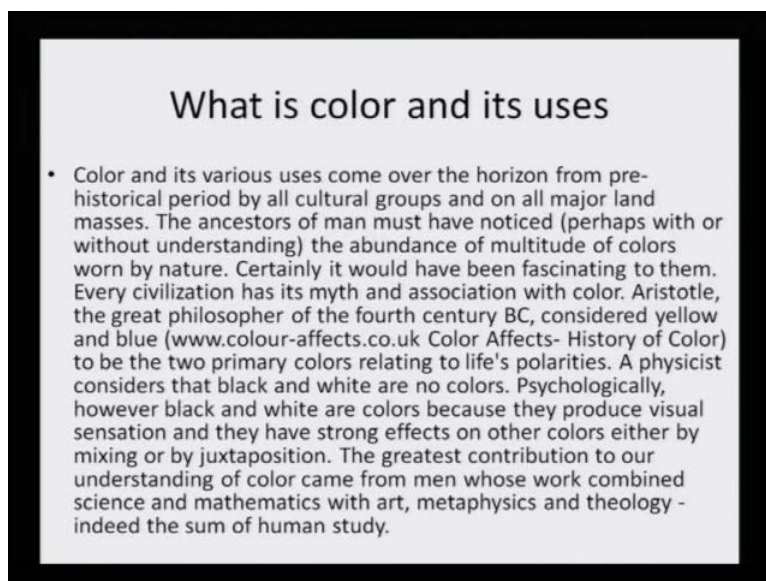


**Natural Dyes**  
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**Department of Chemistry**  
**Indian Institute of Technology, Kanpur**

**Lecture No. # 01**

This is a new course related to dyes and dyeing. We are going to learn a lot of things related to what dye stuff is, what color is, and how do we interpret color, how do we see color, what are the complementary colors and so on. We will also take an overview of synthetic dyes briefly, and then go into the details of natural dyes, their sources, their structure elucidation, their extraction and how they can be used in a more innovative manner for dyeing. So, let us begin this new course on dyes and dyeing; and let us start with the first lecture related to History of Dyestuff.

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What is color and its uses? Color and its various uses come over the horizon from pre-historical period by all cultural groups and on all major land masses. The ancestors of man must have noticed perhaps with or without understanding the abundance of multitude of color worn by nature. Certainly, it would have been fascinating to them. Every civilization has its myth and association with color. Aristotle, the great

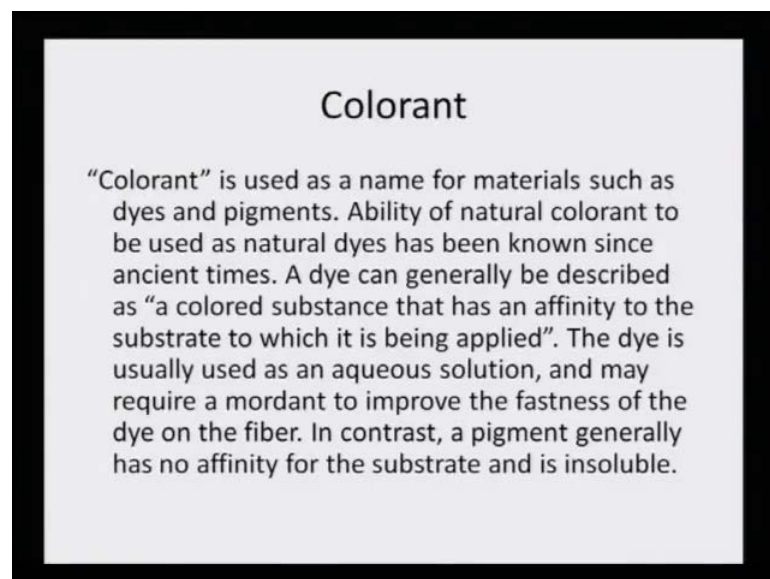
philosopher of the fourth century BC, considered yellow and blue to be the two primary colors related to life's polarities. A physicist considers that black and white are no colors.

Psychologically, however black and white are colors, because they produce visual sensation and they have strong effects on other colors either by mixing or by juxtaposition. The greatest position or contribution to our understanding of color came from men, whose work combines science and mathematics with art, metaphysics and theology, indeed the sum of human study.

Now, you will also appreciate that color was known and observed from pre-historic time and it was man whose first notice this variation and it was through the visual effect. Secondly, every civilization had this association of color it was not that any civilization grew up without the observation of color. And the third point that you know, people may have a different perspective about color, but they all boil down to the fact that there is black, there is white and all the colors lie in between these two exhibitives or there is yellow and blue and all the **the** colors lie between these two extreme colors.

