Natural Dyes

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Lecture No. # 06

In the last lecture, we were looking at the adverse effects of the synthetic dyes. And now we came to a conclusion that synthetic dyes are toxic, and natural dyes are safe. Let us make a comparative you know, study has to if it is really so, then why is it so, and what are the main characteristic, which make the synthetic dyes, now no more wanted in the food industry or in the textile industry, and what is it that makes the resurgence or the revival of natural dyes.

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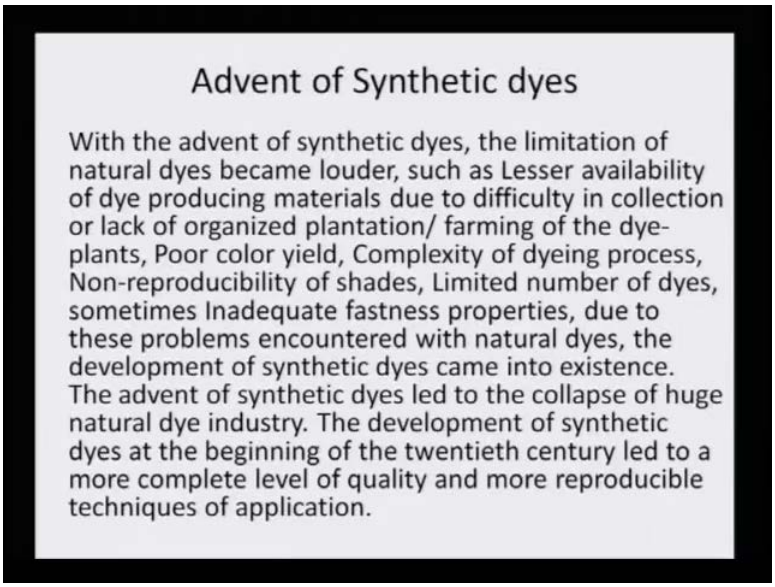

So, with the advent of synthetic dyes, the limitation of natural dyes became louder such as lesser availability of the dye producing material due to difficulty in collection or lack of organized plantation; farming of the dye-plants, poor color yield, complexity of dying process, non-reproducibility of shades, limited number of dyes, sometimes inadequate fastness properties, due to these properties, due to these problems encountered with natural dyes, the development of synthetic dyes came into existence. The advent of synthetic dyes led to the collapse of huge natural dye industry. The development of

synthetic dye at the beginning of the 20th century led to a more complete level of quality and more reproducible techniques of application.

So, one thing has to be accepted that no product is full proof; it has its own set of advantages, and it has an its own set of disadvantages. But natural dye, which was practice in earlier times, in ancient times, when we were studying the history of dye stuff. We said earlier in the ancient time in the pre-historic time, and even in the before Christ period in the era or before Christ period and after Christ period, every time we saw that it was only natural dye, natural dye, natural dye. There was no synthetic dye till 1857 so or 1896, because that was the time, when there was a, you know invention of natural synthetic dyes.

So, but when synthetic dye came into the market, it completely over powered the market, for the following reason that it could give a very even kind of dying; and that the application technique was very easy. On the other hand, there were several, several problems related to natural dye, its collection, its extraction, its poor yield, its complexity of dying process. And then after all that, if the shades were not reproducible or they were very limited number of shades, and some times of fastness property would not be very desirable that means, it would just run off, the color will run off in one or two washings. So, these were the kind of you know, comparative situation for synthetic dye and natural dye.

Now in that kind of a situation, it is very hard for the manufacturing unit to decide what to choose, because obviously, when one is doing business, one need to have a quality control and the evenness of dying must be acceptable. If the dyes are in patchy description, no buyer is going to buy; that is a common sense. So therefore, it was important that these factors are the drawbacks that were with natural dyes; how they can be tackled; and how it can be brought apart with synthetic dye. So, unless and until we make a comparative analysis of the two, we will not know how to deal with the problem.

