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### Lecture No-03

Yesterday, we look at the history of dye stuffs and we also looked at the functioning of light and its relation with color. In today's lecture, which deals with classification of Natural dyes and Synthetic dyes, based on their structure and by color; how they are classified; we will try to look at this aspect of dyes. Because it is important to know that the dyes have a systematic classification, whether it is natural dye or synthetic dye based on their chemical structure, they are designed in they are categorized in such a manner that they have to be put under different classification, according to their structure or there is a classification according to their color.

(Refer Slide Time: 01:24)

## Natural dyes

One can get coloring matter from almost all-vegetable matter. However, only a few of these sources yield colorants which can be extracted and work out to be commercially viable. Similar is the case of colorants obtained from animal origin.

Basically, three primary colors are required to get any given hue (or color). This type of approach has been worked out for synthetic dyes. However in the case of natural dyes, the dyeing procedures are different for different dyes and they cannot be blended to get required color easily

Natural dyes: If we try to look at natural dyes. One can get coloring matter from almost all vegetable matter. However, only a few of these sources yield colorants, which can be extracted and work out to be commercially viable. Similar, in the case of colorants obtained from animal origin. So, it is true that every colored substance in nature can yield color that means color can be extracted from any vegetable source or any animal source if they are colored. But how does it react with the material, whether it is a dye which is to be considered for commercial purpose, whether it is a dye which is in substantial quantity is what actually makes the viability of the use of that dye. Primarily, three primary colors are required to get any view or color. This type of approach has been worked out for synthetic dyes as well. However, in the case of natural dyes, the dying procedures are different for different dyes and they cannot be blended to get required color easily.

So, it is important to understand that there are three basic colors, and these three basic colors are hue, are what actually they make the whole Gamut of colors. Now whether it is series or a dye from synthetic dye series or whether it is a natural dye component is what matters.

(Refer Slide Time: 03:19)



How and why natural dyes are different? Never-the-less, while looking for different colors one finds that it is better to have a limited number of dyes with good fastness properties rather than having too many colors or sources with limited fastness properties. Now, it is very important for a dye to be having some qualities, particularly the fastness quality. If suppose, I dye a cloth with turmeric, and turmeric is considered to be a fugitive dye, fugitive means that it does not hold to the fabric or material very well. It is washed off in one go, now in such a case why and how natural dyes are different? Let us try to look at this aspect that what makes natural dye different from synthetic dyes.

Never-the-less, while looking for different colors one finds that it is better to have limited colors of dyes, with good fastness properties, rather than having too many colors or sources with limited fastness properties. So now, you see that whether there is a choice of having fewer dyes, but their fastness properties is good or they should be larger number of dyes a very poor fastness property. Obviously, the first option is better. I will give you an example like for example, if turmeric is used for cotton dying, it is a fugitive dye. A fugitive dyes means that a dye which runs off in water while washing. So, it does not adhere to the fabric and the color is very at the fastness property is very poor and the color runs off, so therefore, turmeric is not considered to be a good dye.

So, in order to have a good dye from the natural dye series, the main criteria is to have good fastness properties. Now these fastness properties include light fastness, washing fastness, perspiration fastness, these are three tests that a dye must go through in order to be proven that it is a good dye for fabric. While selecting the proper pellet of color, one would like to have at least one blue, one red and one yellow to start with. As I earlier said that there are three primary colors, one is red, the other one is blue, and the third one is yellow. Out of these three colors, many, many colors can be generated by proper combination.

Due to the limited number of natural dyes available, the correct choice of dye is very important. Information of some important natural dyes will be shown on the next slide. So, it is very important to keep in mind that these are the three hues or colors, which are important while selecting a dye; and what are the three hue colors? Blue, red, and yellow.

