Natural Dyes

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Lecture No. # 27

Today, again we will talk about Anthocyanin pigment. Why because it is so important and it is so widely naturally occurring that it needs another lecture to discuss.

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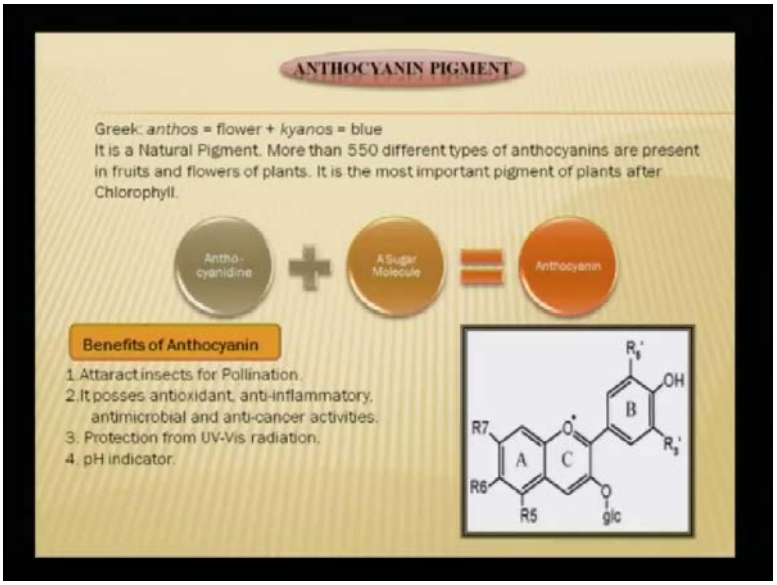

And one very common plant that we see around us, which is a very big source of anthocyanin dye and that is rose flowers. You must have seen that you know there are so many varieties of roses, but the native red colored rose has so much of anthocyanin pigment that it can be a source of huge source of this natural dye. Another thing, because it is you know use for offering to the god and goddesses, this flower is abundantly also available from the temple ways. So, it can be a real good source of natural dye, and therefore we will dedicate one more lecture to this anthocyanin pigment and its use. And today's focus will be on the rose pigment that is derived from the rose flower.

As you all know that it is a natural pigment, and more than 550 different types of anthocyanins are present in fruits and flowers of plants that grown in India. It is the most

important pigment of plant after chlorophyll. So, you see, I mean chlorophyll is the green pigment which we all know and the entire photosynthesis and all that happens, because of the chlorophyll pigment.

And next to that is the anthocyanin; so it is that widely and abundantly available. When anthocyanin, when we talk about anthocyanin dye, we are talking about anthocyanidin plus sugar and as what I would go back again to the slide and show you what it means. These anthocyanin dyes have other roles also to play. They attract insects on pollination; it posses antioxidant and anti-inflammatory, antimicrobial and anti-cancer activities and protection from UV is radiation. And it has also been use as a p H indicator for the first time in our laboratory. So, you see that it has a lot of features that need a tension to describe.

Now, so today we are going to look at the newer dyeing approach with rose anthocyanin, and therefore we must dedicate some time to the way the rose anthocyanin is extracted. We must see how it is use for dyeing and what are the shades and the color depths that can be derived on different fabrics that is cotton silk and wool. So that we know that there is a huge applicability and we can prove that.

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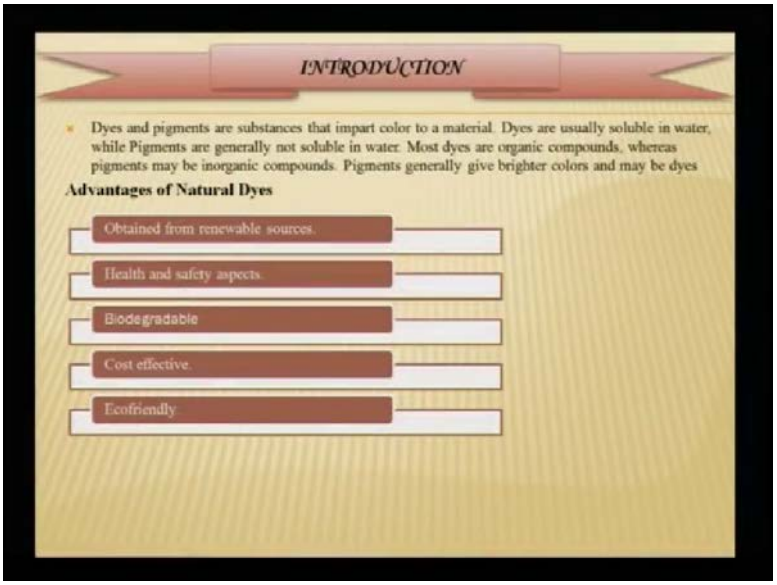

As we all know that the dyes in pigments are substances that impart color to a material. This is now time and again we have been talking about this dyes are usually soluble in water, while pigments are generally not soluble in water. Most dyes are organic

compounds where as pigments may be inorganic compounds as well. Pigments generally give brighter colors and may be dyes. If in are also they are brighter than the dyes, but still dyes have more applicability. Pigments are only use for printing and other purposes because of their insolubility or because of their insoluble nature.

