FOOD SCIENCE AND TECHNOLOGY

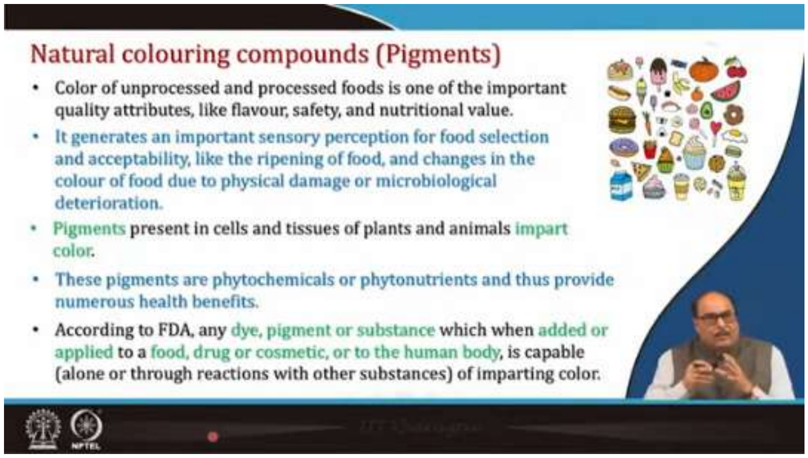
Lecture29

Lecture 29: Pigments and Colours

Hello friends, Namaste.

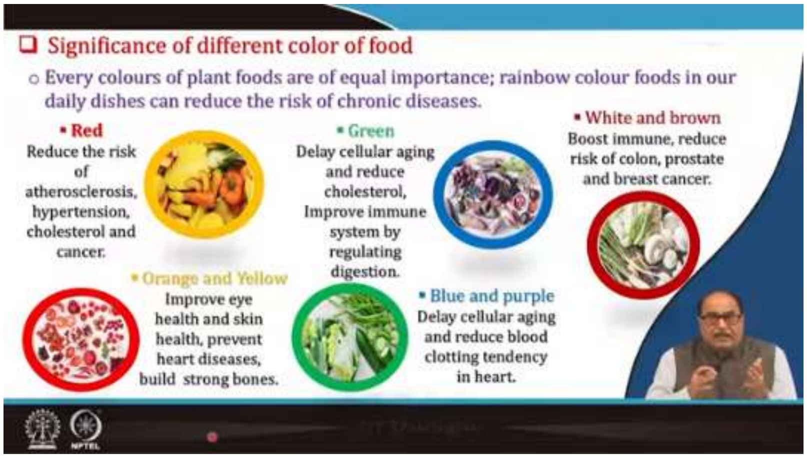
Now, in this lecture, which is lecture 29, we will talk about pigments and colors.

The concept that we will discuss in the next half an hour or so. Include natural coloring compounds like chlorophylls, myoglobin, anthocyanins, tannins, quinones, xanthones, flavonoids, carotenoids, etcetera. These are the various coloring compounds which give color and contribute to the color naturally of various biological materials. Then we will also talk about structural changes and their effect on the color hue, particularly during processing and other process steps, environmental conditions. And then, in the end, we will also touch upon synthetic colors.

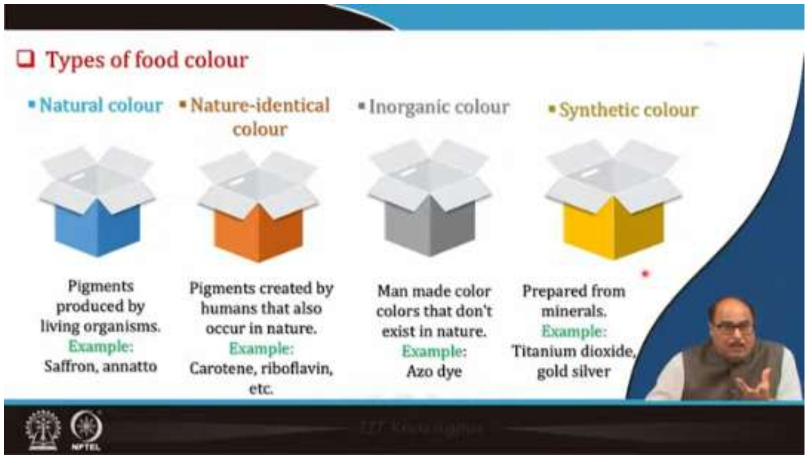


So, the natural coloring compounds, like you know, the color or hue of various natural materials, agricultural materials, biological materials is because of the various compounds which are naturally present in them, and these are called pigments. Natural coloring compounds are pigments. This is both in unprocessed and processed foods; color, you know, is one of the very important quality attributes like flavor, safety, and nutritional value, color is also one very important criterion. It generates an important sensory perception for food selection and acceptability. When you go to the market to buy some food, particularly fruits, vegetables, etcetera, many times we get attracted to the color of the food and it decides whether we should accept it or not. Even like in the ripening of the fruits, when a vegetable or a fruit ripens, its color changes. So, during the ripening process, various compounds are naturally synthesized, they are formed, and which contribute to the color of that particular fruit/vegetable. Like a mango, a green mango becomes red or orange or of different color depending upon the type of the compounds which are formed during the ripening process. Also, there are changes in the color of the food due to physical damage or microbiological deterioration. Sometimes if the food or fruits or vegetables are physically damaged, then there are various microorganisms and other reactions, the causative factors there act on this, and they change the form in which these natural pigments are present. So, their color hue is reduced, or the color is sometimes, depending upon the type of reaction or type of process, it may completely be bleached. So, these pigments, basically, the natural pigments, are basically the phytochemicals or phytonutrients, and therefore, they also provide numerous health benefits. In the last lecture, we discussed the health benefits of the phytochemicals. So, the pigments which are present in the cells and tissues of plants and animals impart their color and also have various health benefits.

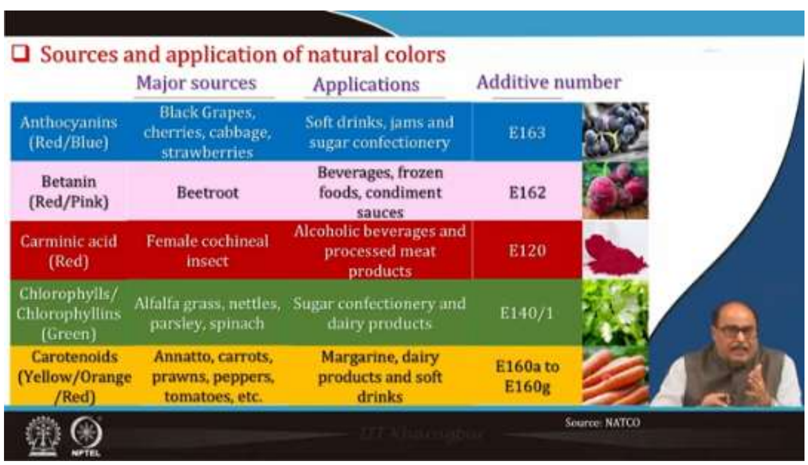
According to the Food and Drug Administration, any dye, pigment, or substance which, when added or applied to a food, drug, or cosmetic, or to the human body, is capable alone or through reactions with other substances of imparting color. That is the FDA definition of colors or pigments.