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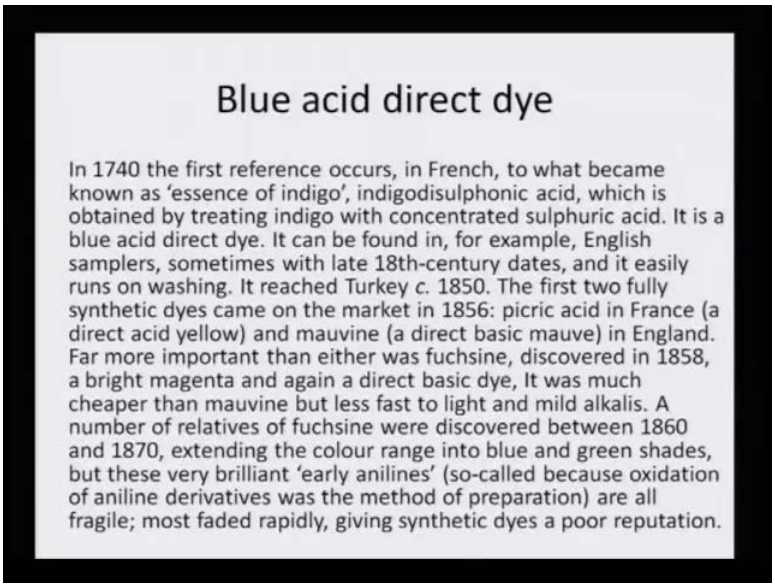

Blue acid direct dye: In 1740, the first reference occurs in French, to what became known as the essence of indigo; indigodisulphonic acid, which is obtained by treating indigo with concentrated sulphuric acid. It is a blue acid direct dye. It can be found in for example, in English samplers, sometimes with late 18thcentury dates, and is easily run on washing. It reached Turkey in 1850. The first two fully synthetic dyes came on the market in 1856; picric acid in France, a direct yellow; and mauvine, a direct basic mauve in England. Far more important than either was fuchsine, discovered in 1858,a bright magenta; and again a direct basic dye, it was much chipper then mauvine, but less fast to light and mild alkalis.

A number of relatives of fuchsine were discovered between 1860 to 1817, extending the color range into blue and green shades, but these very brilliant early anilines, so-called because oxidation of aniline derivatives was the method of preparation and are fragile; most faded rapidly giving synthetic dyes a poor reputation. So in fact, the beginning of synthetic dyes was also not very bright and very easy; why because it was it develops slowly, but as an when it developed, it became a boom in the dying industry.

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Synthetic dyes: A second important group of dyes, the direct acid azo-dyes, were introduced in 1875and provided shades of yellow, orange and red. They did not fade, but many ran easily. So, they were run off in water, but they were not faded by the light. Other major and minor groups of synthetic dyes followed, and before long the whole spectrum was covered. The new dyes, essentially pure chemical compounds, were more consistent, and often more brilliant and cheaper than the natural dyes previously used. However the many other qualities needed by the user were not always available and the synthesis of improved dyes continued to be the main preoccupation of organic chemists.

So in fact, thus you know, the history of synthetic dyes shows that in the beginning, the dyes were not having the two main requisites; that is fastness to light and fastness to washing. And some of them were light fast, but they would, they did not have good wash fastness, and such a category will not really fit into the market very well, because for a dyer, it is important that any dye be it syntactic dye or be it natural dye must have two basic criteria full filled. And what are these two basic criteria? One is the light fastness property, and the other one is the wash fastness property. If they both have acceptable limits of these, then they are actually fit to be in the dyeing market.

And therefore, the chemist, organic chemist of that era started making newer and newer and more stabled dyes. They started understanding the structure and the structure that would be more compatible with the fiber, so that the dye adherence is better, and there is

no fading due to light. So, dye adherence better would save it from running off by water, and if it did not get affected by the absorption of white light, it would not fade. So, these were the two aspects on which newer synthetic dyes were being developed at that time.

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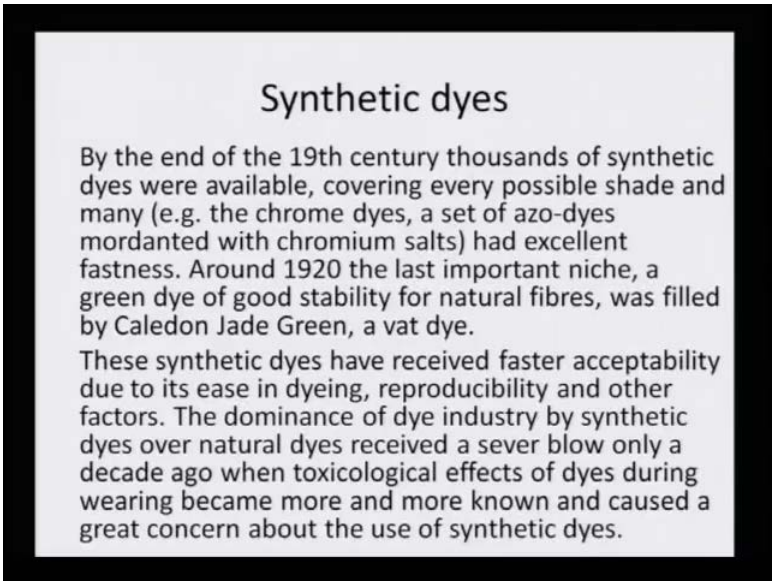