Now, there are several advantages as I have been talking about the advantages of natural dyes, but let us recap and you know let us have a relook at it. They are obtain from renewable sources and our emphasis has been that we should use plan parts which grow again and again instead of taking the roots and destroying the plant ones for all. It is better to take either the flower or the leaves or the stamp which can be regenerated. They have health and safety aspects; they are bio degradable, and now they have been proven to be cost effective, and they are echo friendly because of the bio degradability as well as compatibility with the nature.

Now, one thing that there was a myth that it is not cost effective because that time they were no organize forming the availability was a big factor and they were very few companies were making natural dyes. So, therefore, they were selling at a very exorbitant price, but that scenario has completely change in the last few years, and now we have natural dyes available from several companies who select almost at a very nominal price. And when we were trying to look at the dissemination of the natural dye technology lecture, I had also shown you that there is only a marginal change in the dyeing cost, a cost varying from 4 to 9 rupees in the case of a shirt and may be 50 rupees in the case of a saree. So, that is a kind of you know little cost enhancement, but look at the other aspect the value addition that the natural dyed fabric brings in is far more than the cost that is you know enhanced.

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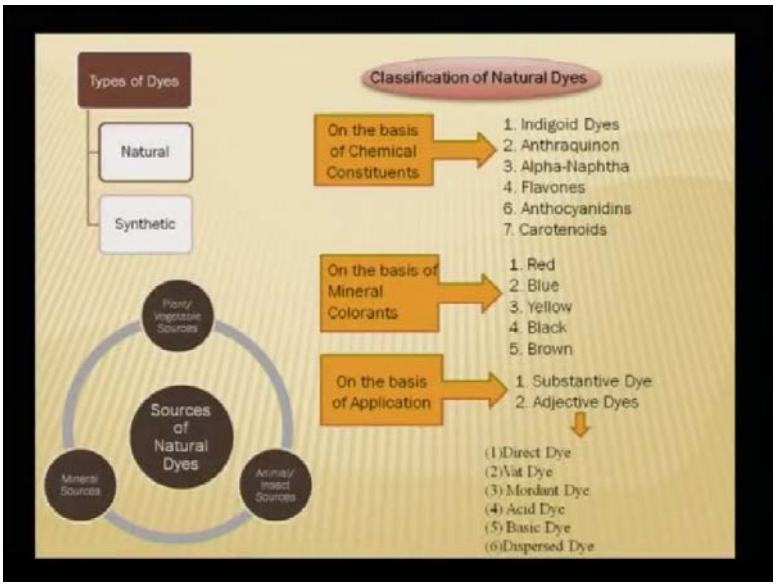

Now, we just recapitulating the whole scenario of dyes and natural dyes. So, let us try to look at this particular slide where we know that there are two types of dyes - natural dyes and synthetic dyes. We have been talking about both, because I want to give you an overview and then it is up to you to decide what is good, what is bad. Because there are goods with synthetic dyes also, there are bad points with natural dyes also. So, one has to out way and whatever is available that must be trapped.

Now, classification of dyes we have seen that on the basis of chemical constituents they can be indigoid dyes, anthraquinon dyes, alpha-naphtha dyes, flavones dyes, anthocyanin dyes and carotenoid dyes. Now today's lecture will be mainly emphasizing on the anthocyanidin dyes. On the basis of their colorant or color present that is there the dyes can be segregated in to red types of dyes or blue types of dyes or yellow dyes or black dyes or brown dyes.

However on the basis of their you know, how they hared to the fabric again another definition can come that they are substantive dye or adjective dye and among the adjective dye it could be direct dye, vat dye, mordant dye, acid dye, basic dye and dispersed dye. So, these are the various nomenclatures, but when we are talking about natural dyes they as we saw that they were mostly mordant dyes, and therefore we have to concentrate only on the mordant dyes.

So, this is how they can be also source from plant source all the anthocyanin dyes are source from plant source, but there are other natural dyes sources like animal source particularly for cochineal and lack dye and there are mineral sources like some of the salts have transition metal salts are color they can be used as dyes also.

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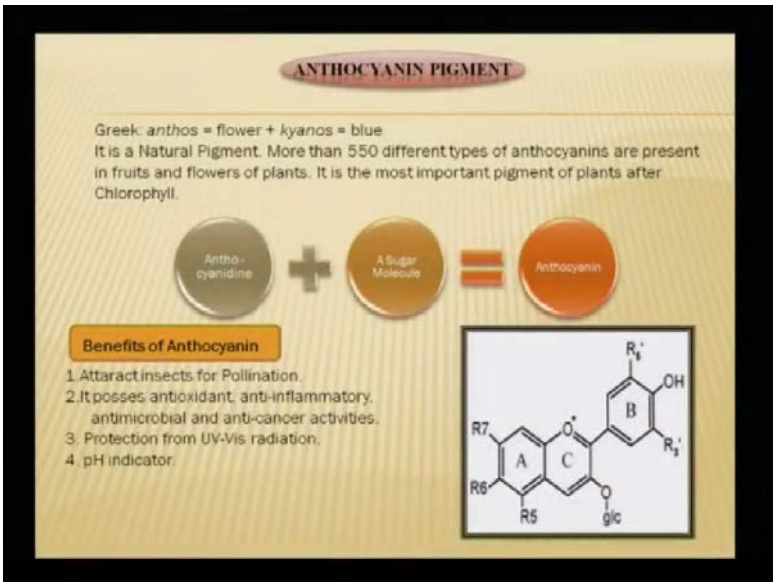

Now, this is the most important slide that we must concentrate now this particular moiety you see A, B and C. They are three rings which are now nicely beautifully connected and you see that I wanted to draw this picture and make it very clear to you because you see this B rings functionality and A ring functionality is very important and that sugar moiety that is hanging at the position of in the C ring is also very consequence. Now because of this kind of arrangement in the molecule, it is possible that the molecule can adjoin the metal very easily.