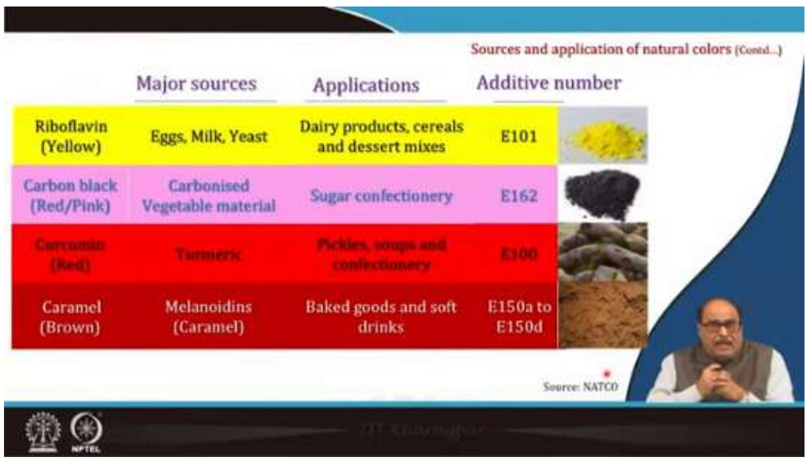
So, the significance of different colors of food, like you know, every color of plant food is of equal importance. The rainbow colors of foods in our daily dishes can reduce the risk of chronic diseases. That again, we discussed earlier, that these colors mainly are the phytochemicals. Phenolic compounds and such other compounds, which, in addition to imparting the color properties to the food, they also have various health-promoting activities. Like, for example, let us see the red color. The red color reduces the risk of atherosclerosis, hypertension, cholesterol, and cancer. The green color delays cellular aging and reduces cholesterol. It improves the immune system by regulating the digestion process. White and brown colors boost immune function and reduce the risk of colon, prostate, and breast cancers. Orange and yellow colors improve eye health and skin health. It prevents heart diseases, build strong bones, whereas the blue and purple colors delay cellular aging and reduce the blood clotting tendency in the heart. So, these are the different various foods shown in this picture which provide this, like white and brown colors, such as mushroom and cauliflower. Green color is found in various green leafy vegetables, etcetera, blue also. Then red color in various red vegetables, red fruits, and so on.



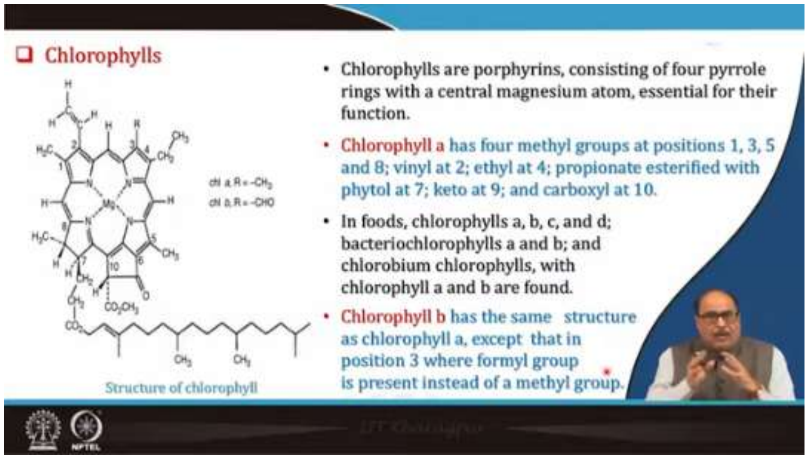
So, the various types of food colors in this slide, I have tried to give you like there is one, obviously, the natural color that is pigments which are produced by living organisms, living cells, bio cells, etcetera. For example, saffron, annatto, etcetera, these are the natural colors. Then, nature-identical color, the other category of color may be nature-identical colors. For example, carotene, riboflavin, etcetera, these are the pigments that are created by humans that also occur in nature. Then, inorganic colors, inorganic colors are man-made colors. They do not exist in nature. For example, azo dye, they are basically man-made colors. Finally, comes the synthetic color, they are prepared from minerals like the synthetic color examples include titanium dioxide, gold, silver, etcetera.



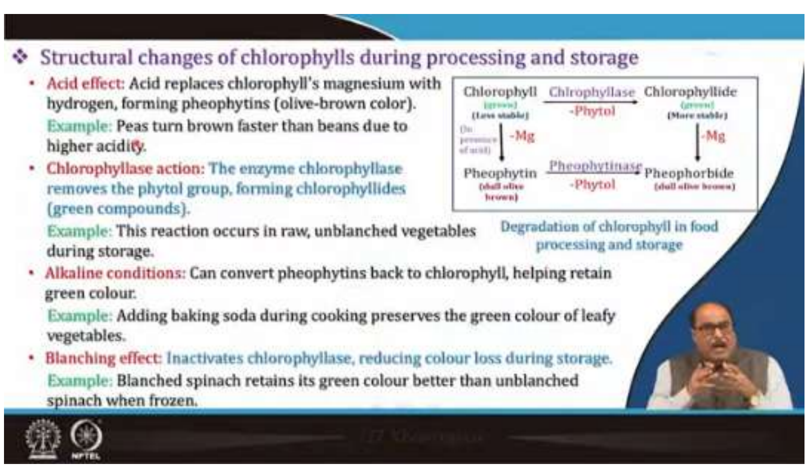
Now, I have tried in this slide to give you an overview of the major sources. The applications and additive numbers of the major colors, that is, natural color pigments. For example, anthocyanins, which are red or blue colors, are found in black grapes, cherries, cabbage, and strawberries, and they are used majorly in soft drinks, such as fruit juices, etcetera, and are found in jams and sugar confectionery. These compounds are used, and their additive number, as per the FDA and Codex, is E163. Then, betanin is the red pigment, red or pink, found in beetroot. It is used in beverages, frozen foods, and condiment sauces. Its additive number is E162. Then, carminic acid, which is again a red pigment. It is found in female cochineal insects, and its applications include alcoholic beverages and processed meat products. Its additive number is E120. Chlorophylls and chlorophyllins are normally of green color and they are found in alfalfa, grasses, nettles, parsley, spinach, etcetera, and they are used in sugar confectionery and dairy products. Their Codex Alimentarius number or additive number is E140 by 1. Carotenoids, which are yellow, orange, or even red pigments. They are found in annatto, carrots, prawns, peppers, tomatoes, etcetera and their applications mainly include margarine, dairy products, and soft drinks that is annatto, you see, it is used in margarine, that vegetable butter, to give its yellow color like that, they are naturally present in dairy products. Its additive number is E160A to E160G, depending upon the source from which they are found.



