Natural Dyes

Prof. Padma Vankar

Department of Chemistry

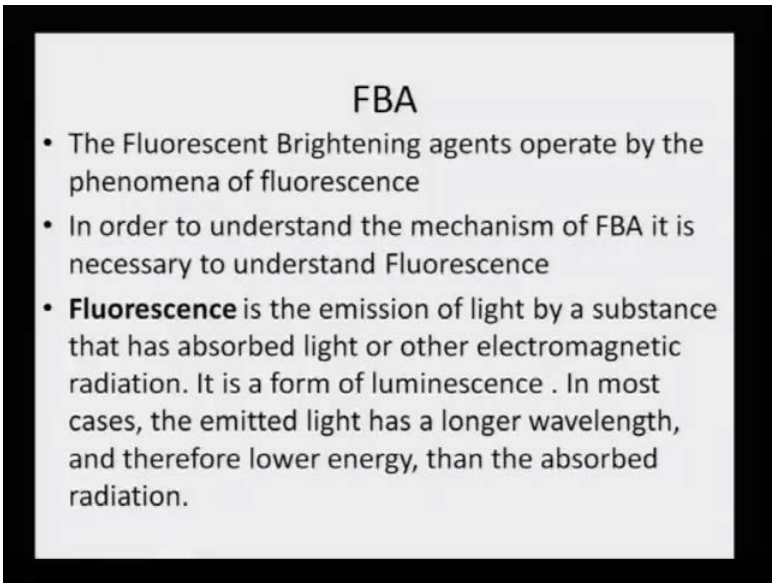
Indian Institute of Technology, Kanpur

Lecture No. # 39

Today's lecture is on a very different material fluorescent brightening agent. Now this is if I do not cover this agents with you, it the chapter on dyes will not be completed. Because after all everybody wants to wear bright colored clothes or even white clothes which are pale nobody wants to wear them. So, the fabric even if it is not dyed needs to be treated with chemicals which are brightening agents and they are optical brightness, because to the vision they appear as bright objects. And if you recall there was a product called tinopal. Now this tinopal is nothing but an optical brightener which is used with the fabric.

Many times these brighteners are added into the dye bath; many times these brighteners are added during the process of spinning, but whether they are added at the time of spinning the yarn or whether they are added after that after dying, after you know washing, after covering, after bleaching, but they are definitely used, and so I thought of spending one lecture to make you aware of what is the chemicals structure of these optical brighteners, and why are they used what is the role and with different types of synthetic and natural materials, how differently these compounds are used and so on and so forth. Because now you have to understand one thing that a finish product must have brightness, any product which is dull looking will never be pass for commercial purposes. So, let us try to devote one full lecture on fluorescent brightening agents, which are used extensively in the textile industry.

(Refer Slide Time: 03:01)



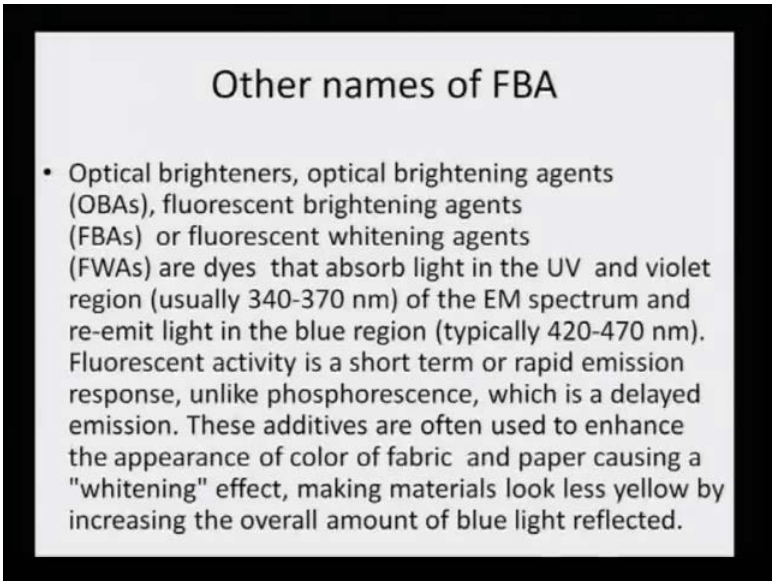
The fluorescent brightening agents operate by the phenomena of fluorescence. So, there is chemistry all around you cannot escape because it is a phenomena physical, chemistry phenomena that you know the light behaves in a little different manner to give us some kind of deceptive look, but the deceptive look is on the beneficial side. In order to understand the mechanism of fluorescent brightening agent it is necessary to understand fluorescence. Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence. In most cases the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation. So, as what we know any light that is absorbed must be transmitted. Now, if the transmitted light has a longer wavelength or lower energy some of the light obviously has been absorb and this absorb is the one which will then create fluorescence effect.