By the end of the 19thcentury, thousands of synthetic dyes were available, covering every possible shade and would many, such as the chrome dyes, a set of azo-dyes mordanted with chromium salts had excellent fastness. Around 1920, the last important niche; a green dye of good stability for natural fibers, was filled by Caledon Jade Green, a vat dye. So, you see that you know, how from 18th century to 19thcentury, in a beginning of 19thcentury, most of these synthetic dyes were already synthesized and were getting more stable and more acceptable, because their properties of were overcome, and they became a more marketable product.

These synthetic dyes have received faster acceptability due to its ease in dyeing, reproducibility and other factors. The dominance of dye industry by synthetic dyes over natural dyes received a severe blow only a decade ago when toxicological effects of the dye during wearing became more and more known and caused a great concern about the use of the synthetic dyes.

So, you see how from the natural dye market suddenly with the advent of synthetic dyes, the natural dyes faded, and it was only in the 19thcentury; the 18thcentury towards the end and the 19, entire 19thcenturyit was only synthetic market. But what started happening

that by the end of the 19 century and the 20th century, beginning of the 20th century people started noticing the adverse effect of the synthetic dyes. And therefore, there was a resurgence or revival of natural dyes again now. So you see, how you know, the whole… All the time the synthetic dye and the natural dyes have been in competition with each other, and the effect of that is, because they have been found to be toxic.

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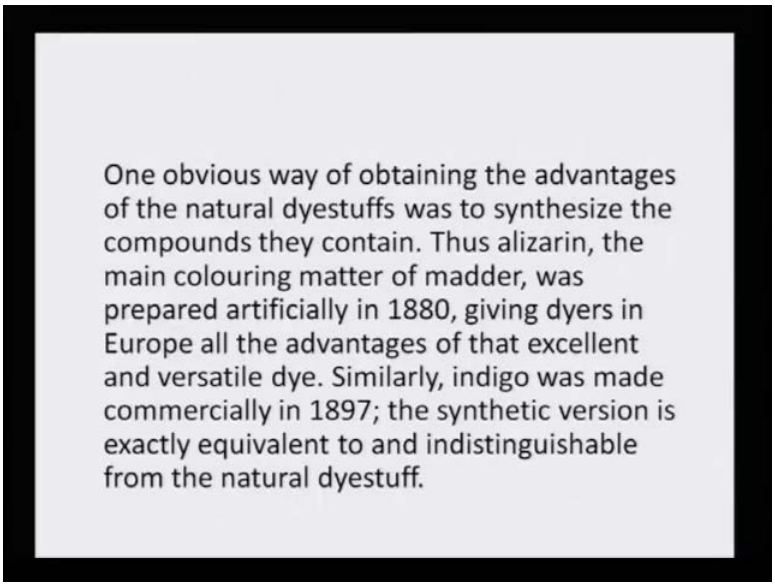

One obvious way of obtaining the advantages of the natural dyestuffs was to synthesize the compounds they contain. Thus alizarin, the main coloring matter of madder, was prepared artificially in 1880, giving dyers in Europe all the advantages of that excellent and versatile dye. Similarly, indigo was made commercially in 1897; the synthetic version is exactly equivalent to and indistinguishable from the natural dyestuff. So, you see the other alternative was that, that because synthetic dyes were found be so dangerous and toxic and soon and so forth, it was then thought by organic chemist that is why not to synthesize very molecules, which are very similar to the natural analogs. And therefore, the simplest of the simple molecule that is the alizarin. Yesterday we were looking at the structures of alizarin, it is an anthraquinoid dye, and it has an orthohydroxy groups.