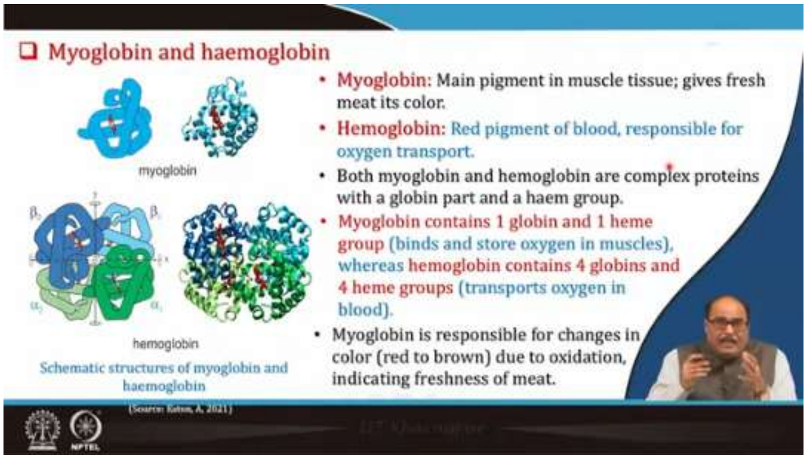
Then riboflavin, which is a yellow pigment, is mainly found in eggs, milk, and yeast. The yellow color of the egg is mainly because of riboflavin and its application is in dairy products, cereals, and dessert mixes; its additive number is E101 Then carbon black, that is the red or pink They are carbonized vegetable material or used in sugar confectionery; its additive number is E162. Then again, curcumin, which is red curcumin, is mainly found in turmeric. It is used in pickles, soaps, and confectionery, and its additive number is E100 And the caramel brown, which is melanoidin, that is the caramel, is used in baked goods and soft drinks, etcetera, E150 A to E150D is the additive number. So, these are the natural pigments which are found in various agricultural materials or biomaterials or food materials naturally, and there are various methods of extraction processes by which they are extracted, characterized, and purified for use in various food applications. So, that is what I summarized in this.



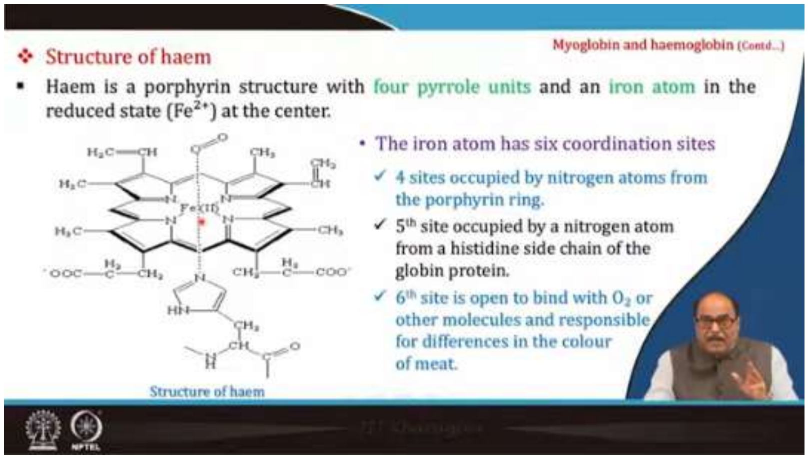
Now, let us talk about some important chemistry of some major pigments present in food materials. The first such chemical to come up is chlorophyll. See, the chlorophyll, it is a very, very big and huge structure. They are basically porphyrins consisting of four pyrrole rings. In the center, there is a magnesium ion. This magnesium ion and the pyrrole rings are essential for their biological functions, etcetera. Chlorophyll mainly has two groups: chlorophyll a and chlorophyll b. Chlorophyll a, as you can see in this structure, has four methyl groups at positions 1, 3, 5, and 8. It has a vinyl group at position 2, an ethyl group at carbon position 4, and also it has a propionate esterified with phytol at the 7th position and a keto group at position 9 and a carboxyl group at position 10. So, this makes the very complex structure of chlorophyll. So, in the foods, in fact, chlorophyll A, B, C, and D, that is bacterial chlorophylls A and B and chlorobium chlorophylls with chlorophyll A and B are found. The chlorophyll B has the same structure as that of chlorophyll A except that in position 3, if you see here, it is the R. So, when this R is a methyl group, it becomes chlorophyll A. When this R is a formyl group CHO, then it becomes chlorophyll B. So, otherwise, the structure is the same for chlorophyll A and B; the only difference is the group at the carbon position 3.