Optical brighteners or fluorescence brightening agent or fluorescent whitening agents, you know they are all like are some sort of dyes that absorb light in the UV and violet region. So, let us you know now conceptualize in terms of dye molecule which only absorbs in the UV region. So far, you had known the dyes only absorb in the visible region and that is why they appear color and that is the complementary color is what is absorbed by our eye.

Now, if I have to describe and optical whitener or brightener or and you know a fluorescent brightening agent I would say that it is a dye because it is an organic

molecule with lots of substitution and with lots of conjugation. And because it has chromophoric groups and oxochromes and it usually absorbs in the ultra violet and violet region that is why we are not able to see it as a colored compound.

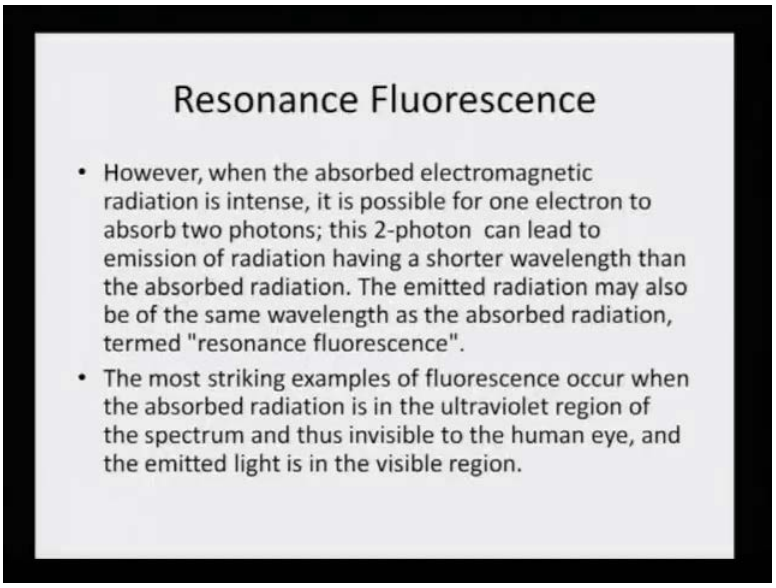
(Refer Slide Time: 05:35)



The usual concept of a dye that is why and they are able to absorb light in the region of 340 to 370 nano meter which is will in the UV region, and from 400 to 800 is the visible region and re-emit light in the blue region that is typically 420 to 470 nano meter. The fluorescent activity is a short term or rapid emission response unlike phosphorescence which is delayed emission. So, it does emit light immediately and but the wavelength is higher, and therefore these addition are often used to enhance the appearance of the color of the fabric or even paper causing a whitening effect making material look less yellow by increasing the overall amount of blue light that is light reflected.

Because of the you know transmittance or reflectance of the bluish ting of light they look brighter in color that is all there is no other functionality, it is completely a physical phenomenon and there is a light which is absorb and this light is then reflected at with a higher wavelength and because there is some amount of energy that has been absorbed.

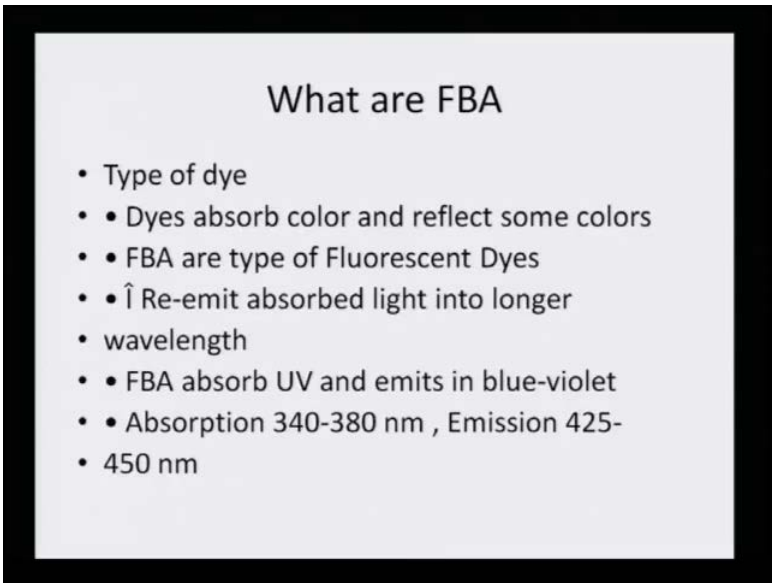
(Refer Slide Time: 07:22)