Whatever be the situation, there are two polarities, and whether we consider as black and white has two polarities or yellow and blue has two polarities, but color range ranges between these two polarities. Now, how do we describe a colorant?

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“Colorant” is used as a name for materials, such as dyes and pigments. Ability of natural colorant to be used as natural dyes has been known since ancient times. So, now this colorant is a common term, it can be used for dyes and pigments and definitely, if we are saying dyes and pigments. That means these two entities are different, how different they are we will learn during the course of our study.

But right now for you, it is an important to know that colorant is a common name for either referring to dyes or to pigments. Ability of natural colorant to be used as natural dyes has been known since ancient **ancient** times. Why because see, initially there was no synthetic dyes, it was all if there was a color source, it was through the natural source. And natural sources could be from plants or animals. Plants which were some color object either in terms of their, flower or their seed or their fruit or their bark or their leaves.

So, they are even roots. So, these are the various sources from where the color can come from plants, similarly animals can have different types of shells, which are colored and or some kind of covering or their body, can have some color from which the color can be extractive. The dye can generally be described as a color substance that has an affinity to the substrate to which it is be applied. So, common terminology for dye is that a chemical substance, which can have affinity for another substance and it, can be applied.

So, that is why the dye is used for dyeing. The dye is usually used an **an** as an aqueous solution and may require a mordant to improve the fastness of the dye on the fiber. In contrast, a pigment generally has no affinity for the substrate and is insoluble. So, the basic difference between dye and pigment is now very **very** clear. From these two announcements, dye is soluble and has affinity for the substrate; pigment is insoluble and has no affinity for the substrate, where it is applied to...

And in dyeing there is one very important factor that a particular salt of metal or any other compound, which can enhance this affinity on application part of the dye, is called mordants. So, these three terms should be absolutely clear, dye pigment and mordant. With natural dyes or synthetic dyes, we use the term mordant also may or may not, but with pigments, we just use pigment as it is... But pigment cannot as it does not have an affinity for the fiber or it is insoluble as well their needs to be a carrier or modifier, which can adhere the pigment to the fabric, so that we will learn during the course of this

lecture, but right now the definitions dyes pigments and mordents should be absolutely clear.

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Now what are the chief sources of color? The chief sources of coloring matter, until about a century ago, had been nature in general and vegetation in particular. Man learnt to use different kinds of natural coloring matters to dye cloths. Now, it as I just told you a while ago initially they were no synthetic dyes. So, the main source of dyes for ancient people were from nature and **and** from nature particularly from the plants.

So, vegetation was the main source for the coloring matter. Biochemists have identified that the vital activities of plant is also dependent on colorants in the way that the bright colors of flowers are important in attracting insects and birds to act as pollinators. When these are used for dyeing fabrics, they not only impart color to the fabric, but also act as antifungal agent, whereby they impart protection to fabric against bacterial or fungal infections or as moth repellent. Some dyes like indigo has a cooling sensation also.

So, you see that apart from being a source of vegetation, being a source of dye, it also brings in many added advantage. Some of these dyes have this special property of antifungal and antibacterial agent, and because of that once it is applied on the fabric **the fabric** also becomes antibacterial and antifungal, and it kind of reduces any kind of biotic attack, from the fungus of the bacteria or the moth. And some of these dyes like indigo dye is known to have a very cooling sensation. A lot of natural dyes you will learn later

on in one of the lectures that possess special medicinal properties, we will take a very deep look at it at a later stage.

But right now, so what we conclude from this type that colorants the name chief source of coloration, for man has been natural source and that to factors from the source of vegetation, very few animal extracted dyes have coming to the market are being used. But more so much, these dyes are absolutely a very, very a special, because they not only impart color to the fabric, some of them also have antifungal and antibacterial properties, which add to a kind of a value addition to the dyed fabric. What is color? If we have to understand as kin ease, how this color concept came into being, we will try to understand it from the chemist point of view very specifically.