So, when it has two hydro toxic groups in the last string of the aromatic, it has the good chelating effect; and this is naturally also available; and synthesizing this small molecule was not a big challenge. Similarly, indigo is another naturally occurring dye; but it could

be easily synthesize in the laboratory, and it was found that both the synthetically made alizarin and indigo were quite similar in their reactivity towards the fiber; and in their wash fastness and in there light fastness with the computability was similar. Therefore, the market for the red dye could be substituted with synthetic alizarin, if the natural alizarin could not be obtained in those quantities; and as I said a while ago, a few lectures ago that the entire denim industry is thriving on synthetic indigo. All the blue genes that you see are dyes by indigo, but they are not natural indigo, they are dyed fabrics.

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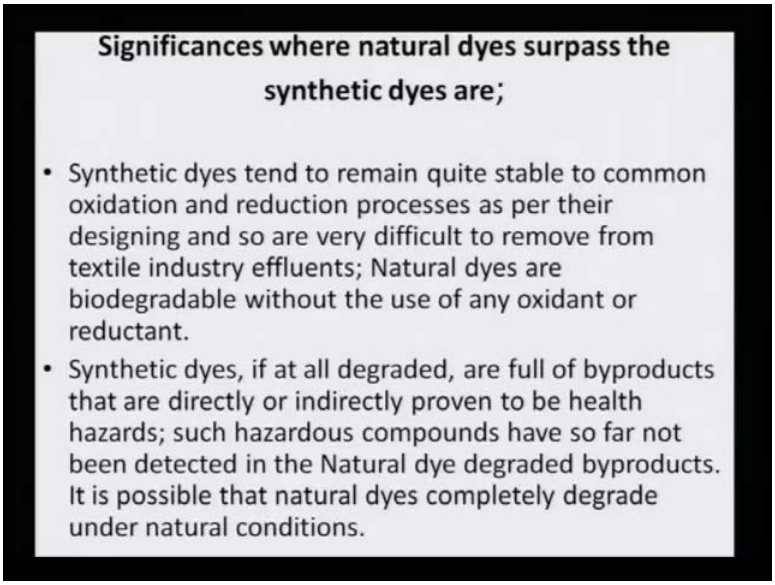

Significances where natural dyes are passes through the synthetic dyes; so, when we are making comparative data or a comparative analysis of how the synthetic dyes and the natural dye were; we can take a most closer look and understand. Synthetic dyes tend to remain quite stable to common oxidation and reduction processes as per the designing and so are very difficult to remove from the textile industry effluents. Natural dyes are biodegradable without the use of any oxidant or reductant. So, you see that synthetic dyes are very hard to break, and special oxidative and reductive processes are required, if the dye effluent has to be you know, decolorized; but that is not the case with natural dye, why because all the natural dyes are coming from the biotic material, and they are very easily biodegradable.

Synthetic dyes, if at all are degraded, are full of byproducts that are directly or indirectly proven to be health hazards; such hazardous compounds have so far not been detected in the natural dye degraded byproducts. It is possible that natural dyes completely degrade under natural condition. So, you see that we just took look at the degraded product of azo-dye; and we found that this one and amino two naphthol, which comes from the breaking of the azo linkage is the most notorious and toxic material. But we do not find such components are metabolize or degraded products from natural dyes. And therefore, they are safe, and they do not interfere, and they simply degrade under natural conditions, and they do not release any harmful chemicals.

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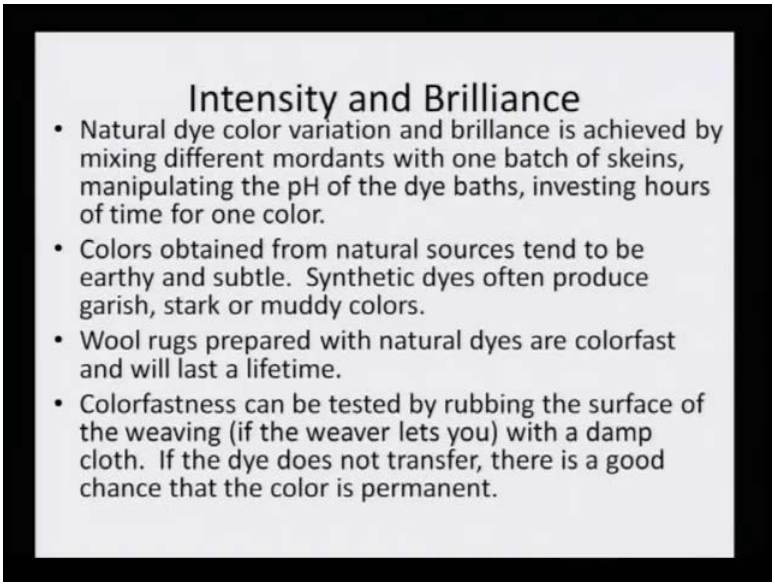