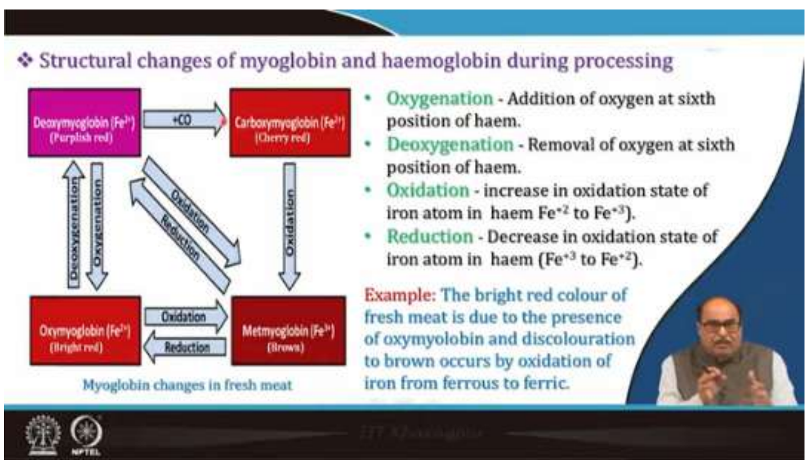
Now, there are various structural changes in the chlorophylls during processing and storage of the food, and these structural changes in the chlorophyll influence even color hue of the food materials. particularly fruits and vegetables, etcetera when they are heated. When they are cooked the green color converts into the dull brown color, etcetera, the changes, etcetera, in the color. So, that is mainly because of the structural changes of the chlorophyll during cooking, similarly during processing and storage, etcetera. So, there are these structural changes, and they are influenced by various factors, like the acid effect, which means this acid replaces in the presence of acid, this magnesium which is present in the center of the chlorophyll structure, is removed. The chlorophyll, which is generally of a green color, is less stable in the presence of acid. When magnesium is reduced, the chlorophyll is converted into pheophytin and this pheophytin is basically of a dull olive-brown color. So, particularly, you can take the example of peas, which turn brown faster than beans due to their higher acidity. Peas have a comparatively higher amount of acid in comparison to beans. When beans and peas are heat-processed under similar conditions, the change in color is more pronounced in peas compared to beans. This is mainly because of the presence of more acid in peas. Additionally, the structural change is due to the action of the chlorophyllase enzyme. So, the enzyme chlorophyllase can remove the phytol group from the chlorophyll structure, and by this, chlorophyll is converted into chlorophyllide. In this change, there is the removal of the phytol group from the chlorophyll. It makes the less stable green colour into a comparatively more stable green colour. These chlorophyllides are mainly green compounds and more stable and this reaction occurs in raw, unblanched vegetables, particularly during storage. If the vegetables are not blanched, then if their enzymes are active during storage, this action will take place. Then, if there are alkaline conditions, like the alkaline condition, they convert pheophytins back into chlorophyll, helping retain the green colour like this again. Adding baking soda during cooking preserves the green colour of leafy vegetables. Similarly, there may be a blanching effect, as I told you, that blanching effect if the vegetables are blanched, then it inactivates the chlorophyllase enzyme and then reduces the colour loss during storage, meaning that the removal of phytol is stopped. Blanched spinach retains its green colour better than unblanched spinach when they are frozen. So, this is a reaction that gives the pheophorbide a dull olive brown colour, then pheophytin, if phytol is removed, it becomes pheophorbide, a dull olive brown colour. These are various ways by which the structural changes during processing and storage of the food materials occurs which finally affects the color hue and even also its biological property.



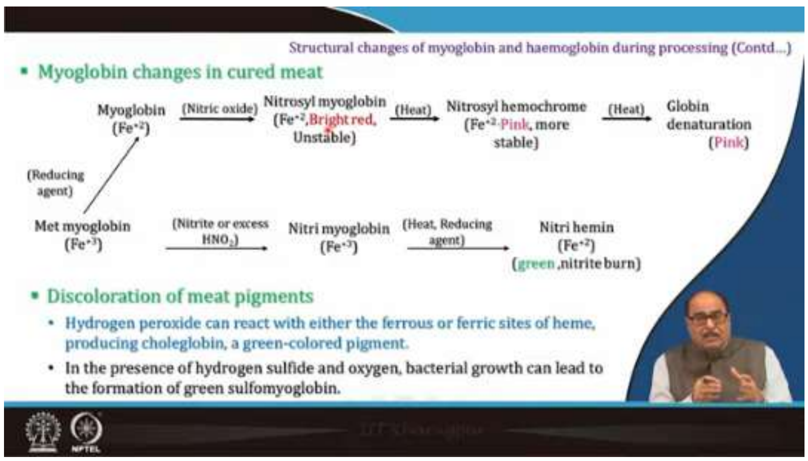
Then another very important compound and pigment, a natural pigment in the biological material, is the myoglobin. In the chlorophyll, it was the major pigment present in the plant material or even some algae, etcetera. That myoglobin and hemoglobin are the major red pigments present in the animal material. Myoglobin is the main pigment in the muscle tissue; it gives fresh meat its color, the fresh color of the meat. Whereas, hemoglobin is the red pigment of blood, and it is responsible for oxygen transport. Myoglobin and hemoglobin are basically complex proteins, and they have a globin moiety; there is a protein part and a non-protein part. There is a complex protein with a globin part and a heme group. So, normally myoglobin contains one globin and one heme group and, this binds and stores oxygen in the muscles, whereas hemoglobin contains four globin and four heme groups; that is, one globin and one heme group is myoglobin. Four globin and four heme groups become hemoglobin, and this hemoglobin transports the oxygen in the blood. Myoglobin is responsible for changes in the color, that is, from red to brown, due to oxidation, indicating the freshness of the meat, that is, when the animal is slaughtered. Then, there are significant changes, such as oxidation, etcetera. that is myoglobin converted into oxymyoglobin and then red metamyoglobin, and this causes the changes. There are all these three colors present with the fresh meat, that is myoglobin, oxymyoglobin. There is a dynamic system, you can say, of this myoglobin, oxymyoglobin, and metamyoglobin and these depend upon the availability of oxygen, that is the oxidation-reduction process, and accordingly, the color of the meat gets stabilized or gets changed. So, if you look at the structure here again, you see like the chlorophyll structure.



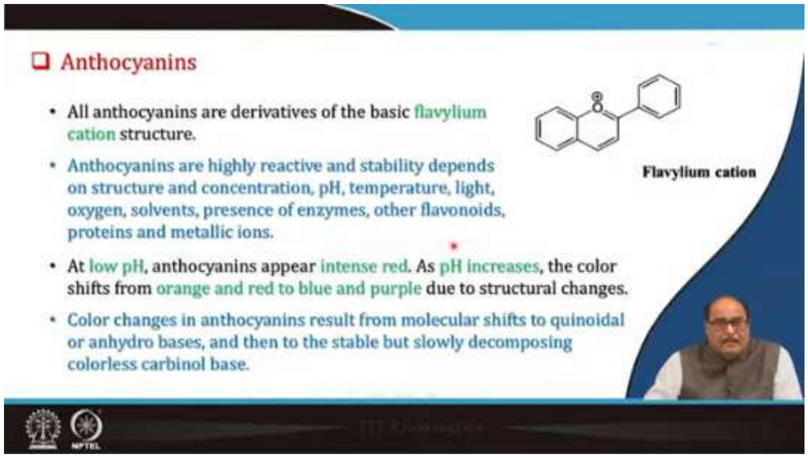
Similarly, here also it is a very complex structure, it is particularly the haem, it is a porphyrin structure with 4 pyrrole units, and here, in the chlorophyll, it was the magnesium in the center and here, in this myoglobin, it is the iron, Fe, in the reduced state. There is Fe^{+2} in the iron ferrous state at the center. So, this iron atom basically has a 6 coordination sites, among which 4 sites are occupied by nitrogen atoms from the porphyrin rings, that is, 4 porphyrins are there, whereas the 5th site is occupied by a nitrogen atom from a histidine side chain of the globin protein. There is a haem, and the sixth site is open to bind with oxygen or other molecules and it is the sixth side that is responsible for differences in the color of the meat.