The resonance fluorescence: However, when the absorbed electromagnetic radiation is intense, it is possible for one electron to absorb two photons; this 2-photon can lead to emission of radiation having shorter wavelength than the absorbed radiation. The emitted radiation may also be of the same wavelength as the absorbed radiation, termed as resonance fluorescence. So, three things can happen three things can happen one is that it can emit after absorbing certain radiation longer wavelength or it can emit the same wavelength without any absorption. And the third thing is that it kind of emits radiation with the when it is same wavelength then it is call resonance fluorescence, but; however, if the two photon systems happens then the radiation has a shorter wavelength.

The most striking example of fluorescence occurs when the absorbed radiation is in the ultra violet region of the spectrum and thus invisible to the human eye, and emitted light is in the visible region. So, you see that bluish ting or the brightening ting which is at the border line.

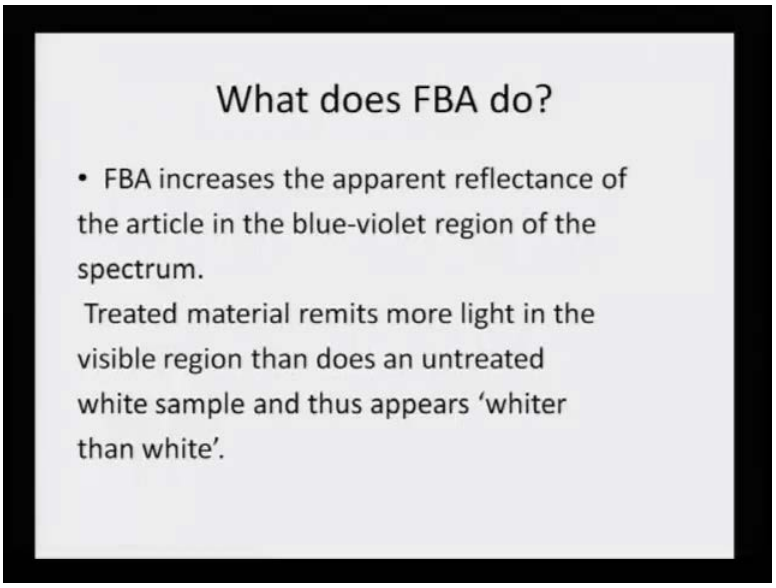
(Refer Slide Time: 08:40)



What are fluorescent brightening agents? So, having understood the phenomenon as to what is actually this fluorescent brightening agent, how do they work, what is the kind of light they absorb? And they are like equivalent to dyes these chemicals and they absorb light in the UV region and they emit light only at the border line of the visible region that is why they appear, so brighter in color.

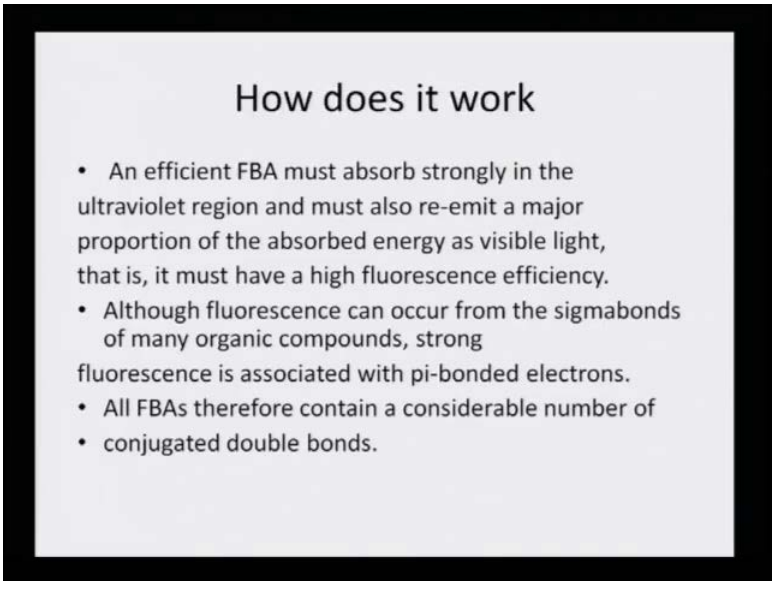
Dyes absorb color and reflect some color, these have certain qualities. So, we are just talking about these you know properties of a fluorescent brightening agent, they are like a type of dye as what I describe. But instead of being a conventional dye which has colored you know color in it these are colorless dyes let us put it this way. The fluorescent brightening agents are type of fluorescent dyes and they re-emit absorb light into longer wavelength. The fluorescent brightening agents absorb UV and emit in blue-violet region absorption took takes place at 340 to 380 nano meters, whereas emission is typically at 425 to 450 nano meter. So, it has a bluish tinch and which causes the brightening or the lightening effect.