Intensity and Brilliance: Natural dye color variation and brilliance is achieved by mixing different mordants with one batch of skeins, manipulatingthe pH of the dye baths, investing hours of time for one color. Now that is true that when one is working with natural dyes, one has to do a lot of permutation combination, and it is very slow process, and then only the color variation and the brilliant can be achieved. Colors obtained from natural sources tend to be earthy and subtle. Synthetic dyes often produce garish, stark and muddy colors. So, they are very strong and brightly color. Wool rugs prepared with natural dyes are colorfast and will last a lifetime. Colorfastness can be tested by rubbing the surface of the weaving if the weaver lets you with a damp cloth. If the dye does not transfer, there is a good chance that color is permanent.

So, these were various ways of, simplified ways of testing whether a dye is you know, permanent dye or a dye is fugitive dye and soon. But there are very, very discrete differences between the synthetic dyes and the natural dyes; it is not only the degraded product that makes them different; even the ease of using is very different. Natural dyes are a little tedious process require a tedious process in dying; whereas, in synthetic dyes the ease of application is much simplified and the color obtained is much brighter; whereas in the case of natural dyes, it is more earthy color and most you know, sober in nature. So, these are the kind of differences, which cannot be matched one is to one; one is different from the other, this is what has to be accepted.

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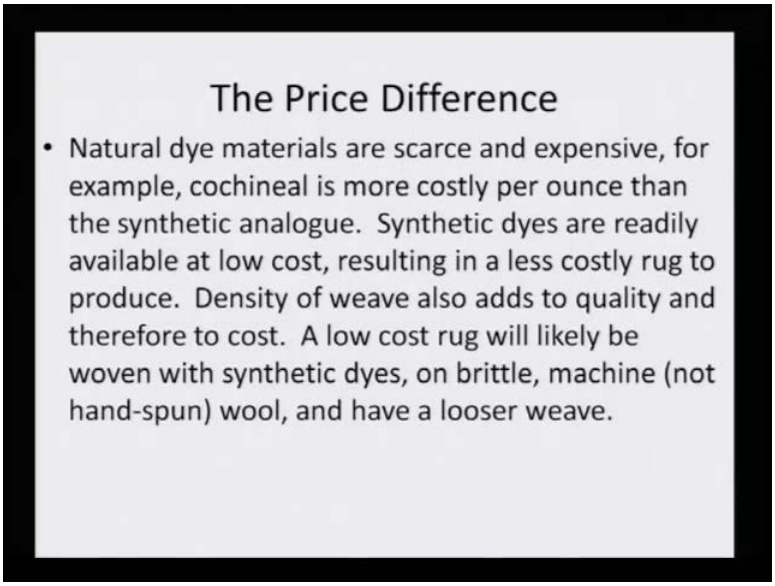

Of course, there are price differences; no doubt about it, because the process of collection, extraction, isolation, and use is tedious in the case of natural dyes. The material, because they are scarce and expensive, for example, cochineal is more costly per ounce than its synthetic analogue. Synthetic dyes are readily available at low cost, resulting in a less costly rug to produce. Density of weave also adds to quality and therefore to cost. A low cost rug will likely to be woven by synthetic dyes, on brittle, machine and not hand-spun wool, and therefore, it will have looser weave.

So, you see the synthetic dye rug can be identified so easily, whereas hand woven rug; rug means carpet. These one can make a very distinct evaluation or whether a carpet is hand woven or it is machine made, and if it is machine made, whether it the dye that has

been used in coloring the various wool, shades are synthetic or natural even that can be evaluated.

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Advantages of natural dyes are also there. As I was telling you that every commodity has its own advantages as well as disadvantages. Therefore, even natural dye it is not very difficult to handle natural dyes, there are some very positive aspects of natural dyes, which has brought them back again in to the market. Natural dyes cover the area of green chemistry. A great need of research is required for green dyes to replace toxic synthetic petroleum based dyes. It has been a matter of debate that synthetic dyes give a better glow and a range of color, while the natural ones are limited to dull and muddy colors only. It is not at all true, as natural dyes not only give us a feel of superior, a superior quality, sensory experience but also provide a spectrum of colors.