Also they can kelate with the metal and the kelate of the metal can then add on to the fabric the natural fabrics; that is cotton silk and wool. So, therefore, we can say that anthocyanins have a very good structural detail very compatible to what is required for an ideal natural dye. Because as when we were talking about anthoquinon dyes. I have told you that the alpha hydroxyl groups can bring in the metal kelate very easily and that is what makes eliserine a good dye. Similarly, because of these R prime, R 3 prime, R 5 prime and R 5, R 6 and R 7. These functionalities can be hydroxyl groups or they can be other groups which can be helping in the metal kelation.

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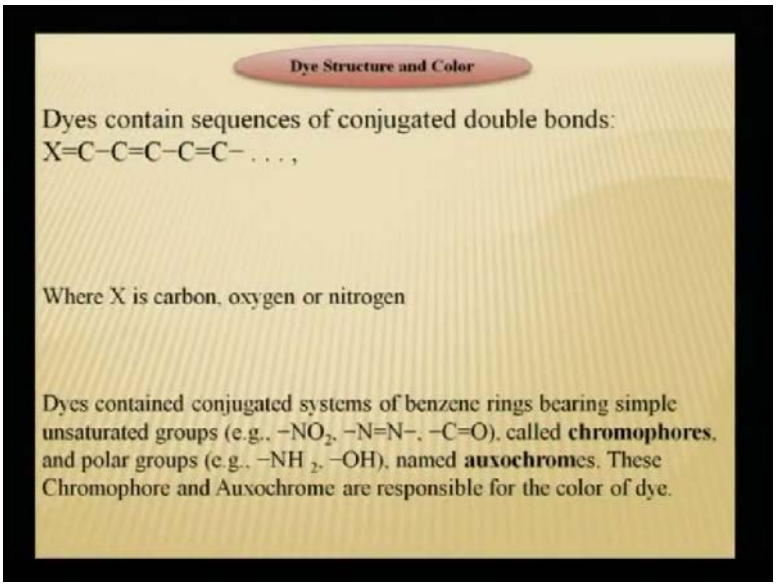

Now when we try to understand, because we know that the dye and its structure has a great importance in the fact that the more the conjugation in the dye the better or the dark is the color. Dyes contain sequence of conjugated double bonds that is you know you have C double bond c and so on where X is carbon oxygen or nitrogen.

Dyes contained conjugated system of benzene rings bearing simple saturated groups like nitro groups HO group carbonyl groups and these are called chromophores. We have already learnt all these this is just like a recapitulation. So, that now we can connect two and two and understand it in a much better manner.

And the polar groups like NH 2 or OH groups which act as not only help in the keylation of the metal atom, but also are called auxochrome because they enhance the activity of the chromosphore. these chromophore and auxochromes are responsible for the color of the dye.

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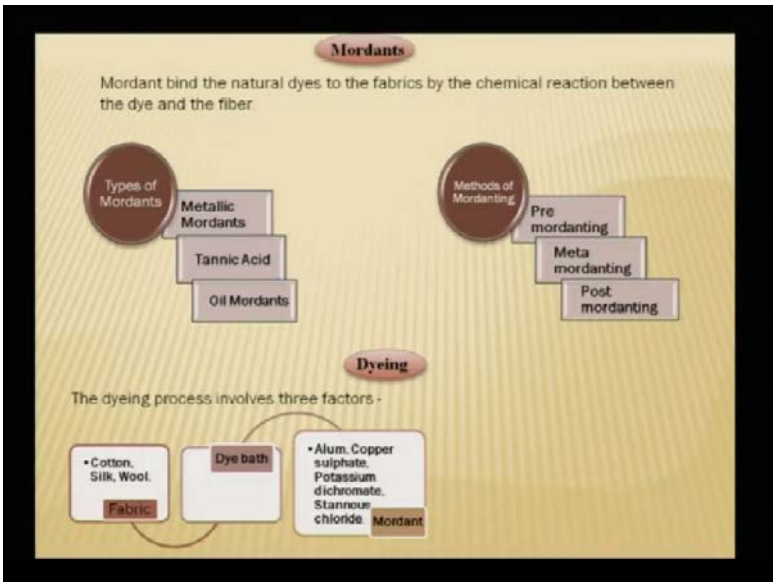

Now, when we come to now ones the dye part is understood dye is actually whether natural or synthetic must have conjugated system. This is one of the most important criteria to be categorize as dye plus it must have a chromophoric group and an auxochromic group only. Then it you know actually becomes an ideal model for being called as a dye.