(Refer Slide Time: 10:25)



What does fluorescent brightening agent do? Fluorescent brightening agent increases apparent reflectance of the material in the blue-violet region of the spectrum. So, all it does thereby it is near presence and by the absorption of a light of the wavelength of 320 to 370. It only kind of emits light which is in the blue violet region of the spectrum and makes apparent reflectance. Treated material reemits more light in the visible region than does an untreated white sample and thus appears whiter than white. So, that is what it does? It just is on brightening agent.

(Refer Slide Time: 11:12)

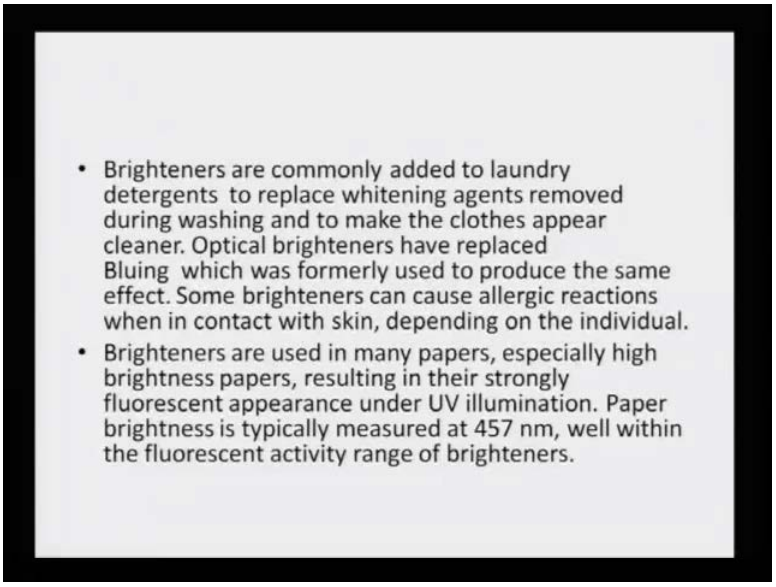


How does it work? An efficient fluorescent brightening agent must absorb strongly in the ultraviolet region and must re-emit a major portion of the absorbed energy as visible light, that is, it must have a high fluorescent efficiency. So, you see that unless and until a compound which we called as fluorescent dye satisfies these two factors - what are these factors that it should strongly absorb in the UV region and must re-emit a major portion of the absorbed energy as visible light, but that should have a good high fluorescence efficiency.

Although fluorescence can occur from the sigma bonds of many organic compounds strong fluorescence is associated with pi-bonded electrons. So, the molecule must have a good conjugated system where there are ample of pi-bonds. So, there now you understand that excitation of electrons are very facile when we talk about pi-electrons.

All the fluorescent brightening agents therefore contain a considerable number of conjugated double bonds - which means that they have double bond, single bond then double bond conjugated system. So, by now after having learn so much about dyes and the conjugated system and the visible spectrum and the ultra violet spectrum - you must have develop a some understanding of what I am referring to. So, these fluorescent dyes which are colorless must have lot of conjugation in the system, we will see those structures in detail and then you will be able to appreciated.