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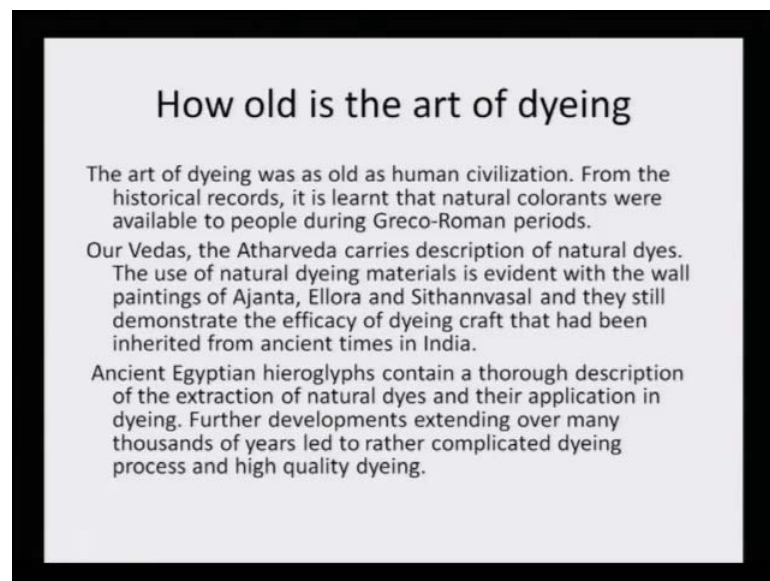
Color is one of the elements of nature that made the human living more aesthetic and fascinating in the world. They are supposed to be associated with emotions, human qualities, seasons, festivals and passion in our life. In the past, at dawn of the civilization, the people tried to ornament their surrounding similar to that of natural colors observed in plant, soils, sky and other sources. This gave birth to a new science of colors from natural origin.

So, how did the application of color **came** come into existence. It was due to the seasonal changes, there were some particular flowers, which bloom that a particular season and those flowers were then used during that seasonal time to color the fabric, and people

wore that fabric, at festivity. And so, all that was connected to the civilization, and everything was in harmony with the nature. So, whatever nature offered at that time, whatever flowers were blooming at a particular seasonal time, it was made us off.

I will give you an example; you must have heard the name of the flower called tesu. It is actually yellow in color, and it blooms at the time when there used to be bezant season. Now, this bezant season is a period of festivity and people wore this tesu flower dyed oh cloths, in order to show that yellow is the color of the season. And it really had a very positive impact on the minds, of the people and then that is how people started co-relating with nature. How old is the art of dyeing? Now we know that dyes have been there from ancient times. But let us try to lay it take a closer look, at when they did it all start, it must started at one period or at least it must been recorded at that period. So, let us try to look at that.

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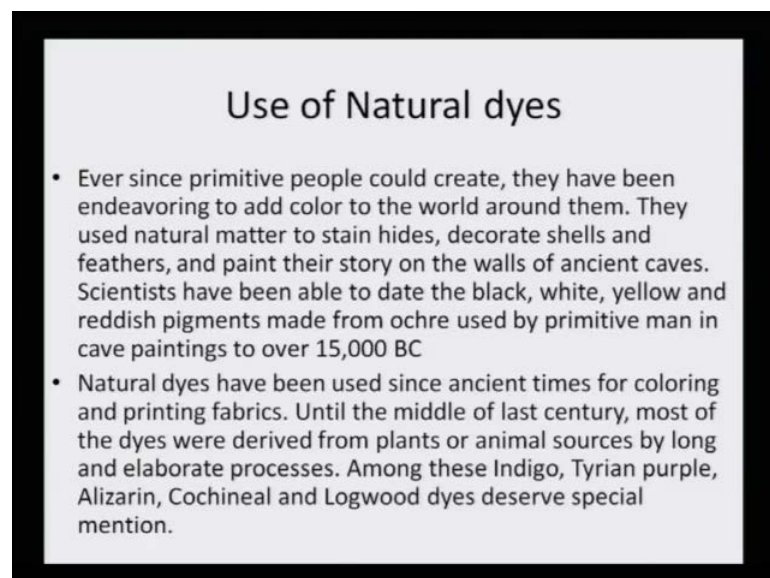
The art of dyeing was as old as human civilization from the historical records, it is learnt that natural colorants were available to people during Greco-Roman periods. Our Vedas, the Atharveda carries description of natural dyes. The use of natural dyeing material is evident with the wall paintings of Ajanta, Ellora and Sithannvasal and they still demonstrate the efficacy of dyeing craft that had been inherited from ancient times in India. So, you see, it is as old as a description, which was mentioned in one of the Vedas called Atharveda. And there it it carries the description of how people try to dye fabric

and do art on the wall, with these natural colorants. And still in the remains of the caves of Ajanta and Ellora the painting on the wall, show that all the colors that were used, at that time were from natural source. The archaeological samples collected from various museums, all over the worlds have been analyzed and they have been found to be one or the other natural dye.

Ancient Egyptian hieroglyphs contain a thorough description of the extraction of the natural dyes. Ancient Egyptian hieroglyphs contain a thorough description of the extraction of natural dyes and their application in dyeing.

Further developments extending over many 1000's of years, left to rather complicated dyeing process and high quality dyeing. So, it is as old as a very ancient Egyptian method. That is how the first started that first method of dyeing was carried out by the Egyptian civilization, and how they I mean the description at least is a also available in the other part of the world, and they describe the natural dyeing process in great details. And over a period of time as the science advance, from time to time new methods were incorporated into this ancient methodology. And more complicated became the dyeing process. But the nevertheless it always was done for the sake of improvement.