Now, ones we have understood about the dye we also know that natural dyes need mordanting because they are mordant dyes. So, mordant binds the natural dyes to the fabric by chemical reaction between the dye and the fiber. So, as I told you that here is the dye here is the fiber and the mordant act as reign hire. So, be it any type of fiber cotton fabric cotton silk or wool when it is put in the dye bath along with you know mordant such as alum copper sulphate, potassium dichromate, stannous chloride. These are the four mordents that we try that dyeing can be carried out it can be also pre mordenting, meta mordenting or post mordenting.

So, we know that there are three modes of mordant can be added in the beginning after the scouring of the fabric and in the case of cotton we use tannic acid treatment and then after scouring there is a tannic acid pre treatment and then mordenting. So, if the mordenting is done before hand it is called pre mordenting. If the mordant or the dye are put in the same dye bath and both are done simultaneously it is called simultaneous mordenting or meta mordenting and the third option is that first after discovering and

after the dyeing it is then finally, mordents with these mordents. So, the mordents that are used are alum copper sulphate, potassium dichromate and stannous chloride.

Now, time in again I have mention that the use of copper and chromium should be minimal and if possible if one can avoid it is even better. But many a times what happens is that we need to have shade variation and from the same dye extract it is possible to get different shades by altering these mordents.

So, as what I told you that there are different types of mordents and here we will only discuss the metal mordant and the tannic acid which is used as a pre treatment metals of mordenting we already know that pre mordenting, meta mordenting and post mordenting I have just explain to you. So, it is now you know more like recapitulating what we had done in the last class with the anthocyanin dyes and also to make you understand that not only hibiscus even rose which is. So, abundantly available can be a very rich source of anthocyanin dye.

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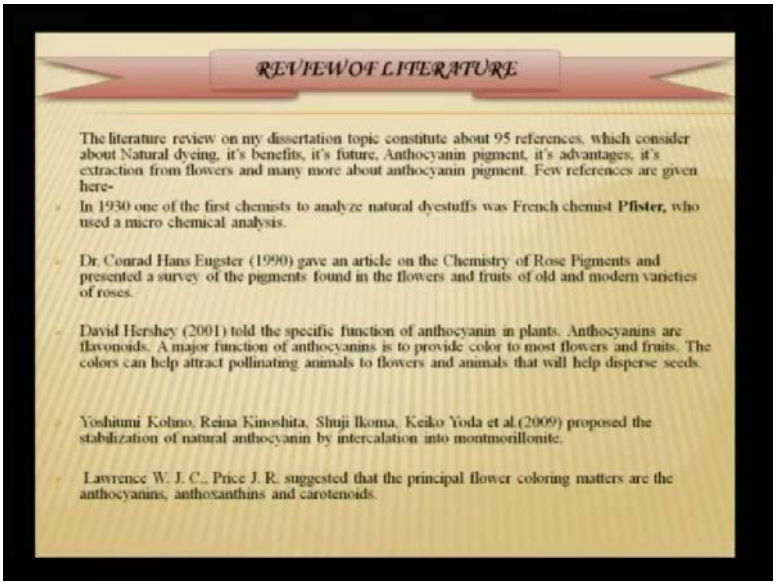

And not many people actually have been in to the use of this literature review, shows that no there are 95 references and not many people have worked on the chemistry of rose pigment and looked at it from this point of view of the source of textile dye. However, they have been some you know sporadic information here and there, but nobody has actually worked on anthocyanin dyes people have worked in the various you know

chemistry; that means, what are the chemical components present in the anthocyanin dyes derived from rose.

But they have not seriously looked in to a possibility of using this anthocyanin dye as a source of textile dye. So, Lawrence at all have found out that the principle coloring matter or anthocyanin, anthoxanthins and even some carotenoids exact present similarly. You know the analysis done by Yoshiumi Japanese group they propose that stabilization of natural anthocyanin can be done by intercalation with montmorillonite.

So, you see they were only working at an aspect as to how to trap this dye and how to because as you would know that because of the positive charge on the oxygen. It is a dye which is very pH sensitive and this we had discussed in great detail in the last lecture that because of its pH sensitivity anthocyanin dyes were not considered so far for textile dyeing.

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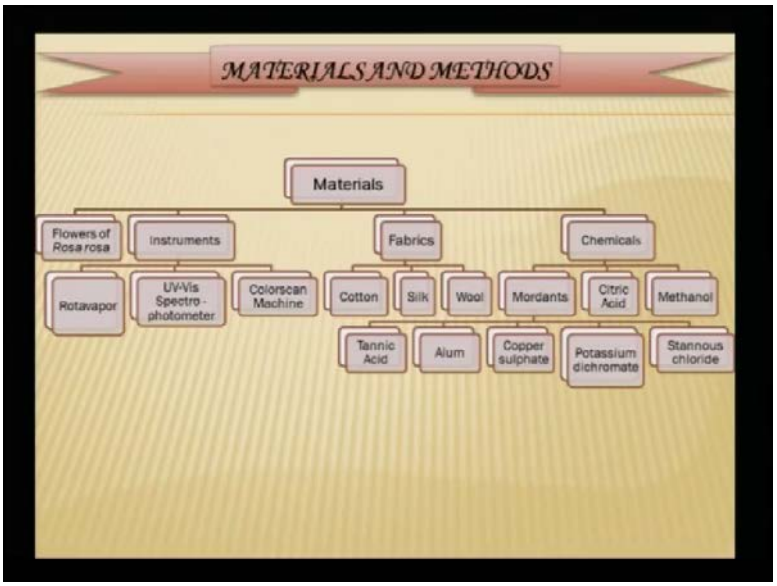

So, now if one has to take a look at how the material can be used for dyeing purpose the flowers of rose which the botanical name is rosa rosa is actually taken and it is extracted and the instruments that were used for the measurements were UV is spectrometer and color scan machine and the fabrics. They were three types of fabric they which were used that was cotton silk and wool.