#### (Refer Slide Time: 06:54)



Now looking at the Blue dyes: The color index list only four natural dyes that is Natural Indigo, sulphonated Natural Indigo, Kumbh that is particularly found in Manipur and the flowers of Japanese 'TsuyKusa' used for making awobana paper. Now, these are the four main sources of blue dye, which are popularly used of course, blue dye can be extracted from many other flowers, but are they very good in their fastness properties. As I said in the beginning itself that vegetables having colored part, that means, colored flowers or fruits or bark or stem or leaves can yield color, but the question is that do these extracted color, adhere to the fabric and do they have a good fastness property, is what is of importance. And if they pass in this test of fastness property, they are good material and they can be considered in the series of natural dyes.

The only viable choice among the blue natural dyes is indigo. Natural indigo is obtained by fermenting the leaves of various species of Indigofera, running off the liquor and oxidizing it to precipitate the dye. So, it is not that the direct extract can be use as a dye. There is a certain amount of procedures and oxidation reduction reaction, and only after it is kind of oxidized the dye actually comes up with its true color. Woad which is Isatis tinctoria is another important source of Indigo. The plant is grown mostly in North Europe and British Isles.

With the synthesis of indigo in 19 in 1880 and its successful commercial exploitation in 1897 by BASF, it is a big chemical dye company; the production of natural dye

decreased. The king of natural dyes went into oblivion. There are some sciences of its revival. The current demand of Indigo in US is estimated to be around 800 tunes per year, priced at about 20 million dollars. The main ingredients in natural indigo are indigotin and indirubin.

Now, the structures I will show you in a while, but it is important for you to understand, how important is this dye which has been used from primitive time; and it is because it has a very good coloring agent. But this coloring agent requires a little bit of processing on the fabric. It is not that simply the extract is taken and the fabric is dip and that is it, and it takes the color on it. It has good fastness property. And I was as I was telling you yesterday that the entire denim industry those who wear jeans and I am sure every one of you wear jean, must know that all the jeans are dyed by this color, which is either natural indigo or synthetic indigo.

So, that is why a there was because of the grade demand of indigo, the natural indigo could not be supplied in that much demand, and since the structure is fairly simple structure. It could be easily synthesized in the year 1880 and finally, production of synthetic indigo was facilitated by a very big company BASF in 1897.

(Refer Slide Time: 11:18)



Now we try to look at the structure. You see there are carbonyl groups, and there is an N H group and there is aromatic ring. Yesterday, we were talking about, how these functional groups are the chromopores. Let us now not call them functional group, but

chromo pores. So, the chromopores here are C O N H, and then there is a benzene ring, which is having delocalized electron, and the C C double bond, which is connecting the two indigo tin, moieties together is all in conjugation. The more the conjugation, the more it shifts from color less to colored compound. Similarly the same thing the same kind of moieties, but they are joined in a little different orientation make the indigo Rubin. So, you see that the structurally similar compound, forms the very simplified structure of this natural dye and it can be also synthesize in the laboratory very readily.

(Refer Slide Time: 12:29)

## **Red Dyes**

- The color index lists 32 red natural dyes. The prominent among them are madder (Rubia tinctorum L.), manjistha (Rubia cordifolia L.), brazil wood/ sappan wood (Caesalpina sappan L.), Al or morinda (Morinda citrifolia L.) cochineal (Coccus cacti L.) and lac dye (Coccus laccae).
- Manjistha or Indian madder is anthraquinone based red dye. The most important colorants in madder are the anthraquinones, alizarin (III), purpuroxanthin (IV), rubiadin (V), manjistin (VI), purpurin (VII) and pseudopurpurin (VIII).

Red Dyes: now let us try to look at the red dyes. The color index lists about 32 red natural dyes. I will come to color index in a while, but at least for the time being, you just understand that color color index is a kind of cataloging numbering system. The prominent among them are madder, which is Rubia tinctorum, Manjistha which is Rubia cordifolia, brazil wood or sappan wood, which is Caesalpina sappan and all which is Morinda citrifolia, cochineal, which is Coccus Cacti and lac dye which is Coccus laccae.