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### Use of Natural dyes

- Ever since primitive people could create, they have been endeavoring to add color to the world around them. They used natural matter to stain hides, decorate shells and feathers, and paint their story on the walls of ancient caves. Scientists have been able to date the black, white, yellow and reddish pigments made from ochre used by primitive man in cave paintings to over 15,000 BC
- Natural dyes have been used since ancient times for coloring and printing fabrics. Until the middle of last century, most of the dyes were derived from plants or animal sources by long and elaborate processes. Among these Indigo, Tyrian purple, Alizarin, Cochineal and Logwood dyes deserve special mention.

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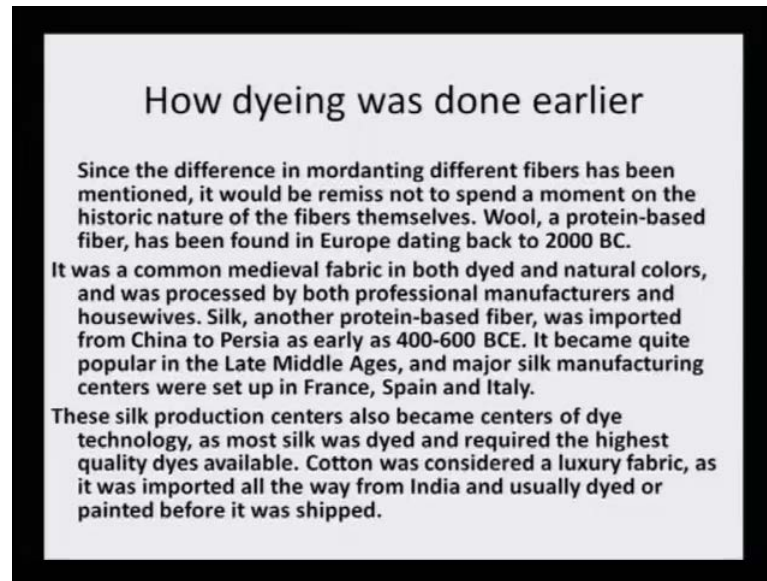
Scientists have been able to date the black, white, yellow and reddish pigments made from ochre used by primitive man in the cave paintings to over 15,000 BC, BC - Before Christ. So, you see it has been as old and as primitive as they, you know the date tells you. And from that period the civilized or the process of civilization had begun, and people were using different sources of natural dyes to color not only their clothes, but also they were wearing hides that is leather clothing.

They were also decorating shells and they were writing their own stories, on walls of the caves with these colored paints or dyes. Natural dyes have been used since ancient times for coloring and printing fabrics, until the middle of last century. Most of the dyes were derived from plants and animal sources by long and elaborate process, among these indigo, tertian purple, alizarin, cochineal, logwood dyes, deserve special mention

So, the dyes that were used from time to time and time and again were mainly from the plant sources, and some of them were from the animal sources. And common one that were used what indigo, which was from a plant source, from the leaves of a indigo plant, tertian purple was extracted from a shell, alizarin, was a extracted again from a plant, mother plant, cochineal was from another kind of animal source, logwood dyes were extracted from wood lumen, and so, these dyes were particularly very, very deep in color, very colorful and gave a very nice spectrum of color range, how dyeing was done earlier. Now, let us try when we are learning the history of dyeing, let us also understand, how they use these dyes, which were from the natural sources only. And at that time what was the methodology that was adopted by them.



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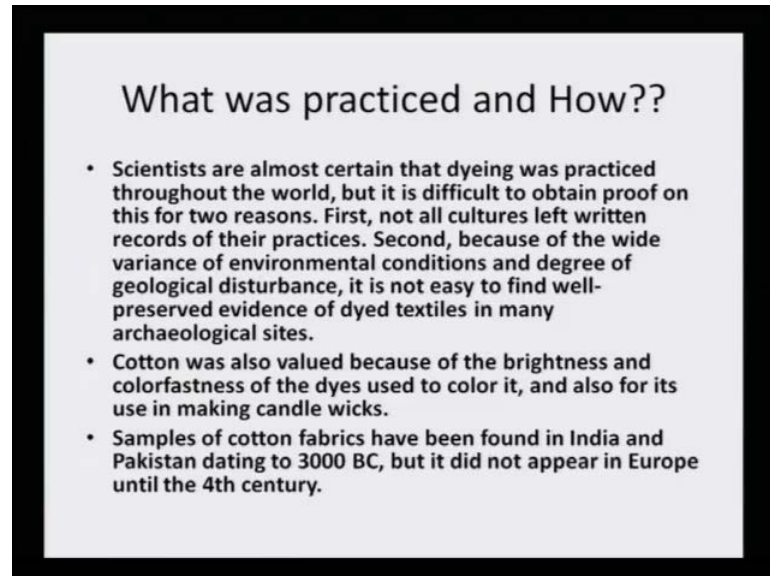
Since the difference in mordanting different fibers have been mentioned, it would be remiss not to spend a moment on the historic nature of the fiber themselves. Wool, a protein-base fiber, has been found in Europe dating back to 2,000 BC. So, you see it is first important to understand, what are the fibers that have that were used for dyeing, and then see the fiber and dye connectivity or affinity, unless and until we have an understanding of the material on which the dye has as to be applied, one cannot be able to appreciate the process of dyeing, and mordanting as I mention the while ago is a very important step, when we deal with natural dyes.