The chemicals that were used were mordents that is the metal mordents alum copper sulphate, potassium dichromate and stannous chloride and citric acid and methanol and cotton was treated with tannic acid only, but silk and wool were only treated with the mordents that is the alum copper sulphate, potassium dichromate and stannous chloride. So, this is how the whole from overview of the procedure what all was used and how they were used.

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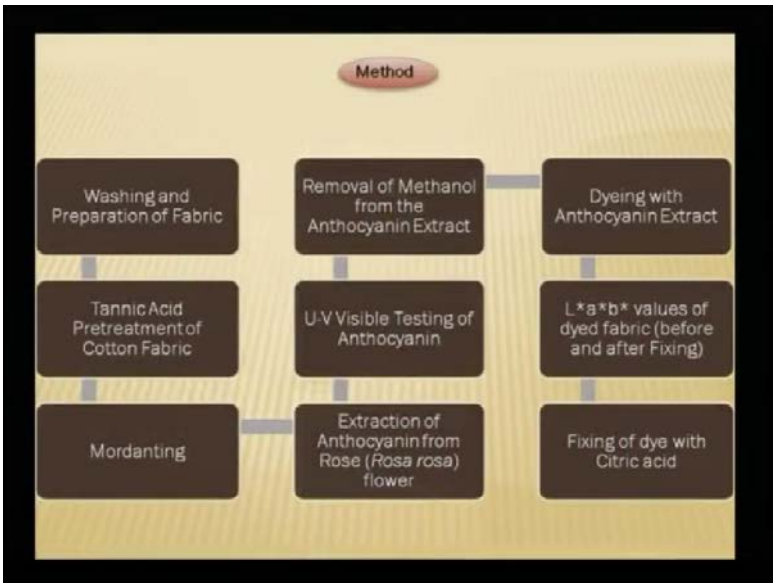

The methodology is that washing and preparation of the fabric is carried out first then the extract of the methonolic extract of anthocyanin is done. But while doing the methonolic extract little bit of citric acid addition can always enhance the extract quality and the more and more dye can come in to it.

Then the dyeing of the citric this fabric with the anthocyanin extract can be done, but before we do the dyeing of cotton fabric tannic acid treatment is carried out then it is dried then mordenting is carried out. Now in order to see whether the dye is really anthocyanin or not UV Visible spectrophotometer testing is carried out of the extract.

The extraction of anthocyanin dye actually is the most crucial part because the more we can extract the color from the biotic material the fade the more concentrated will be the solution and that can be figured out. If the biotic material is getting faded; that means, all the colorant has come in to the methonolic acidified methonolic solution. So, that is you know test to evaluate whether all the dye has to come or not it is not required to heated

for two long time only slight heating can actually bring out the color and ones that is done ones the dyeing is carried out the L a b values are evaluated.

And before doing that you know dye before the dyeing rather before the dye fixing and after the dye fixing the L a b values to show. How much of the dye has actually impregnated in to the fabric. And therefore, there is a need for dye fixing and citric acid is one very good example which was tried out it is a mild acid and it does the retention of the color on the fabric the dye at haration enhances.

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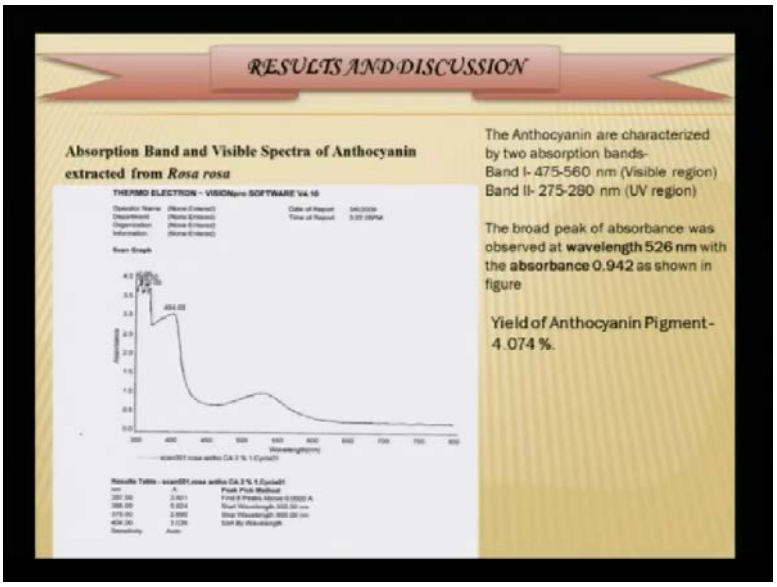

Now, if we try to look at the you know the UV visible spectra of the anthocyanin derive from rose. You can see that there is a very distinct peak and anthocyanin are known to have peak between one bond in between 475 to 560 as what we saw in the case of viscous also which falls in the visible region and the second band which is at 275 to 280 is in the UV region and rightly so we found a very appropriate band at 526 nano meter which shows an absorbance of 0.94 and the yield that was calculated was about 4 percent. So, you see that this dye this dye source already has just from the flower petals 4 percent of dye can be extracted readily from the rose dye.