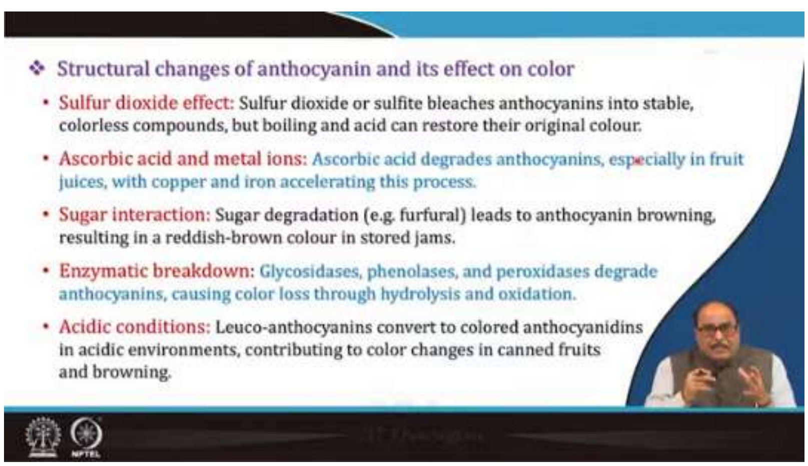
So, the structural changes again in the myoglobin and hemoglobin during processing, etcetera. As I told you, there is a dynamic system of myoglobin, oxymyoglobin, and metmyoglobin. That is the oxymyoglobin where iron is in the reduced state, the ferrous form, and it is a bright red color. Then, oxidation results in converting it into metmyoglobin and it is a bright red color or brown color comparatively, where ferrous is converted into the ferric state. Similarly, deoxymyoglobin, which is purplish red, is converted into carboxymyoglobin in the ferric state, which is cherry red. So, depending on it, oxidation and continuous oxidation and reduction processes are even interchangeable, depending upon the availability of oxygen. Oxygenation is the addition of oxygen at the sixth position of the haem. Deoxygenation is the removal of oxygen from the sixth position of the haem. Oxidation increases the oxidation state of the iron atom in the haem, that is, from Fe^{+2} to Fe^{+3}, and then reduction decreases the oxidation state of iron in the heme, that is, from Fe^{+3} to Fe^{+2}, which is ferric to ferrous. If you see the example, the bright red color of fresh meat is mainly due to the presence of oxymyoglobin and its discoloration to brown occurs by the oxidation of iron from ferrous to ferric, and oxymyoglobin is converted into metmyoglobin.



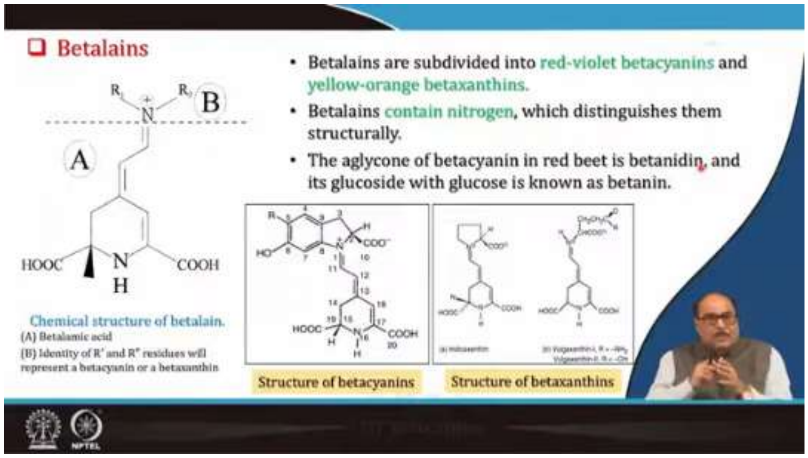
Then, there are again the myoglobin changes in the cured meat. That is the curing, which is considered to be a good process for the storage of the meat and also for the fixation of the bright red color. So, during curing, sodium salt and a curing mixture, basically, nitrates or nitrites compounds of sodium are added with other compounds, then there is a series of reactions, as you say. There is myoglobin; metmyoglobin is reduced, and it becomes myoglobin. Myoglobin combined with nitric oxide becomes nitroso myoglobin. So, here, ferrous is still in the ferrous state; it is in the +2 state, it is bright red and unstable, but when this meat is mixed with a smoke curing mixture, when it is smoked or when it is given heat treatment, then nitrosomyoglobin is converted into nitrosyl hemochrome and here, the iron is again in the ferrous state, but its color is pink, and it is more stable. Further, if you make it heat-treated, then it becomes globin, which is denaturation pink. Another way is that metmyoglobin reacts with HNO_2, which is nitrite, or excess HNO_2, that is nitri myoglobin and it is heated either by it is nitri hemin, that is, it is in nitrate burn. So, mainly, the discoloration of meat pigment, that is, hydrogen peroxide, can react with either the ferrous or ferric sites of the haem producing. Choleglobin is a green-colored pigment. In the presence of hydrogen sulfide and oxygen, bacterial growth can lead to the formation of green sulfomyoglobin.



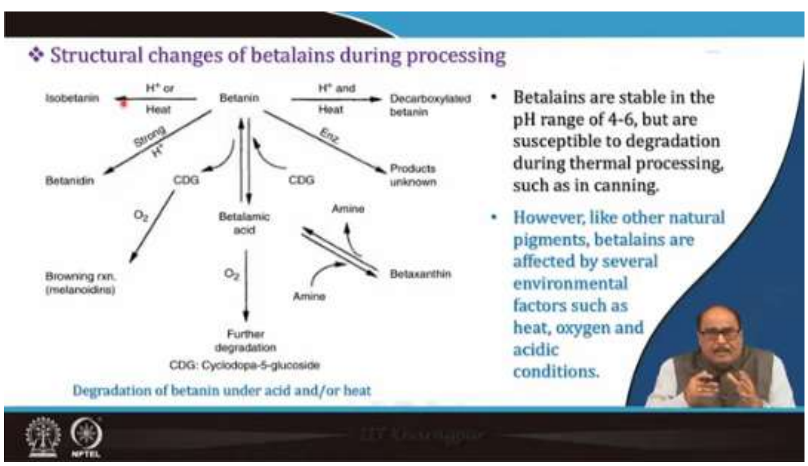
Then, anthocyanins, which are the derivatives of the basic flavium cation. Anthocyanins are highly reactive, and their stability depends on the structure and concentration, pH, temperature, light, oxygen, solvents, as well as the presence of enzymes and other flavonoids, proteins and metallic ions. At low pH, anthocyanins appear in an intense red. As the pH increases, the color shifts from orange and red to blue and purple due to the structural change in the anthocyanins. Color changes in anthocyanins result from the molecular shift to a quinoidol or anhydro base and then to a stable, but slowly decomposing, colorless carbinol base.