It was a common medieval fabric in both dyed and natural colors, and was processed by both professional manufactures and housewives. Silk another protein-based fiber, was imported from china to Persia as early as 400 to 600 BCE. It became quite popular in the late middle Ages, and a major silk manufacturing center was set up in France, Spain and Italy. So, you see most of these fibers were also natural, because there was no synthetic fiber available at that primitive time.

These silk production centers also became the centers of dye technology, as most silk was dyed and required the highest quality dyes available. Cotton was considered a luxury fabric, as it was imported all the way from India and usually dyed or painted before it was shipped. So, you see we were the pioneers in cotton, but silk and wool were actually established or used in other countries, but the nevertheless whenever silk was imported

from here. Whenever cotton was exported from India, it would be either dyed or painted before it was actually sent out.

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What was practiced and How? Was it done Scientist are almost certain that dyeing was practiced throughout the world, but it is difficult to obtain the proof on this for two reasons. First, not only not all cultures left written records of their practices and second because of the wide variants of environmental conditions and degree of geological disturbances, it is not easy to find well-preserved evidences of dyed textiles in many archaeological sites.

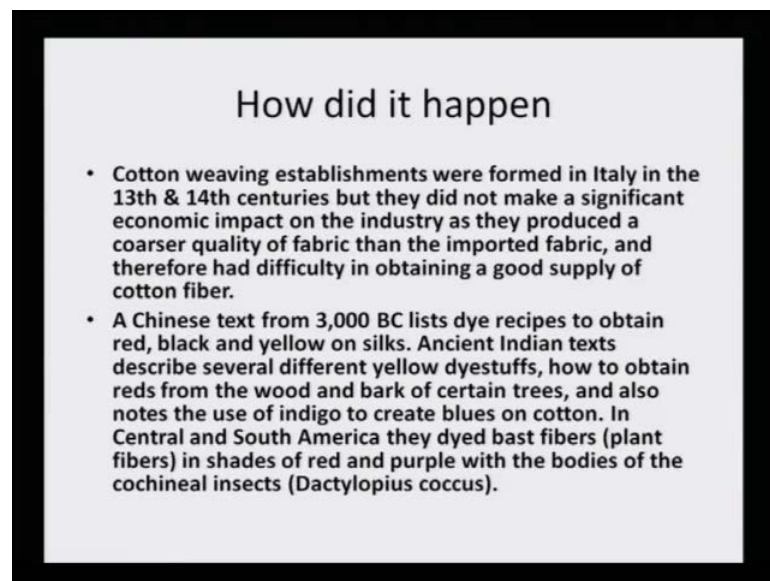
So, now you see it to be able to understand or to know the history of dyes and dyeing is not an easy task. Why because for two reasons, it is quite difficult first thing is that the cultures did not reserved some times, what they were practicing the art of dyeing. And Secondly, because of the geological condition variation, they had different climatic conditions and. So, there the art of dyeing varied from one country to another country, and because it was not well documented, it was kind of difficult to preserve.

Cotton was also valued because of the brightness and colorfastness of the dyes used to color it, and also for it use making candle wicks. So, cotton was very good material for dyeing. Samples of cotton fabric have been found in India and Pakistan dating 3,000 BC, of course that time Pakistan did not exist, but what is presently the Pakistan was what a part of India, and an extended part of India, their samples of cotton have been obtained

from which dated 3,000 BC. Before, Christ but it did not appear in Europe until fourth century.

So, you see cotton was our primary fabric and therefore, we have an art of dyeing cotton mainly, but European countries. It was silk and wool, which are all protein-based fabrics. How did it happen?

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Cotton weaving establishments were formed in Italy in the 13th and 14th centuries as late as that, but they did not make a significant in economic impact on the industry as they produced a coarser quality of fabric than the imported fabric, and therefore, had difficulty in obtaining a good supply of cotton fiber.

