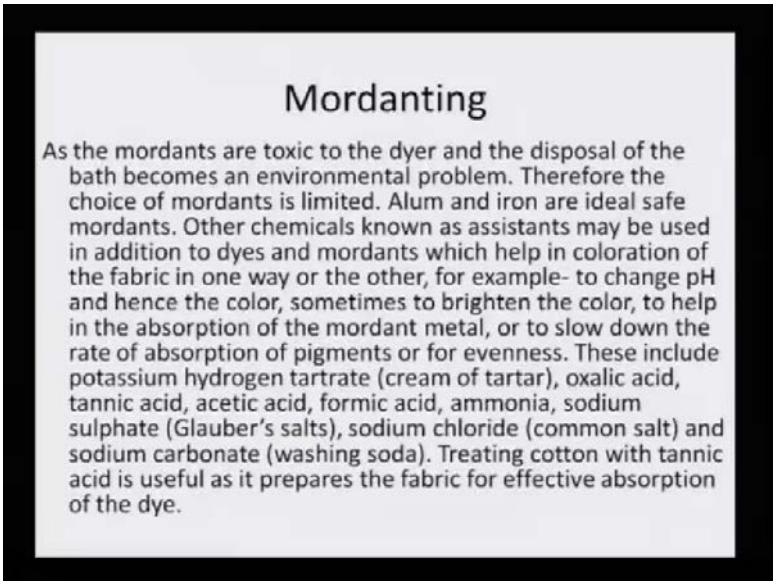
So, using natural dyes mordanting is one very important step. The first step of actual dyeing process is mordanting. A mordant is a chemical that when cooked with the fiber, attaches itself to the fiber molecules. The dye molecule, then, attaches itself to the mordant. Different mordants give different colors when combined with the same dye; this is a very important factor.

Now today you have learnt, so many new things about natural dyeing, but when you are talking about natural dyeing, you need to understand this whole fundamental of mordant; it was not necessary to use a mordant in the case of synthetic dye and the synthetic dyeing. But when it comes to natural dyeing, the role of mordant is very prominent. And mordants are nothing but different types metal salts of transition metals or they could be some kind of pretreatments of the tannin types or they could be enzymatic pretreatments or they could be pretreatments with poly ethylene glycol and so on.

So, at least you must be able to understand that mordants in natural dyeing play a very vital role. For example, the dye, cochineal when use with a alum sulfate gives a fuchsia color; when use with tin, the color is more scarlet, and when use with a copper, it is purplish. Mordants except for alum and iron, are considered toxic and therefore, should be avoided in the preparation of eco-textile otherwise the whole exercise will be self defeating.

So, you see that the same dye extract can give different dye colo, if the mordant used is different. And they the example of a cochineal is a very beautiful example because it is a nice dark purplish dye - a pinkish purplish dye and when it is used with alum sulfate it remains in that color mostly. But when tin mordant is used, it becomes scarlet and when it is used with a copper, it becomes more on the purple or the bluish site. So but copper chromium these are very toxic mordants. So, it should be a practice that these should be avoided unless and until they are used in very small quantities and the eco-friendliness test shows that they are in trace quantities on the surface of the fabric; otherwise, they should be avoided and the use of only safe mordants like alum, iron should be encouraged, to some extent even tin can be used. So, with this we now move onto the next chapter of mordanting and at least you will now appreciate that mordanting will bring in many more new information.

(Refer Slide Time: 38:33)



As the mordants are toxic to the dyers and the disposal bath becomes on environmental problem. Iron and alum are the ideal mordants.