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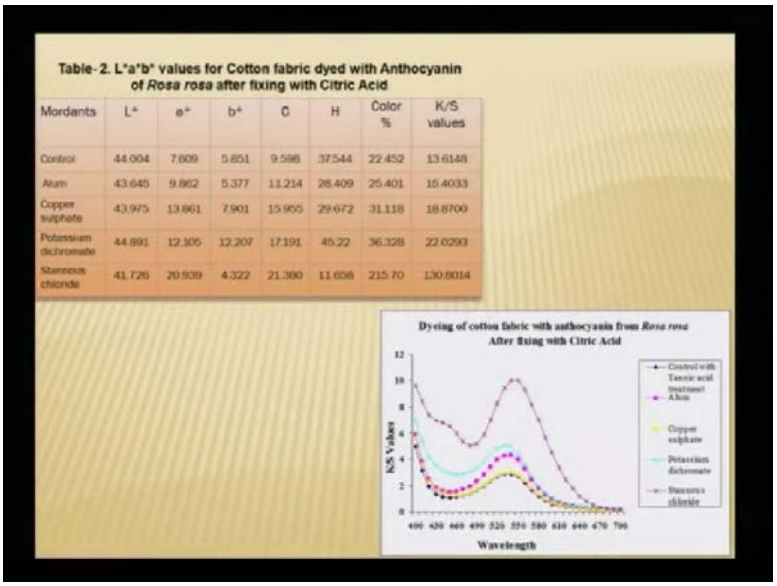

Now, when the L a b values for cotton fabric dyed by the rose anthocyanin was characterize before fixing with citric acid the value showed that the k by s values were between 62 or rather 52, 132 and the highest being for stannous chloride. This is the same observation that we had in case of hibiscus anthocyanin also. So, you see that stannous chloride seems to be the ideal mordant for this rose anthocyanin and it is also.

So, we can conclude that for anthocyanin dye stannous chloride mordent seems to be having good functionality and it is does not fall in to the you know dangerous category like copper and chromium. So, it can be safely use, but every time we are using mordent it should be kept in mind that the minimum amount of mordent should be used. Otherwise there could be problems arising in the a fluent treatment or in the a fluent management.

Now, when the same cotton dyed fabric is treated with citric acid. That the dye fix shows that lot of dye has run off you see; that means, that dye fixed now what is the situation of the k by s value we should not get you know pattered by the fact that oh so much of dye has run off even then it has very rich color and we will see the fabric very soon and we will then understand and here also the k by s value shows that pass stannous chloride the value is 130. So, if we go back from 130 to it has only reduce to 130.

So, treatment with citric acid has not reduce the color strength in the case of stannous chloride where as in the case of other mordents and in the case of control fabric it has

shown considerable change. So, this also goes to indicate that for rose anthocyanin the ideal mordant is stannous chloride.

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Now, you see that as compare to the hibiscus fabric which we had seen last time. The controlled fabric look at the controlled fabric which is been just treated with the pre treatment tannic acid and the alum peace and the copper sulphate peace, the potassium dichromate peace and the stannous chloride peace. So, you see stannous chloride shows very deep color. Similarly, if we take a look at the silk fabric before the treatment of the citric acid before fixing with citric acid you will find that the k by s values vary from 48 to 137 and here also the compatibility is best for stannous chloride.

Similarly if we go to the fabric treated after fixing with citric acid the values have decreased from 137 it has decreased to 111, but still it is showing good values for k by s values and therefore stannous chloride is also rightly suited for the compatibility of rose anthocyanin. And the fabrics look little faded in this case, but the definitely stannous chloride is much darker for silk as well.

Now when we try to look at the wool samples and we try to see what is the situation of the anthocyanin dyed fabric before citric acid treatment they range the k by a value ranges from 63 to 222, which shows very good dye up take you see k by s value shows that dye up take, but some of it only a hearing to the surface. So, the moment the citric acid fixing is done you will see that the color runs off here also the compatibility goes to

show that stannous chloride is showing the best result in the k is a in the terms of k by s values, which is the color strength.