Now these are the various sources of red dye. Manjistha or Indian madder is anthraquinone based red dye. The most important colorant in madders are the anthraquinone, which are alizarin, purpuroxanthin, rubiadin, manjistin, purpurin and pseudopurpurin. So, these all make the color which is obtained from madder - Indian madder or manjistha. Now, it is not that natural come dyes occur in isolation molecule, they are always a combination of similarly, structurally, you know similar compounds and they have structural detailing a little bit different from one another, but they have a basic skeleton, which is similar. And in this case the basic skeleton is anthraquinone; it is the functional groups on the anthraquinone main basic structure that differs in these verities of red dyes.

(Refer Slide Time: 14:29)



Now, if you look at the structure, you will see that the simplified alizarin has two hydroxyl, which are ortho to each other. In the second case the hydroxyl are meta to each other, in the third case there are two hydroxyl, which are meta and in between there is a methyl group. Similarly in the fourth case there are two hydroxyl in the meta position, but there is a carboxylic group in the ortho position, rather in the middle position and similarly we have the fifth molecule, which as three hydroxyl compounds two ortho and one Para and there is the fourth fifth type of molecule, which is pseudo perpurin and it has a carboxylic group at the Meta position. So, you see that these are slightly structurally different, but they all have one basic common similarity, and that is the anthraquinoid that is benzene, carbonyl benzene ring, which is to be noticed here.

#### (Refer Slide Time: 15:43)



More red Dyes are from the verity of Brazilin, which is which as a C. I. number - Natural Red 24; and is the main coloring component from Ceasalpinia echinata Lam that is the Brazil Wood. It is as the name suggest the these wood verity must be available only there, and that is by the name common name Brazil Wood and Ceasalpinias sapan wood, or sappan wood. These two have very similar structure, Brazilin has shown in the figure and that gets a oxidized to red Brasilein has indicated. Now, these compounds are the the carbonyl compound does not have a very good color, but when it is in the enolic form Brasilein, it is brightly red colored dye.

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Red dye from the lac dye variety this also when we looked at the different types of red dyes, this was also one of the verities, which is isolated from the animal source. Lac is perhaps one of the oldest of all known red dyes. However, cochineal and kermes were widely use in the western world for the production of bright purple and red colors. The lac dye is extracted from lac, the resinous protective secretion of tiny insect, Luccifera lacca, which is a pest on a number of plants both wild and cultivated. It secretes a thick resinous fluid which envelops their bodies; and secretion from a hard continues encrustation over the twigs. They contain only 1 to 2 percent of the dye.

There are four coloring components in lac, designated as laccic acid A, B, C and E. Laccaic acid A being the most abundant, Laccaic acid is called Xanthokermesic acid, and it closely resembles kermesic acid in structure. Lac dye being an acid dye can be directly dyed on protein fiber such as wool and silk. It also produces very dark shades on nylon. The hues can be modified by post mordanting treatment with metal salts. The dye has very good light and washing fastness.

So, you see that this also is not a single dye, it is a component made out of various types of laccaic acid A, B, C, D and E. And among them A component is present in maximum and it is being secreted by a tiny insect called Luccifera lacca. Now, this Luccifera lacca insect can thrive on wild as well as some of the cultivated plants. And it secretes some kind of resinous fluid, which encrust the or which covers the twig and then from that it

can be taken out and extracted. The extraction only gives 1 to 2 percent of the dye, but the dye is so, rich in color that it is sufficiently that very small quantity is required, for dying because it is very rich in color.



(Refer Slide Time: 19:41)

Now if you try to look at the structure of Laccic acid you will see that structures of Laccic acid, where all is represented as CH 2 NHCOCH 3 and in the case of laccic acid B the R is represented by CH 2 O H and in Laccic acid C. It is R is represented by CHNH 2 COOH. And in the case of Laccic acid E, R represents CH 2 NH 2. So, it has a carboxylic acid moiety that is why it is an acid Laccaic acid, but it also as an amino group, which causes good aderation to the fabric.