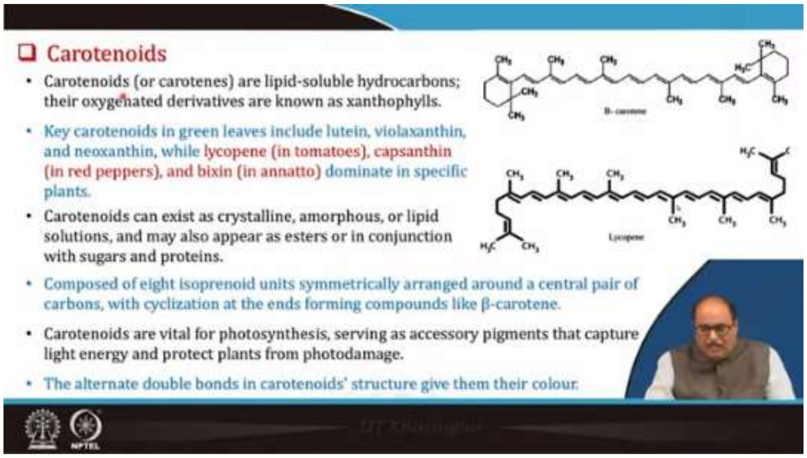
Structural changes of anthocyanins and their effects on color are due to various factors like the sulfur dioxide effect. Sulfur dioxide or sulfite bleaches anthocyanins into stable colorless compounds, but boiling and acid can restore their original color. Similarly, there may be ascorbic acid and metal ion effects. Ascorbic acid degrades anthocyanins, especially in fruit juices, with copper and iron accelerating this process. Sugar interaction, like furfural, leads to anthocyanin browning, resulting in a reddish-brown color in stored jams. Enzymatic breakdown, like glycosides, phenolases, and peroxidases, degrades anthocyanins, causing color loss through hydroxyl and oxidation. Then, acidic conditions such as leukoanthocyanins convert to colored anthocyanidins in acidic environments. This contributes to color changes in canned fruits and vegetables, etcetera, and also causes browning.



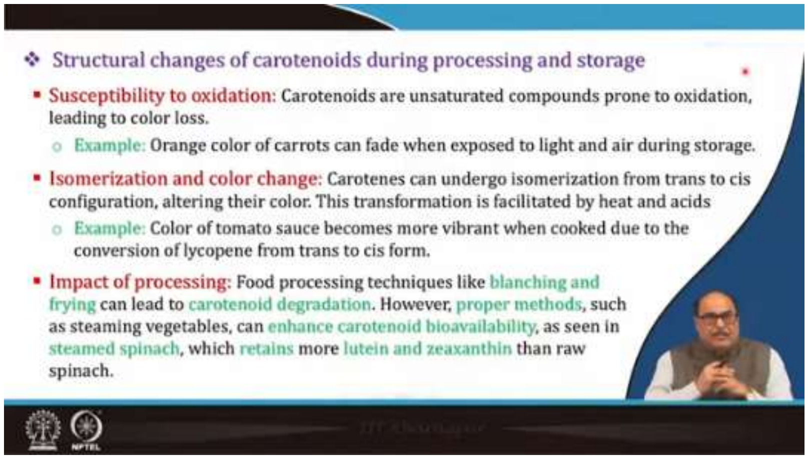
Then, betalains are another group of compounds. Betalains are subdivided again into red-violet betacyanins and yellow-orange betaxanthins. Betalains contain nitrogen, which distinguishes them structurally. The glycone of betacyanin in red beet is betanidin, and it is glucose with glucoside and known as betanin. This shows the structure of betalain and the structure that is here, A and B. A is betalamic acid. And B identifies R and R', R1 and R2 residues, which represent betacyanins and betaxanthins. So, depending upon the R1 and R2 positions, various compounds are formed.



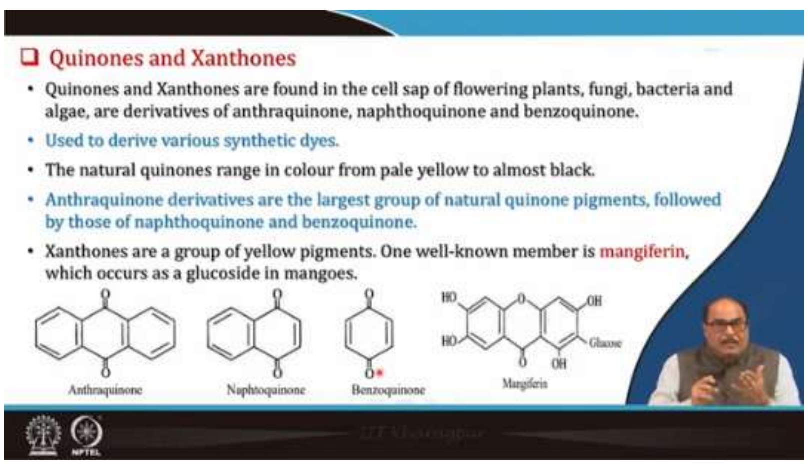
Then, during processing, there are various structural changes in betalains. Although betalains are stable in the pH range of 4 to 6, they are susceptible to degradation during thermal processing. Such as canning, etcetera. However, like other natural pigments, betalains are also affected by several environmental factors, such as heat, oxygen, acetic acid, etcetera, and various forms like isobetalains, decarboxylated betanins, and betaxanthins. Browning reactions, etcetera, melanoidin, betanidin, or even many decomposition products are formed, which actually affect the color of the food material.