So, you see although even it started in Italy in the 13th and 14th centuries, they could not match with the quality that was exported from India and therefore, it was not very high quality. A Chinese text from 3,000 BC lists dye recipes to obtain red, black, yellow and silk. Ancient Indian texts describe several different yellows dyestuffs, how to obtain reds from the wood and bark of certain trees, and also notes the use of indigo to create blues on cotton. In central and south America they dyed best fibers (plant fibers) in shades of red and purple with the bodies of the cochineal insects So, as I told you that the they insect body had a lot of color, which was in the range of red and purple and that was being used mainly in the central and south America.

However and the Indian people mainly use reds from the wood and bark, and indigo and these were some of the common colors and of course yellow, the one which the story of tesu that I told you was primarily used in India.

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The Greek Artifact now even Greek culture or civilization shows that there was a use of natural dyes. A Greek artifact known as the Stockholm papyrus details dyestuffs and techniques in almost a recipe fashion as it was practiced in Egypt in the third and the fourth century. The great detail in which the preparation of the fibers and dyeing materials, and the dying process itself was recorded has led scholars to believe that it had to have been practiced for 1,000s of years previously, in order to raise the process to such a science and art.

So, the process that was documented was much later, and therefore it shows that it is a very evolved process, which has been documented. It discusses mordanting the fibers using alum, copper and iron oxides to darken or “sadden” the red, blue, green purple dyes, as well as the occasional use of tin and zinc. It describes over ten different recipes for using alkanet root as a dye employing camel and sheep urine, lentils, vinegar, wild cucumber and barley malt among others as aids to producing beautiful color. It also gave recipes on maintaining purple hues by over dyeing the alkanet with woad or madder or kermes from the dried bodies of the female shield louse or scale insect and the heliotrope plant.

So, you see that they use various types of combination not only they use metal mordanting, but they also use a very common substance is for enhancing the colors, which were rich in some chemicals, like urine, sheep urine, lentils and vinegars, therefore they were trying to make a very a unique kind of permutation and combination, for dye affinity, for enhancing the dye affinity.

Excavated Coptic textiles dating from 4th to the 6th century, show use of weld to produce yellow, madder and woad for dark purple, and blue from indigo. Scientists have been able to date a red obtained from Egyptian madder root from the 14th century BC. So, you see there have been lots of evidences, what I am trying to draw your attention to the history of dyestuff that it is not a very recent science. It is a very, very old science, which was practiced by the primitive man and over a period of time, it evolved to what we see today. How does history tell us?

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The earliest written record of the use of natural dyes was found in china dated to 2600 BC and chemical text of the red fabrics found in the tomb of King Tutankhamen in Egypt showed that the presence of alizarin, a pigment extracted from madder was observed. Tyrian purple, a well renowned natural dye, occupied prominent position in the roman history. Indigo has been used in the textile industry for the last several 1000 years. It is one of the earliest dyestuffs recorded in history and it still retains supreme

importance even today. Even today the entire denim industry uses indigo. So, you see how important this dye source has been from the time it has started to be used.

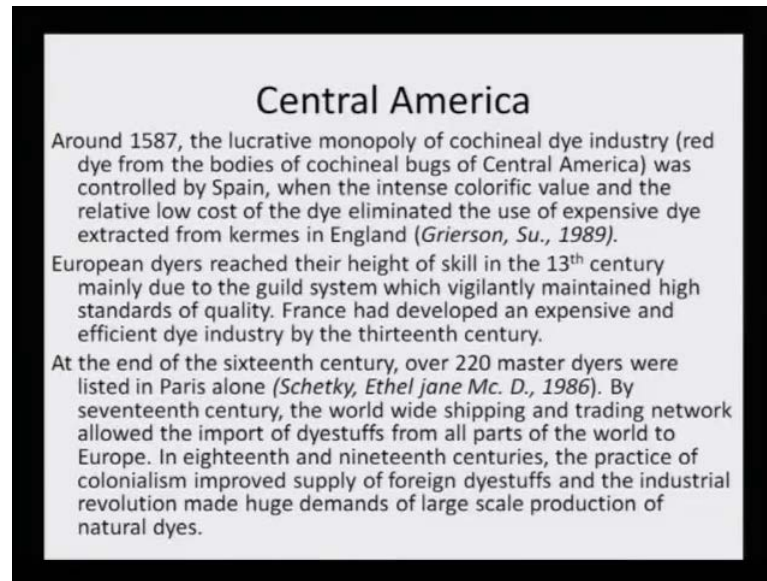
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In Europe how did it all begin: In Europe, the art of dyeing rose to heights influenced by the direct impact of trade, which was instigated by the Crusades and the growing cultural awareness of the renaissance period. Among the major early centers for imported dyestuff was Venice, supplying Brazil wood from the East, Lac and Indigo from India from 15th century AD onwards.