#### (Refer Slide Time: 20:27)

#### Yellow Dyes

Yellow [Mayer and cook, 1943; Goodwin, 1976; Cardon and Chatenet, 1990 and Singh et al., 2001] is the most common color in the natural dyes. However most of the yellow colorants are fugitive. The color index lists 28 yellow dyes. Some of the important yellow dyes are obtained from berberry (*Berberis aristata*), tessu flowers (*Butea frondosa, monosperma*) and kamala (*Mallotus philippensis*).

- Other sources of yellow dye are black oak (Quercus velutina), turmeric (Curcuma longa), weld (Reseda luteola) and himalalayan rhubarb (Rheum emodi).
- Some coloring matters are berberine (XII), its derivatives (XIII), chrysophanic acid (XIV) and luteolin (XV).

Now, trying to understand what are the Yellow Dyes; let us try to look which are the categories of Yellow Dyes, which come under the category of natural dyes. Yellow Dye has been the most common color among the natural dyes. However most of the yellow colorants are fugitive, I just give you an example of turmeric. We saw that how you know, turmeric dye although it dyes very well, but it runs off in the first wash and by second wash no no color is left on the fabric. So, such a dye will be considered as a fugitive dye.

However most of the yellow colorants, which are fugitive. So, there is a big problem which yellow dye to choose and which is the dye that needs to be considered for yellow coloration of the fabric. The color index lists about 28 yellow dyes. Some of the most yellow important yellow dyes are obtained from berberrry that is Berberries aristata, tessu flowers. I just mentioned yesterday about tessu flowers and the festival times associated, because it blooms at a particular basanth festival. It is extracted from the plant, butea, frondosa and kamala, which is malaotus philippensis.

So, these are the few plants from which the yellow dye is popularly extracted, although 28 yellow dyes have been enlisted. Other sources of yellow dyes are black oak that is Quercus, velutina, turmeric which is Curcuma longa, weld which is Reseda luteola and himalayan rhubarb, which is Rheum emodi. So, there are other sources it is not does just the once which I mentioned, some coloring matters are berberine is derivatives

chrysophanic acid and luteolin. These are the main structural compounds in the yellow dyes of course, there are alert other types of structural details, these are just representative that is berberine is one which is from the berberis aristata, and the chrysophanic acid is present in tessu and luteala is also present in many compounds, because it is a very popular flavonol.

(Refer Slide Time: 23:18)



Now, if you try to look at these compounds, you will see that the compound 12 and 13 are basically the berberine structures and the you know, substituted berberines structures. Whereas compound 14 is a typical compound, which is chrysophanic acid, ahchrysophanic acid and the compound 15 is the one, which I was lutherlyn. Now, you see that all of them have popularly got or they have a common feature, they that they have more than one hydroxyl group.

So, there must be some reason for them to be a good dye, because these auxochromes help in color enhancement and even in color adheration. So, you now can understand that either a methoxy group or a hydroxyl group can contribute well to become a good dye model. Now, there are some other dyes, which needs to be a discussed structurally they are different.

## (Refer Slide Time: 24:29)



Dihydropyran: Dyes closely related to flavones in chemical structures are substituted dihydropyranes like the one shown here. Now this dihydropyranes also has hydroxyl group, it has a carbonyl group and an in holmic carbon. So, it has the potential of becoming a very good dye.

(Refer Slide Time: 24:53)



Similarly there are dye molecules, which come under the category of Anthracyanidines. Anthracyanidines: Carajurin obtained from bignonia chica is one dye you know again you will see that there is an o-methoxy, and there is a hydroxyl group, and there are aromatic systems, which make the conjugation; yesterday I was talking about what makes a dye a colored molecule, because only when a chemical has color, it at least can be categorized in the category of dyes. So, the bottom line of understanding the structure is that the dye must have an extended conjugated system. Yesterday, what I whatever I told, I am trying to show you through these structures that all these dyes structures have many, many chromopores, and they have equally high number of oxochrome to add on to the color requirement.