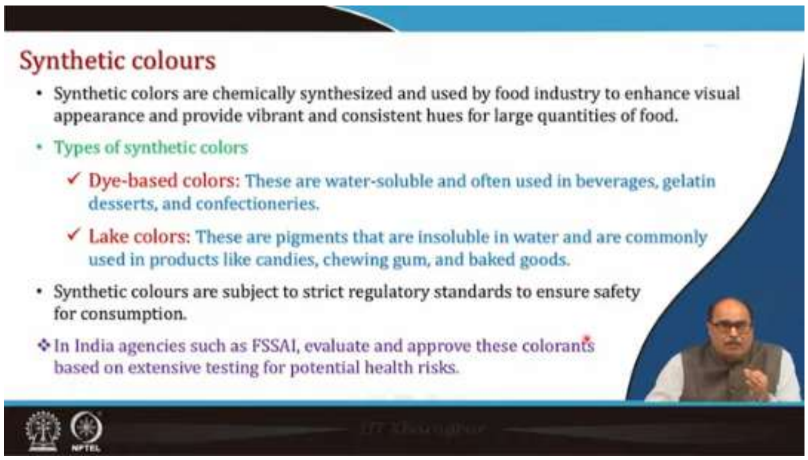
Then, carotenoids, again, a very important group, are lipid-soluble hydrocarbons. They are oxygenated derivatives, which are known as xanthophylls. These carotenoids are key compounds in green leaves, including lutein, violaxanthin, and neoxanthin. While lycopene in tomatoes, capsanthin in red peppers, and bixin in annatto dominate in specific plants. Carotenoids can exist in crystalline, amorphous, or lipid-soluble forms and may also appear as esters or in conjunction with certain sugars and proteins. Carotenoids are composed of eight isoprenoid units, which are symmetrically arranged around a central pair of carbons, with cyclization at the end, forming a compound like beta-carotene. You can see here the structure is given. They are vital for photosynthesis, serving as secondary pigments that capture light energy and protect plants from photo damage. The alternate double bonds in the carotenoid structure give them their color properties. These are the alternate double bonds shown in the figure.



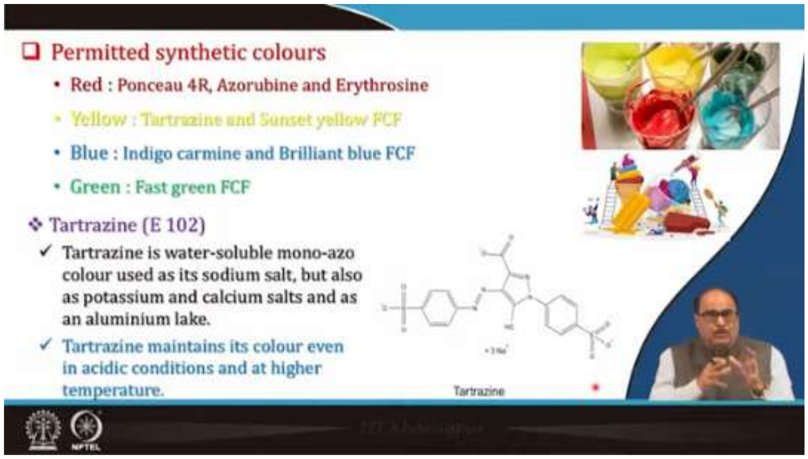
Structural changes of carotenoids during processing and storage. Obviously, they are highly susceptible to oxidation. Carotenoids are unsaturated compounds prone to oxidation, leading to color loss. For example, the orange color of carrots can fade when exposed to light and air during storage. Then there may be isomerization and color change. The carotene can undergo isomerization from trans to cis configuration, altering its color. This transformation is facilitated by either heat or acid or both. For example, the color of tomato sauce becomes more vibrant when cooked due to the conversion of lycopene from trans to cis form. Then there is also the impact of processing, meaning how they are processed, as processing conditions affect the structural changes of carotenoids. Food processing like blanching and frying can lead to carotenoid degradation. However, proper methods such as steaming vegetables can enhance carotenoid bioavailability, as seen in steamed spinach, which retains more lutein and zeaxanthin than raw spinach.



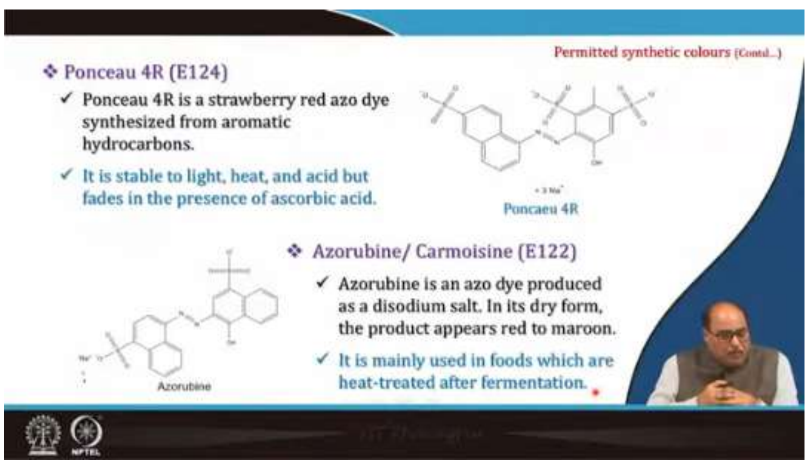
Then, quinones and xanthones are another major pigment in fruits and vegetables. They are found in the cell type of flowering plants. Fungi, bacteria, algae, and they are derivatives of anthraquinone, naphthaquinone, and benzoquinone. You can see this structure. They are used to derive various synthetic dyes. The natural quinones range in color from pale yellow to almost pink. Anthraquinone derivatives are the largest group of natural quinone pigments, followed by those of naphthaquinone and benzoquinone. Xanthones are a group of yellow pigments and one very well-known member of xanthones is mangiferin, which occurs as a glycoside, that is, a glucose glycoside in ripe mangoes. It is one which is responsible for the color of ripe mangoes.