In 1429, the venation dyer's guild documented recipes on different dyes. Woad was grown locally in different regions of Germany from 12th to 14th centuries A.D. That is after the death, and trade fairs were organized with strict legislation on every aspect of trades. So, you see it way goes back to very ancient times and also not. So, ancient times and these are all natural sources of dyes, which have been used even in Central America is what I mentioned this was another very big area, where natural dyeing and dyes were being used.

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**Central America**

Around 1587, the lucrative monopoly of cochineal dye industry (red dye from the bodies of cochineal bugs of Central America) was controlled by Spain, when the intense colorific value and the relative low cost of the dye eliminated the use of expensive dye extracted from kermes in England (*Grierson, Su., 1989*).

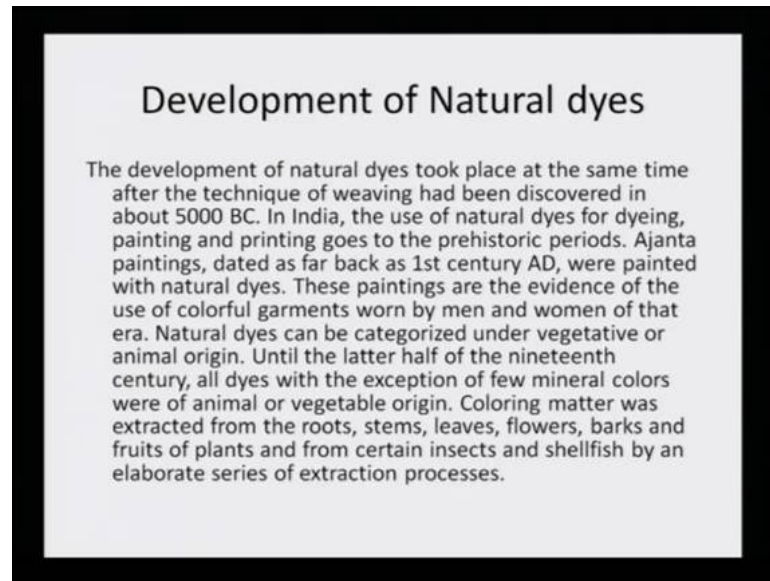
European dyers reached their height of skill in the 13<sup>th</sup> century mainly due to the guild system which vigilantly maintained high standards of quality. France had developed an expensive and efficient dye industry by the thirteenth century.

At the end of the sixteenth century, over 220 master dyers were listed in Paris alone (*Schetky, Ethel Jane Mc. D., 1986*). By seventeenth century, the world wide shipping and trading network allowed the import of dyestuffs from all parts of the world to Europe. In eighteenth and nineteenth centuries, the practice of colonialism improved supply of foreign dyestuffs and the industrial revolution made huge demands of large scale production of natural dyes.

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At the end of the 16th century, over 220 master dyers were listed in Paris alone. By 7th century, the world wide century the world wide shipping and trading network allowed the import of dyestuff from all parts of the world to Europe. In 18th and 19th centuries, the practice of colonialism improved supply of foreign dyestuffs and the industry revolution made huge demands of large scale production of natural dyes. So, you see how the evolution of dyes even took place, how their trading started enhancing and an how this colonial system enhance the supply and the industrial **evolution** revolution help the huge demand.

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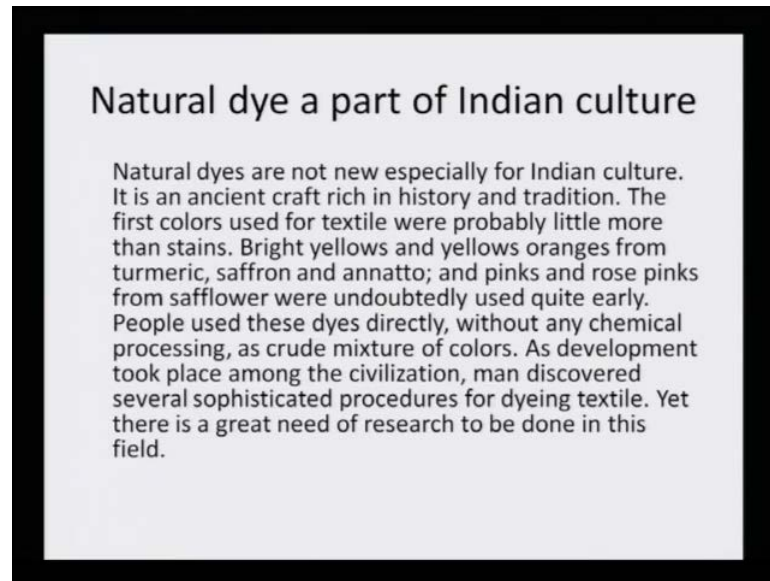


Development of Natural dyes: The development of natural dyes took place at the same time after the technique weaving had been discovered in about 5000 BC. In India, the use of natural dyes for dyeing, paintings and printing goes to the prehistoric periods. The Ajanta paintings, I mention to you dated as far as back as first century AD, were painted with the natural dyes. These paintings are the evidence of use of colorful garments worn by men and women of that era.