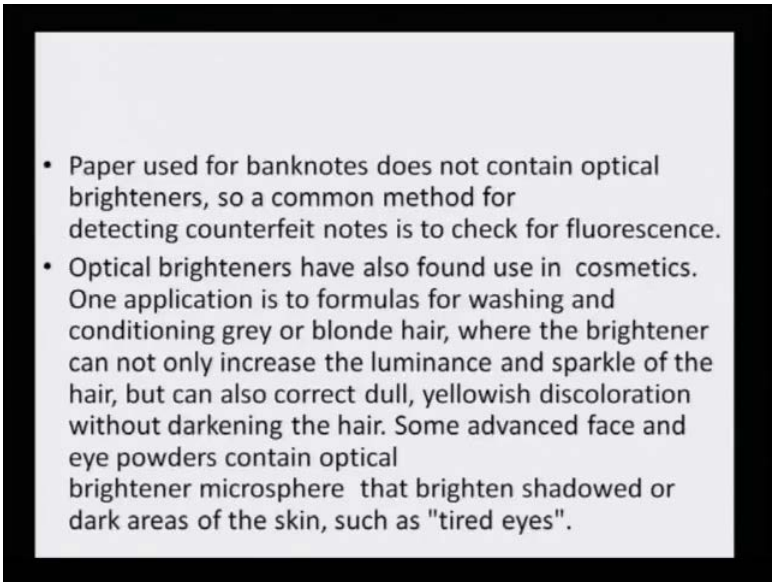
(Refer Slide Time: 13:23)



Brighteners are commonly added to laundry detergents to replace whitening agents removed during washing and to make the clothes appear cleaner. Optical brighteners have replaced bluing which was formerly used to produce the same effect. Some brighteners can cause allergic reactions when in contact with skin, depending on the individual. Now, you see these are chemicals. So, they have their own hazards; they can be allergenic to some people. Earlier, if you recall, they was this robin blue that was use; the robin blue concept was that it was shifting the cloth to more bluer side by making it look brighter. So, the same phenomenon was actually happening in the use of robin blue.

Brighteners are used in many papers also; especially high brightness papers are resulting in their strongly fluorescent appearance under UV illumination. Papers brightness is typically measured at 457 nano meter, well within the fluorescent activity range of the brighteners. So, even its not only just that for textile these brighteners are used, even for paper material they are used in a big way.

(Refer Slide Time: 14:44)



Paper used for bank note does not contain optical brighteners, so a common method for detecting counterfeit notes is to check the fluorescence. So, that is an advantage you can find out whether the banknotes that you have in your hand are actually original or they are counterfeited.

Optical brighteners have also found use in cosmetics. One application is to is to formulas for washing and conditioning grey or blonde hair, where the brightener can not only

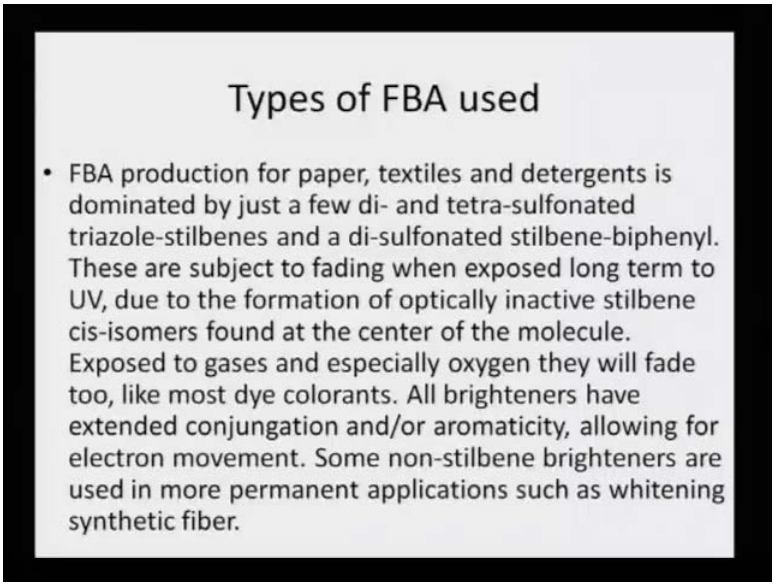
increase the luminance luminance and sparkle of the hair, but can also correct dull, yellowish discoloration without darkening the hair. Some advanced face and eye powders can contain optical brightener microsphere that brighten shadowed or dark areas of the skin, such as the tired eyes. So, now it is also used in paper; it is used in cosmetics; it is used in laundry material, I mean washing powders and the other kind of stuff.