The five classic and popular natural dyes are indigo, madder, cochineal, weld and cutch. So, this will, indigo will give blue, madder will give red, cochineal will give purple, weld will give yellow and cutch will give brown color. So, it is covering almost you know, the whole range; and with the permutation and combination of these dyes, one can generate more secondary colors. These can give rise almost any color, with the exception of a few colors like florescent and electric blues. Natural colors are basically plant dyes, but some of them are of origin, animal origin such as cochineal, which is obtained from insects.

These five dyes show the properties of very strong yields, they are resistance to fading, relatively fast color along with easy availability. So, now you see the main problems of natural dyes, which were identified, where that they were not available in required quantity. They did not have fastness property, they were they did not give too much of dye from the plant material, and they had very poor light fastness all this at least has weaving not so in the case of these five dyes.

And which are the five dyes; indigo, madder, cochineal, weld and cutch; which would give blue, red, purple, yellow and brown, respectively in their shades. Therefore, it is advantageous that one should now switch over to natural dyes, because there are light fastness properties containing dyes even in the natural category. They are now there are organized farming that are producing only these products for the sake of catering natural dye industry.

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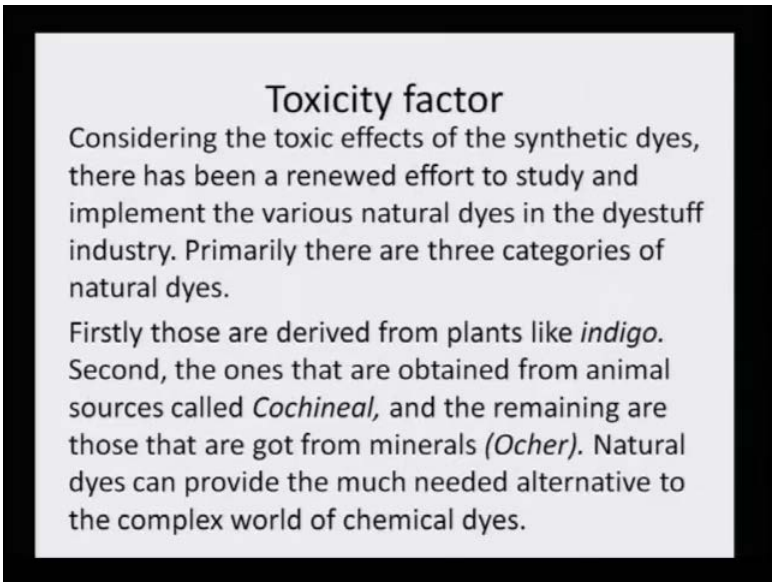

Toxicity factor: Considering the toxic effects of the synthetic dyes, there has been a renewed effort to study and implement the various natural dyes in the dyestuff industry. Primarily there are three categories of natural dyes. Firstly, those are derived from plants like indigo. Second, the ones that are obtained from animal sources such as Cochineal, and the remaining are those that are gotten from minerals that is the Ocher. Natural dyes can provide the much need alternative to the complex world of chemical dyes. So, you see that the even the toxicity factor a I mean, if one considers only that toxicity factor,

one has to understand that synthetic dyes are diffidently very toxic. We have just taken and evaluation in the previous lectures, how toxic these reactive dyes are; how toxic these azo dyes are; and what actually causes the toxicity, we have taken an over view of that.

So, by now you would have understood and would have developed an appreciation, for switching over to natural dyes, but the disadvantages of natural dyes have also been overcome. So, one is trying to make a balance or strike a balance that natural dyes with all it is you know, positivity can be made further better and match the ease with which synthetic dyes came into the market, and was being practicing the market.

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Actually, what happened was that the German ban came in 1996; German struck a severe blow to dyestuff industries, and subsequently other European countries also executed ban on important of textiles and garments, colored with the series of azo-dyes made from aromatic compounds, which were found to be carcinogenic, allergic and poisonous. Azo compounds are reduced by intestinal anaerobic bacteria through scission of azo bond form aromatic amines, which are toxic to living organism. The use of natural dyes however, has not entirely disappeared. Since the 1960s craftsmen have been interested in those dyes that can be grown and used in the domestic environment; and in the 1980s natural dyes were seen as an ideal alternative to the cheap synthetic ones that had damaged the reputation of traditional weaving and dying.