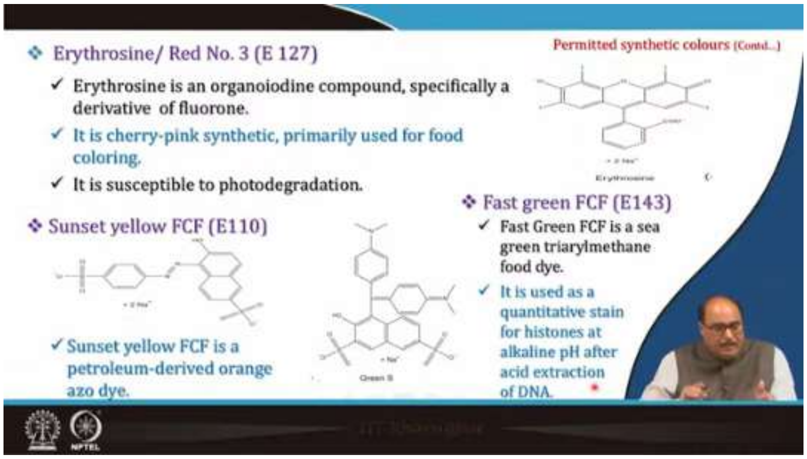
Now, after having a brief description of natural colors or pigments, let us also talk about synthetic colors. Obviously, synthetic colors are chemically synthesized and used by the food industry to enhance visual appearance and provide vibrant and consistent hues for large quantities of food, and sometimes, because of their economic advantages like they are cheap, readily available, etcetera. They are used in a vast majority of various categories of food by the industry. However, they have to be used with caution because there are certain synthetic colors which are toxic and have carcinogenic activities. So many, particularly those which are from the coal tar dyes, are not permitted. So, many synthetic colors which are carcinogenic are not permitted in food materials. So, these synthetic colors should be used with caution. So, there are two types of synthetic colors: one is the dye-based color, which is water-soluble and often used in beverages, gelatin desserts, and confectionery, and the other is the lake color. These are pigments that are insoluble in water and are commonly used in products like candies, chewing gums, and baked goods. So, as I told you, these synthetic colors are subject to strict regulatory standards to ensure their safety for consumption. In India, agencies like FSSAI and at the global level, Codex Alimentarius Commissions and there are even European regulatory authorities for many other countries, they all have their regulatory which evaluate and approve these colorants based on extensive testing for potential health risks and those which are proved by chemical analysis that they are not dangerous, they are approved by the regulatory agency.



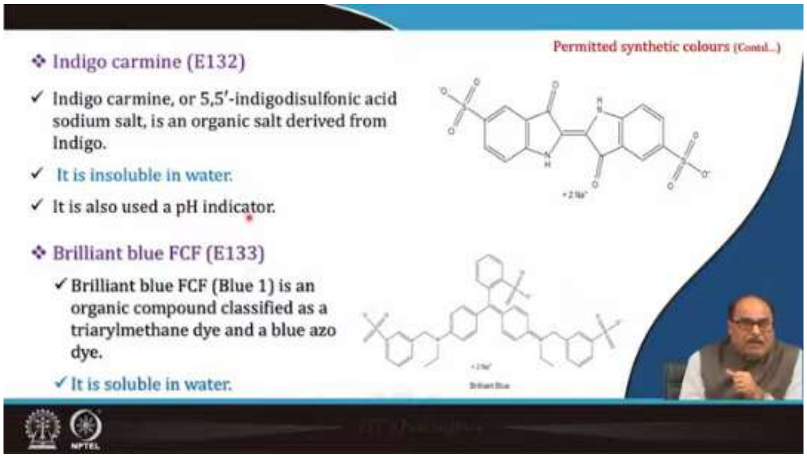
So, some of the approved coloring materials, I will briefly describe in the next 2-3 minutes. Number 1 is the red color that is Ponceau 4R, Azo Rubine, or Erythrosine. Then, the other is the yellow color Tartrazine and Sunset Yellow FCF. Blue color is Indigo Carmine and Brilliant Blue FCF, and green color is Fast Green FCF. So, Tartrazine, its additive number is E102. It is a water-soluble mono azo color used as its sodium salt, but it is also found in its form of potassium salt or calcium salt and as an aluminum lake. Tartrazine maintains its color even in acidic conditions at higher temperatures.



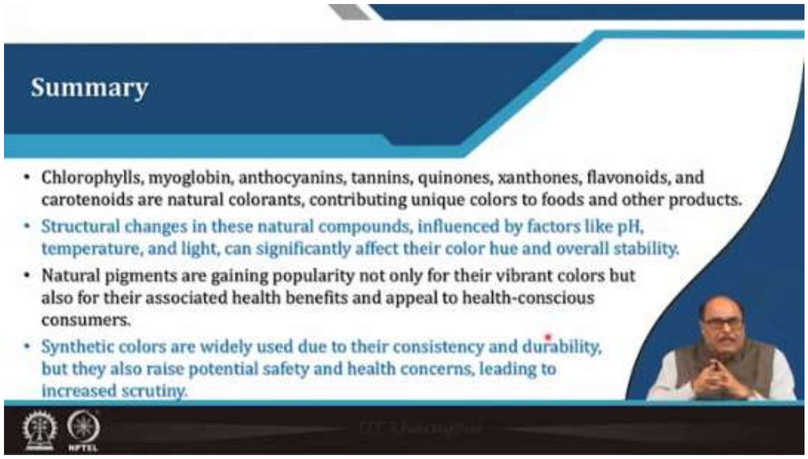
Ponceau 4R, its additive number is E124. It is a strawberry red azo dye synthesized from aromatic hydrocarbons. It is stable to light, heat, and acid but fades in the presence of ascorbic acid. Then azorubin or carmoisine. It is E122 active number. They are azo dyes produced as sodium salts in dry form. The product appears red to maroon. It is mainly used in foods that are heat-treated after fermentation.



Then erythrosine red, it is number 3, and its additive number is E127. Erythrosine is an organoiodine compound, especially a derivative of fluorone structure, as you can see here. It is a cherry-pink synthetic primarily used for food coloring, and it is susceptible to photodegradation. Sunset yellow FCF, it is number E110, is a petroleum-derived orange azo dye. Its structure you can see. The fast green FCF E143 is a sea-green triarylmethane food dye. It is used as a quantitative stain for histones at alkaline pH after acid extraction of DNA. Its structure you can see here.



Similarly, the indigo carmine E132 or 5,5-indigo sulfonic acid sodium salt is an organic salt derived from indigo. It is insoluble in water and is also used as a pH indicator. Brilliant blue FCF E133 is also known as blue 1. It is an organic compound classified as a triarylmethane dye and a blue azo dye. It is also brilliant blue. Its structure you can see here. It is soluble in water.



Finally, as a summary of this lecture, I say that chlorophylls, myoglobin, anthocyanins, tannins, quinones, xanthones, flavonoids, and carotenoids are the major natural colorants. They contribute to the unique colors of food and other products. Structural changes in these natural compounds, influenced by factors like pH, temperature, and light, can significantly affect their color hue and overall stability. Natural pigments are gaining popularity not only for their vibrant color, but also because of their associated health benefits and appeal to health-conscious consumers. Synthetic colors are also available nowadays, and they are widely used in the food industry, particularly because of their consistency and durability. They have economic value; they are cheaply available, but they also raise potential safety and health concerns, leading to increased scrutiny. These synthetic colors should be used only if they are permitted by the regulatory agency in the concerned country.

These are the references that were used for this lecture.

Thank you very much for your patient hearing. Thank you.