(Refer Slide Time: 26:12)



Coming to Carotinoids: In these the color is due to the presence of long conjugated double bond and Annato and saffron's are the examples; even Annato and saffron they give orange color, and we know Carotenoids you have heard about carrots. Carrots are orangish red in color, and that is because they have this beta carotene moiety. And particularly, I have taken this example of beta carotene, because it has extended conjugation and it shows that it is having lot of chromo pores and these chromopores are nothing but double bond, single bond double bond single bond; and because that electrons are highly de localized, throughout the molecule, it absorbs in the ... It moves on to higher wavelength, longer wavelength and reaches the orange red color of the visible region of the electromagnetic radiation. So, these structural details are very important in deciding the color of the dye molecule, whether it is from the natural source or from the synthetic source.

## Triaryl methane dyes- Synthetic dyes

- Triaryl methane dyes. These include the quininoid arrangement as the actual chromophore. The quininoid ring but since all three benzene rings are equivalent there can be rearrangement of the bonds and any of the benzene rings could take up this arrangement.
- There are a large number of dyes used in histology that fall into this category; a few examples are fuchsins, methyl violet, methyl blue and aniline blue

Now, let us consider a few synthetic dyes as well. Triaryl methane methane dyes, these include the quininold arrangements as the actual chromopore. The quininold ring but since all three benzene rings are equivalent, there can be rearrangement of the bonds and any of the benzene ring could take up this rearrangement or arrangement. So, because Triaryl three aryl or aromatic rings are designed or connected to each other; and there could be a lot of rearrangement arrangement in any one of these three rings. So, that makes a still extended conjugation. There are a large number dyes used in histology; histology means tanning in of the cells that fall in to this category. A few examples are fuchins, methyl violet, methyl blue aniline blue. I am sure you must have heard the name of at least these dyes, because they are very common staining dyes.

## Other dye- Synthetic dyes

- Anthraquinone. Here the quininoid ring is seen as the middle of the three fused rings. Examples are alizarin and carmine.
- Xanthene. Here the quininoid ring is the right hand one of the three fused rings and the ring is tilted compared with the previous example. Examples include eosin and xanthene.
- Thiazine. This is very similar to the previous example in overall structure, but the middle ring now has S and N as constituent atoms. This group contains many important metachromatic dyes, such as toluidine blue, methylene blue and azure A.

Other dyes under the category of Synthetic dyes fall in the category of Anthraquinone. Here the quininold ring is seen as the middle of the three fused ring. For Example alizarin just a while ago, we saw the structure of alizarin and carmine. Xanthene is another class of dyes. Here the quininoid ring is the right hand is the right hand on the three fused ring and the ring is tilted compared with the previous example. Examples of xanthenes dye would be eosin and xanthenes itself.

Thiazine, this is very similar to the previous example in over all structure, but the middle ring now as either sulphur or nitrogen as constituent atoms. This group contains many important metachromatic dyes, such as toluidine blue, methylene blue azure A and so on. So, these are various types of structurally different dyes, which come under the categories of either a anthroquinine dye or xanthenes dyes or Triaryl methane dyes and so, on. When we try to look at the chemical structure of the dyes, they are also categorized on the basis of whether they are acidic or basic or neutral.

#### (Refer Slide Time: 30:24)

#### **Basic Dyes**

Basic dyes are cationic and will stain/ color anionic or acidic materials such as carboxylates, sulphates (many complex carbohydrates are sulphated) and phosphates (particularly the phosphates in nucleic acids). Most are used as nuclear stains and staining of cytoplasmic carboxyl groups is deliberately suppressed by using a slightly acid pH. Acidic substances that stain with basic dyes are termed basophilic.

So, let us try to see the classification based on that. Basic Dyes are cationic and will stain/color anionic or acidic material obviously, because acid will stain basic or basic will stain acidic. So, in if it is a basic dye, it will stain the acidic dyes, such as carboxylates, sulphates many complex carbohydrates are sulphated and phosphates particularly the phosphate in nucleic acids. Most are used as nuclear stain and staining of cytoplasmic carboxyl groups is deliberately suppressed by using a slightly acidic p H. Acidic substances that stain with basic dye are termed as basophilic, basophilic base loving. So, basic dyes are very good for acidic material.