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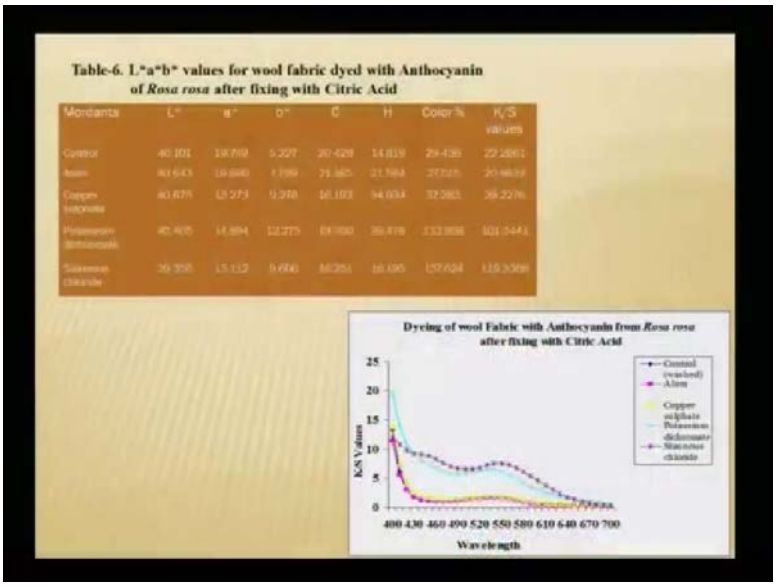

Now when it is fix with citric acid it was found that it has deduced from 220 to 2119 which is almost like going half the way. So, one can see, but even then the stannous chloride values stand out. But here in this case in the case of wool even potassium dichromate shows reasonably good values for k by s. So, both now we can say for wool potassium dichromate and stannous chloride both can be used readily. So, you see it is obvious from the se you know even dyed samples if we see this dyed samples one can evaluate these things what I have told you just now.

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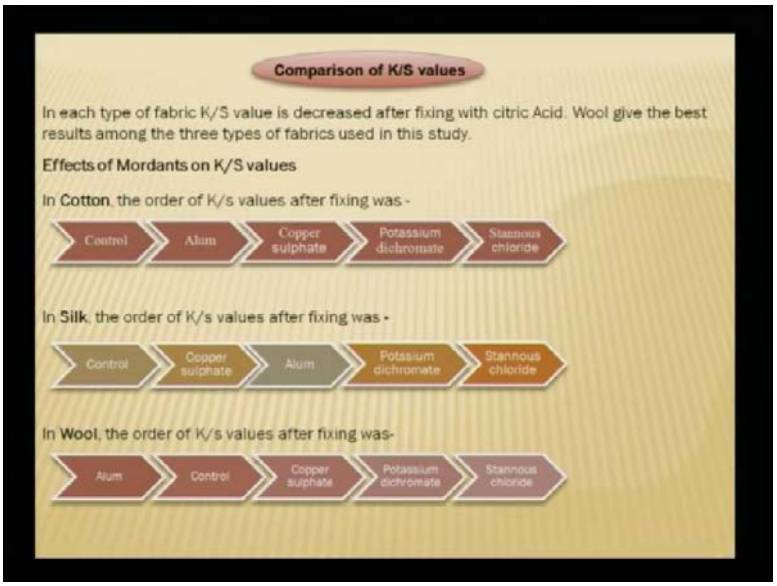

Now, so if we have to take an overview of the k b y s value only. It in each case then let us go in the increasing order in the case of cotton the order of k by s value after fixing was found, because before fixing we cannot say that this is the best method. Because after all the fabric needs to be treated completely. The finishing process must be complete so finishing of the fabric ends only in the step of dye fixing. So, therefore, these values are of more important, but that was more to see how much that dye is taken up and how much is run off in the water. So, if we try to look at the cotton values control is poorest than alum and then copper sulphate and then potassium dichromate and then stannous chloride.

And in the same is the sequence the case of silk control copper sulphate alum. So, you see potassium dichromate and stannous are the two mordents which are quite good for cotton and silk. And similarly we will see that in the case of wool also after fixing alum was the worse it was even worse than the. So, it cannot be recommended at all for wool dyeing. But copper sulphate potassium dichromate and stannous. So, finally, what do we come to a conclusion if we by looking at the case value the potassium dichromate or even better is stannous chloride. That should be used as a mordent for this dyeing of cotton wool and silk by rose anthocyanin.

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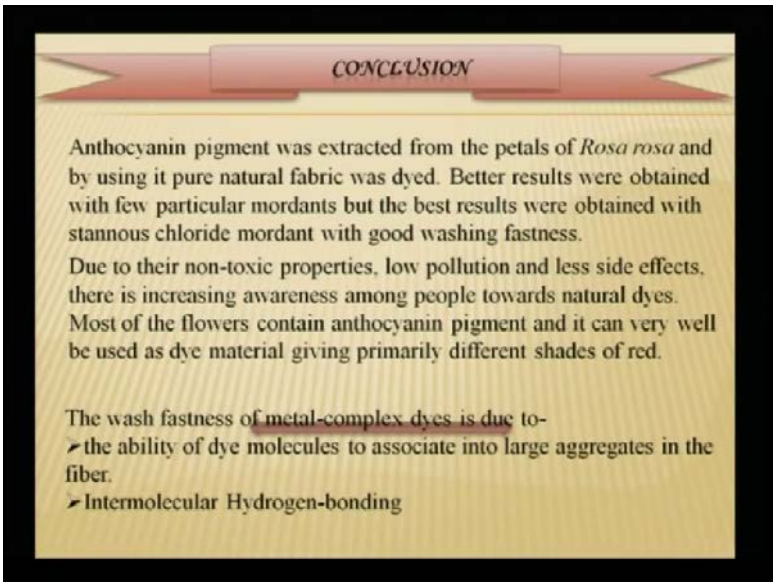

So, if we now have to conclude anthocyanin pigments was extracted from the petals of rosa rosa which is rose and by using it pure natural fabric for dyeing. Better results were obtained with few particular mordents, but the best result was obtained with stannous chloride mordent with good washing fastness. Due to their non toxic properties low pollution and less side effects there is increasing awareness among people towards natural dyes.