Natural dyes can be categorized under vegetative and animal origin. Until the latter half of the 19<sup>th</sup> century, all dyes with the exception of few mineral dyes were animal or vegetable origin. Coloring matter was extracted from the roots, stems, leaves, flowers barks and fruits of plants and from certain insect's shellfish by an elaborate series of extraction processes.



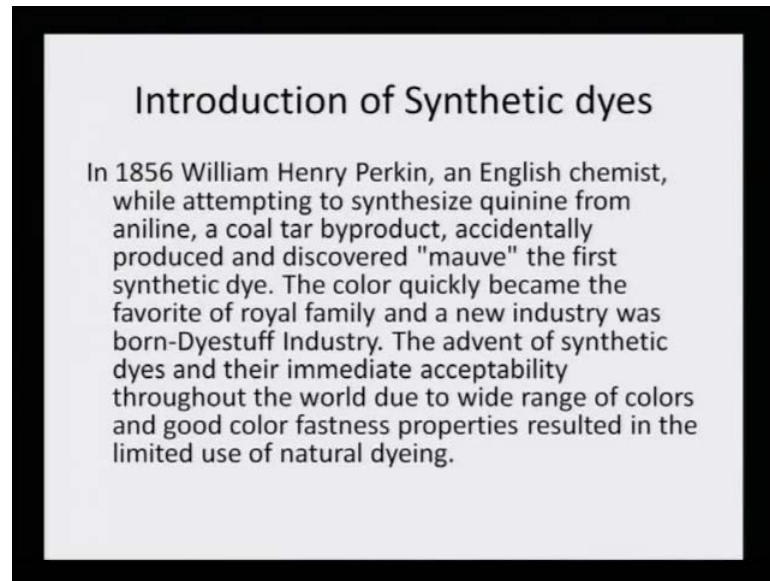
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Natural dye, as a part of Indian culture: We have seen that you know in the history. So, many countries have participated, but what has been a very significant contribution from Indian culture is in the art of natural dyes. Natural dyes are not only especially from for Indian culture. It is an ancient craft rich in the history and tradition. The first colors used for textile were probably little more than stains, white yellows and yellow oranges from turmeric, saffron and annatto; and pinks and rose pinks from safflower were undoubtedly used quite early.

People use these dyes directly, without any chemical processing as crude mixtures of color. As development took place among the civilization, man discovered several sophisticated procedures for dyeing textile. Yet there is a great need of research to be done in this field. So, it is still being a lot of research is going into it, but that is what the history tells us.

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Now comes the introduction of Synthetic dyes: In 1857 William Henry Perkin, an English chemist, while attempting to synthesize quinine from aniline, a coal tar byproduct, accidentally produced and discover “mauve” the first synthetic dye. The color quickly became the favorite of royal family and a new industry was born-dyestuff industry. The advent of synthetic dyes and their immediate acceptability throughout the world due to wide range of colors and good color fastness properties resulted in the limited use of natural dyeing. So, that is when in 1856 as recent is that the synthetic dyes came into existence.

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In India: Until the middle of 19th century all the textiles were, if necessary, dyed/printed with use of natural products. Naturally, various recipes/procedures were in the practice in different parts of the country depending upon the availability of the local special vegetable products and the stage of local standardization/skill achieved by local craftsmen. After independence, the new Indian government recognized the importance of traditional art in Indian society and took steps to support and preserve these and revival by establishing state and local boards for reviving this old art of natural dyeing.

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Indian strong Tradition: India has been prominent as producer of textile and has strong tradition in the making, dying, printing and embroideries embroiling of cloths ancient times. The evidence of madder-dyed cloth is found to be in the excavation of Harrapan culture at Mohenjodero in the Indus river valley dates to the use of mordant-resist dyeing to 5000 years ago. Tinctorial properties of Kala and Asikini, possibly it was a indigo Maharanjana, that is the safflower Manjistha, which is the madder Lodhra, is another dye and Haridra, that is the turmeric were recognized in the Vedic period, particularly in the Athervavedic and succeeding period that is from the 5000 BC to 1000 BC.

So, you see this was a kind of wide range of time period from where it is started natural dyeing in India and the history tells us that India was one of the pioneers.