(Refer Slide Time: 31:33)

#### Acidic and Neutral dyes

- Acidic dyes are anionic and will color cationic or basic groups such as amino groups. Most are used to stain proteins in the cytoplasm and connective tissues. Substances that stain with acid dyes are called acidophilic.
- Neutral dyes are simply compounds of basic and acid dyes. In this case, both ions are coloured. Such dye complexes will stain both nucleus and cytoplasm from a single dye bath. Romanowsky stains are neutral dyes made from more complex mixtures. These are the commonest dyes used in haematology. They are less common in histology but still very useful and include Giemsa, Leishman and Wright's stains.

Now as what I mention the while ago categorizing them in to basic dyes, Neutral dyes and Acidic dyes. Let us try to look at what the Acidic dyes and the Neutral dyes are all about. Acidic dyes are anionic and will color cationic or basic groups such as amino groups. Most are used to stain proteins in the cytoplasm and connective tissues. Substances that stain with acid dyes are called acidophilic. Obviously as the name suggest.

Neutral dyes are simply compounds of basic and acidic dyes. In this case, both ions are colored; such dye complexes will stain both nucleus and cytoplasm from the single dye bath. Romanowsky strains are neutral dyes made from more complex mixtures. These are the commonest dyes used in haematology. They are less common in histology, but still very useful and include Giesma, Leiahman and Wright's stains. Now, these particular classifications come under the category, when we are trying to look at staining of nucleus or cytoplasm.

So, it is not that dyes only meant for fabric or dye is only meant to color the food, dye can be use in various aspects and the dyes, when they are used in nucleic acid dying or in cytoplasm or in in a cell, then what it its role? It the role will come from the acidic or the basic condition of the cytoplasm. And therefore, they are named or there nomenclature is based on the acidity or the basicity or the neutrality.

(Refer Slide Time: 33:20)



Then there are some Amphoteric dyes: Amphoteric dyes both having anionic and cationic group, in the same molecule that is why amphoteric, but these are on the same ion. Amphoteric dyes have both positively chargeable groups and negatively chargeable groups present on the molecule. Depending on the charge actually present these dyes may interact as either positively charged ion basic dyes or negatively charged ion as acid dyes. So, you see that there are COO 3 minus as was as NH 2 plus both are present on the same moiety.

(Refer Slide Time: 33:55)



Natural dyes: Now, if we try to even look at the going back to our Natural dyes, the there are a class of Natural dyes, which have very extended conjugated systems, and then they may be having glycosidic linkages. Natural dyes are simply dye substances extracted from natural sources. Although the main source of dye was from early times, they have largely been replaced by synthetic dyes present time, which I usually more reliable, cheaper and can be supplied more readily. Natural dyes still in use include haematoxylin, carmine, orcein and litmus, although synthetic varieties are also available for some of these.

So, there has been a big debate whether to use good natural dye or a new natural dye or to go over to synthetic dyes, we will not get in to the debate what to use, when to use, but I am simply introducing you to these two different classes of dyes, which are popularly used and the structural details of these dyes are so different. So, you see that among the natural dyes, we have indigoid, we have quinonoid, we have Dihydropyran, we have anthocyanidines and so on and so forth; whereas in the case of synthetic dyes, we have Triaryl methane dyes, we have again anthraquinoid dyes, we have xanthenes dyes, and we have Thiazine dyes.

So, you see because of the structural detail of these dyes, they become different from one another. And it is more that the emphasis on natural dyes will be pain throughout this lecture, because this is primarily a course, which will reflect more information about the natural dyes. So, we will be now dealing more and more with natural dyes, and their structural details. Never-the-less it is important for you to get at least some over view of synthetic dyes, because unless and until you understand the the structural difference between these two dyes. It is not possible for you to have an appreciation of this course.