Most of the flowers of contain anthocyanin dyes and it can very well be used as a dye material giving primarily different shades of reds and pinks. The wash fastness of metal fastness dye is due to the ability of dye molecules to associate with large aggregates in the fiber and because of the intermolecular hydrogen bonding. So, you see the way one can have an overview of why now it is time to accept anthocyanin dyes as textile dyes.

Because they fit in to the category of features that a textile dye must have that is it the dye should be soluble in water, the dye should have good functional or auxochrome group. So, that the metal mordent can attach and the subsequently the metal mordent dye will be able to attach on the fabric. And if a dye follows all these parameters or if it has these characteristics if it is abundantly and cheaply available if it is having the right kind of functionality.

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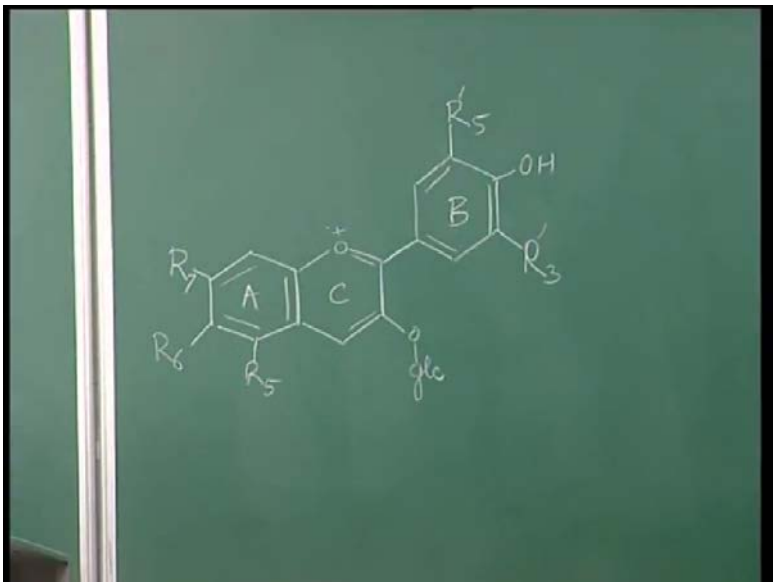

Now you see that there are many chemicals or compounds of this and many possibilities are there where the R 3 prime, R 5 prime, R 5, R 6, R7 in the A ring and the cleavage of this particular. So, the groups the A ring, the C ring and the B ring and the different functionalities and the cleavage of this giving rise to anthocyanidin. They are responsible for good functionality and good linking of the metal ring and metal ring and the rings and the structures and therefore, these dyes are very appropriate for textile because they have the right kind of functional groups.

If we have to now look at the overview that anthocyanins why they were not trapped why is it that this dye had. So, much I mean it was. So, abundantly available from time immemorable, but why is it that it did not enter in to the textile market. Because of the simple reason that extraction process and the dyeing process were not standardize. We try to standardize the extraction process. And we also try to look at; that means.

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We try to standardize the extraction and the extraction of anthocyanin dyes with the help of methanol plus citric acid was evaluated by us for the first time because we thought that if more and more dye has to be extracted, it is necessary to find a method for extraction. Because what was happening? By using just water the dye was not coming completely into the aqueous solution and by using methanol cannot be used for an industrial process. So, we try to take fifty-fifty solution of water and methanol and added a pinch of citric acid just to alter the pH now this alteration of the pH actually help in extraction of the complete anthocyanin that was present in rose.

So, that is where there was an edge; that is where the technology; that we developed harder edge over the existing aqueous extraction process and that really help because we were able now after the extract was obtained either we use it immediately after you know 50 percent concentration or we put it on the rotary evaporator.

See there was a step I will go back to the slide. So, that you can recall that during the process of extraction or methods and materials that we were discussing, this extraction of rose there was a huge of rotary evaporator. Now this rotary evaporator actually can remove the methanol completely and water as well at reduced you know pressure. So, it does not hamper that chemical moiety of the anthocyanin dye and because the dye is in intact and there is the pH slightly acidic; it can be left in the room or on the shelf for months and it can be just used at the time of use. So, the problem that we were facing

about natural dye that it the extract should be immediately use otherwise it goes bad or if the you know the difficulty that natural dyes normally had those we were trying to overcome.

And in the case of rose dye particularly because it was so abundantly available. We have done a lot of standardization not only in the terms of dye, dyeing, but also the major breakthrough was in the process of extraction. And extraction and preservation of that dye can we keep that dye does it get deterviated, no it does not get deterviated even with day light and does not get fungal growth, because there is an slight excess of citric acid which keeps the pH at a level where fungus do not grow. So, that way we were able to preserve this dye paste and use it at a later date. So, that is what made this dye such a good dye and it is such a rich source. So, let us now conclude this lecture that anthocyanins can be a good textile dye because of their cost effectivity, high availability, and good compatibility with the fabric, all the three natural fabrics cotton, silk, and wool.