So, you see that how and why this kind of thing happened; what caused the down fall, I would say of the synthetic dye market; and what cause cause the researches or revival of natural dye that was primarily, because of this particular ban, which came in 1996 and this is called the German ban. So, you should be aware and the German ban was first actually targeting the carcinogenic azo-dyes. And a list of 22 dyes were completely banned from the market that is because by now studies had been done, and it was found that they are highly injurious for human beings; and because they were banned, the dye industry had to be supplemented with some alternative. And therefore, in 1960s, between 1960s to 1980s slowly the natural dyes were being promoted; and after this ban, in India also the Indian ban came in following the German ban; and after that, it was more aggressive movements towards the use of natural dyes.

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Repercussions of German ban: However, due to German ban on azo dyes in 1996, there is currently a move to find renewable sources to supplement the need for safe dye industry. This trend has led to resurgence in research in the production of natural dyes on the commercial-scale. Commercialization of natural dyes which are extracted from vegetative matter and animal residues have become very important in fashion trends. They are not only chemically safe, but also add aesthetic value to the dyed fabric. So, you see as a result or repercussion of this German ban, the Indian ban came into existence. So, even from the Indian textile market or color market, dye market, their synthetic dyes were then banned. Now, if these dyes are banned, obviously people will

not start wearing untied cloth; nobody will you would not see that the whole society wearing only white cloth, because of synthetic dyes have been banned.

So therefore, there was a necessity for having safe natural dyes in the market. So therefore, there was this whole process of promotion of natural dyes by the government, because the ministry of textile, then started approaching people to start working on commercialization factor; organized farming for natural dyes were being promoted. And because of that in many places, these factories were organized, where extraction of natural dyes production of natural dyes was promoted and there was a lot of subsidy given by the government, so that people should plan in to this new area and find business out of it.

And because of this commercialization of natural dyes, lot of organized forming was promoted from, because dyes have to be extracted from vegetative mater or these animals which actually, are color producing very few of them, we just learnt that you know lack dye and cochineal are the two animal origin dyes, others all from the vegetative dyes. And the ones which I mentioned that is indigo, madder, weld and cutch; they are all from plant sources, only cochineal is from animal source. So, it was given great imputers that these dyes should be produced in larger quantity. So, if they have to be produced in larger quantity, and they are not being synthesized as a synthetic analog, then more and more vegetative or animal producing substances should be made available in this factor, so that they can extract these dyes.

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So, therefore, there was a resurgence of natural dyes. The use of non-allergic, non toxic, eco friendly natural dyes on textiles has become a matter of significant importance due to the increase environmental awareness in order to avoid some hazardous synthetic dyes. However, worldwide the use of natural dyes for the coloration of text ails has mainly being confined to artisan/ craftsmen, small scale/ cottage level dyers and printer as well to small scale exporters and producers dealing with high-valued eco friendly textile production and sales.

So, although there is a resurgence of natural dyes, because they are non allergic, non toxic and they do not create an dye effluent, which is you know, which needs to be specially treated because of its toxicity. Therefore, it is you know, eco friendly, it is environmentally friendly dye. And but at the same time, it is not picked up in the market like the synthetic dye; why because you know, it is only being practice by small craftsmen and artisans. And it in small cottage industries, because that is the level that can be handled in small groups, because the amount of vegetative matter that would be required for dye extraction is huge; why because these plants parts have something like 2 to 10 percent of dye only.

So, you imagine if 10 grams of dye have to be obtained, 100 grams or 200 grams or 500 grams of substance will be required, but that is not all, because they have to be made in kgs. So, the magnitudes of vegetative matter that is required is very large. And therefore,

it is important that they are being to understand that they are just being practiced by its small players. It still not come into the main market relay, because if the main market has huge requirements; but there is big drive to have bigger commercial houses, which can produce larger quantities of these natural dyes. And the natural dye quality needs to be standardized; and they should make made equivalent to synthetic dyes, just to be able to use of the shall just the way that synthetic dyes are being used, and all those things are taking place.

As we along in the next few lectures, we will try to look at, how this standardization process takes place; how these dyes are you know they need to be standardized? One thing you have also understand and appreciate that plantation of a particular plant see suppose I taken example of Indigo; Indigo that is grown in Bihar; and Indigo that is grown in Himachal Pradesh, will definitely have different indigotic content. It it is not that both the plantations will have the same amount of indigo. And at the same time they may or may not have some other colorant also in the plant material. So that variation needs to be manipulated or organized, and all those standardization processes, we will try to take a look at it in the next few lectures.