(Refer Slide Time: 16:00)

So, it has a wise spectrum use not only in textile, but in others cosmetic and paper and other industries also. Stilbenes are one of the very prominent fluorescent brightening agents. The most common class of chemicals with this property are the stilbenes and older, non-commercial fluorescent chemicals such as umbelliferone, which absorb energy in the UV portion of the spectrum and re-emit in the blue portion of the visible spectrum. A white surface treated with an optical brightener can emit more visible light than that which shines on it, making it appear brighter. The blue light emitted by the brightener compensates for the diminishing blue of the treated material and changes the hue from the yellow or brown towards white. So, you see the overall effect is that when compounds like umbelliferone or stilbenes or which are nothing but fluorescent dyes are utilized. The overall effect is very simple; they absorb light from the UV region and they emit re-emit light from on the visible side in the bluish violet spectrum of the visible light.

So, if it is coated on a white surface these shine or look brighter simply because you know the yellowness or the brownishness of the dull looking cloth actually with the help of these brightening agents looks more bluish and brighter; that is the because of the reflectance - because of the remittance of the light. So, that is the beauty of these compounds. There are approximately 400 brighteners types listed in the color index, but less than 90 are actually produce commercially and only a handful or commercially important. So, although many, many fluorescent brightening agents have been made, but the importance is that about 90 are available for commercial purposes and still lesser are actually being popularly used.

(Refer Slide Time: 18:48)

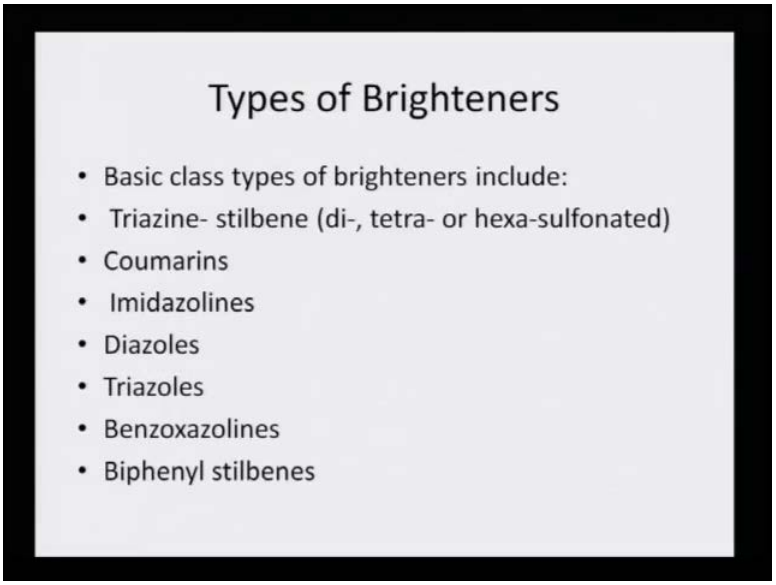


Types of fluorescent brightening agents that are normally used; the fluorescent brightening agent production for paper, textiles, detergents is dominated by just a few di- and tetra-sulfonated triazole-stilbenes and a di-sulfonated stilbene-biphenyl compounds. These are subject to fading when exposed long to long term to UV, due to the formation of optically inactive stilbene cis-isomer found at the center of the molecule. So, over a period of time, they are deactivated because they get converted into the cis-isomer of the stilbene. We will see what is cis-isomer, what is trans-isomer and then you will be able to understand.

Exposed to gases and especially oxygen they will fade too, like most dye colorants. So, they also are oxygen sensitive. So, therefore, if there are gases, if there are oxygen they