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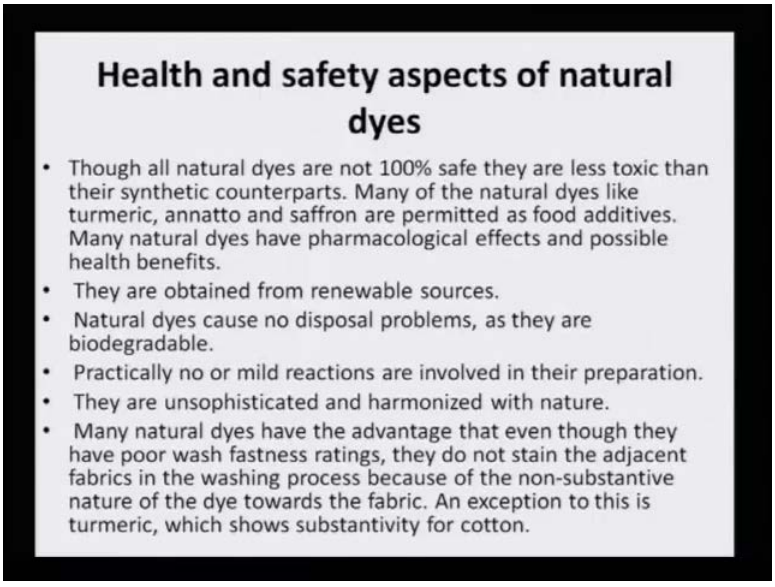

So, therefore, health and safety aspects of natural dye, although all natural dyes are not 100 percent same; they are less toxic than there synthetic counterparts. Many of the natural dyes like turmeric, annatto and saffron are permitted as food additives. Many

natural dyes have pharmacological effects and possible health benefits. They are obtained from renewable sources. Natural dyes cause no disposal problem as they are biodegradable. Practically no or mild reactions are involved in their preparation. They are unsophisticated and harmonized with nature. Many natural dyes have the advantage that even though, they have poor wash fastness rating, they do not stain the adjacent fabrics in the washing process, because of the non-substantive nature of the dye towards the fabric. An exception to this is turmeric, which shows substantively for cotton.

So you see that so many aspects we have learnt. We have seen the difference between the synthetic and the natural dyes; but over all if one has to sum up, one would try to look up and say that looking at the health and safety aspects of the natural dyes. And the biodegradable nature of natural dyes, it is more and more advisable to bring and use only natural dyes and only rarely used those synthetic dyes, which are safe, and which do not give any harmful biodegraded products. So therefore, this natural dyes, because they are also obtained from the renewable sources, the plants can be always harvested and the dying material can be obtained or the dye can be extracted from them.

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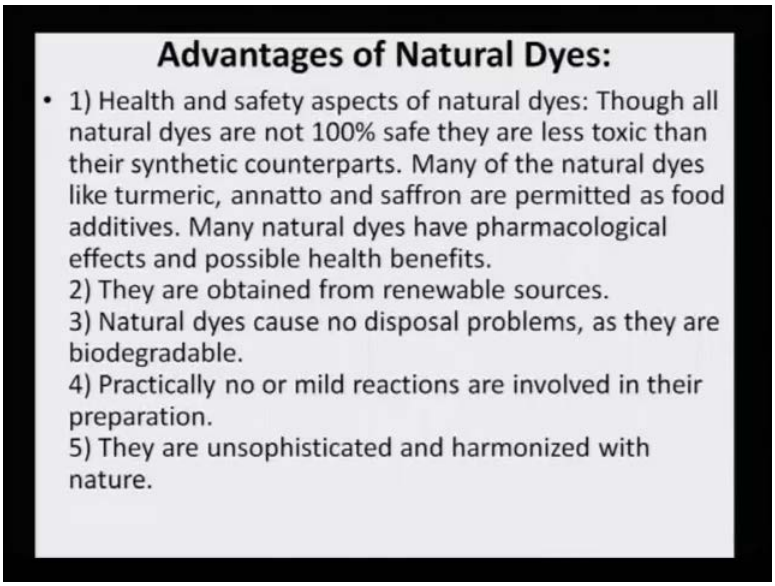

Advantages of natural dyes: Health safety aspects of natural dyes we have just taken a look. Although all natural dyes are not 100 percent safe; but then they are less toxic that we also have seen. They are obtained from the renewable sources we have seen. Very

clearly, that these points are like added advantage to the natural dyes. So if we have to sum up, we can say that natural dye is the (( )) of the day.