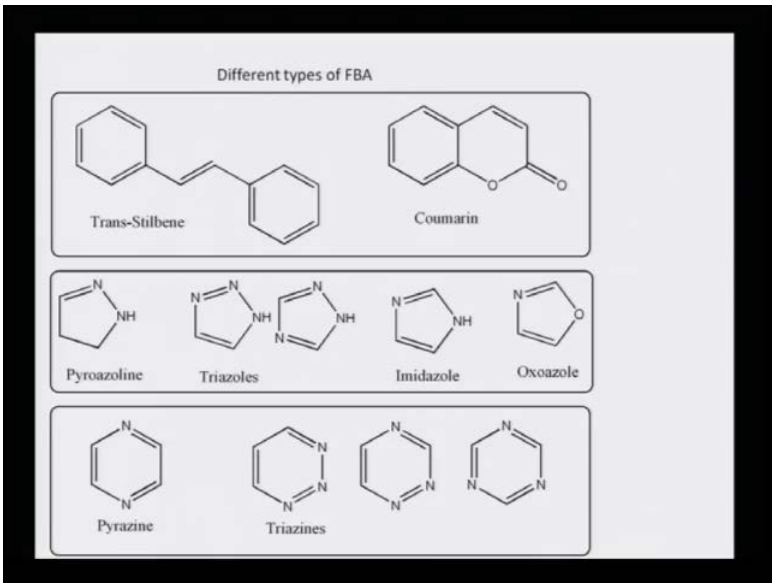
get kind of deactivated. All brighteners have extended conjugation and or aromaticity, allowing for electron movement. Some non-stilbene brighteners are used in more permanent application as whitening synthetic fibers. So, there are a class of different these brighteners which are used for primarily for a permanent treatment on whitening synthetic fibers to makes synthetic fibers brighten whiten there are use on a permanent basis.

(Refer Slide Time: 20:28)



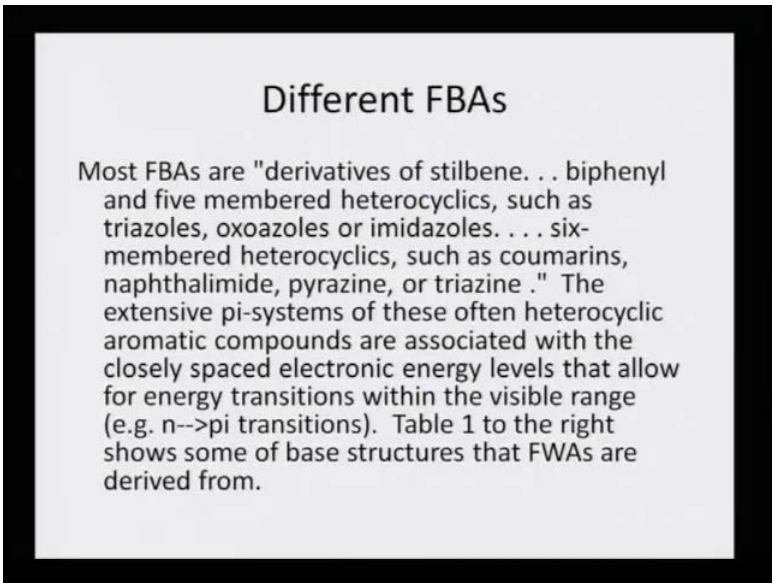
Types of brighteners that are normally available in the market. Basic class of brighteners include triazine or stilbene which can be (di-, tetra or hexa-sulfonated), coumarins, imidazolines, diazoles, triazoles, benzooxazolines. biphenyl stilbenes. So, these are different types of the classes of optical brighteners or fluorescent brightening agents that are available and these are the chemical class based on the chemical structure.

(Refer Slide Time: 21:13)



Now, if let us take a look at the different types of structures trans-stilbene. Only the trans-stilbene acts as an activated fluorescent dye, when it get converts into the cis that is this bond is getting converted into the cis and that is not a very good option. Similarly, coumarins also have a conjugated system pyroaxoline, triazoles, imidazoles, oxoazoles, pyrazine, triazines - these are different types of molecules that are actually used as fluorescent brightening agents. And it is the excitation of these pi electrons either in the aromatic ring or in the you know aliphatic region of the molecule that the molecule act absorbs light and reemits light. So, this is where the UV light is absorbed, and therefore these chromophor groups are an essential part of the optical brightening agents or fluorescent brightening agents it is one and the same.

(Refer Slide Time: 22:42)



Different fluorescent brightening agents: Most fluorescent brightening agents are derivatives of stilbenes or biphenyls and five membered heterocyclics, such as triazoles, oxoazoles or imidazole; six membered hetero cyclic, such as coumarins, naphthalimides, pyrazine or triazine. So, it could be five membered heterocyclics or it could be six membered heterocyclic or they could be derivate of stilbene where it is one aromatic ring in conjugation with the double bond and another aromatic ring. But remember that these rings are actually pose opposite to each other, which means that this double bond which is there is actually trans and not cis once it converts to cis it is deactivated.

The extensive pi-systems of these often heterocyclic aromatic compounds are associated with the closely space electronic energy level that allow for energy transition within the visible range - that is n to pi star transition takes place; table 1 to show that some of the basic structures we have just shown to you in the last slide.

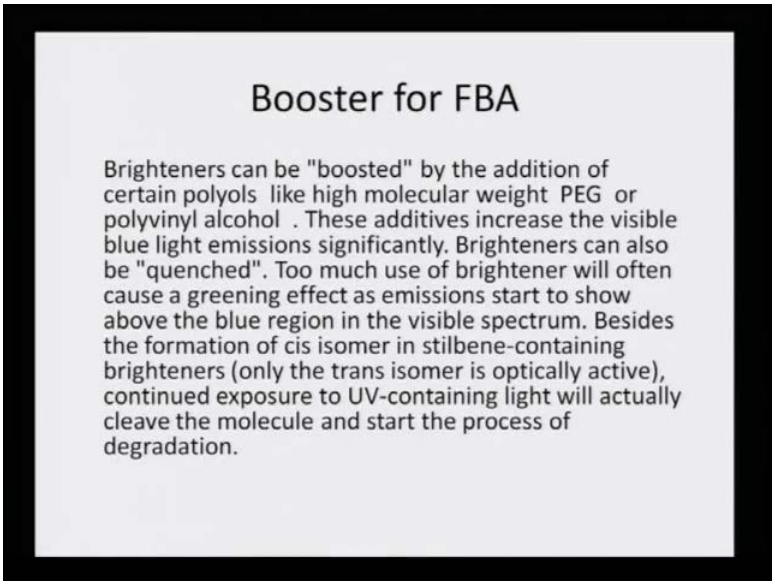
So, you see that it is n to pi star transitions which are taking place by now when I had thought you about the analysis of UV visible spectrometer we had come across what are the probable transitions that are allowed. And in these optical brighteners of fluorescent dyes the allow transition is energetically matching with the n to pi star you know excitation of electrons and that is that is the role of the heteroatom.

You see most of them are heterocyclic; only stilbene is one which has no other heteroatom it is only carbon hydrogen, but coumarins has oxygen. If we go back to the

structure, you will see that the lower two classes that is the pyroazoline, triazoles, imidazoles, oxoazoles, pyrazine, triazines they all have nitrogen or oxygen and nitrogen. coumarin has two oxygen; only stilbene is one which does not have any oxygen or nitrogen.

So, most of them having these heteroatom and the heteroatom consist of lone pair of electron, and it is this lone pair of electron which excites and goes into the you know the the pi anti arbitral of the pi bonds. So, therefore, this is very well suited as the fluorescent dyes or optical brighteners.

(Refer Slide Time: 26:05)

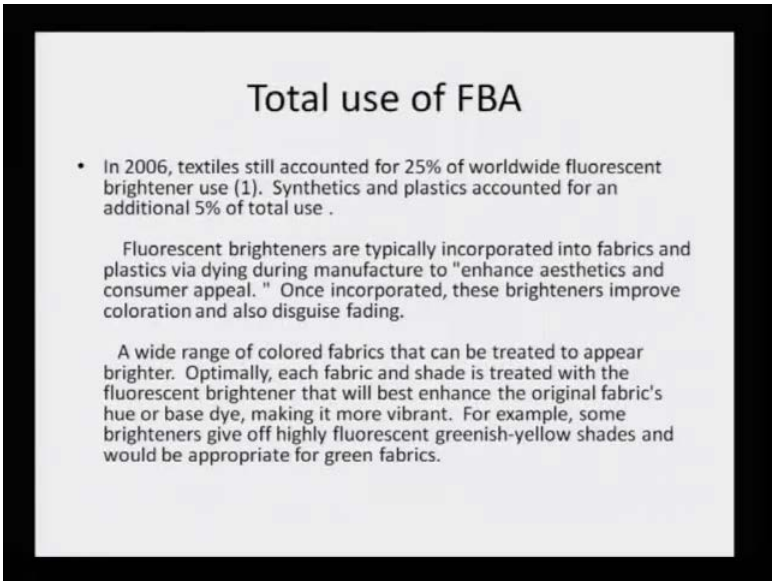


Boosters for fluorescent brightening agent: Brightness can be boosted by addition of certain polyols like high molecular weight poly ethylene glycol or polyvinyl alcohol. Now even they can be you know their functioning can be enhanced by addition of poly ethylene glycol or polyvinyl alcohol - PVA.

These additives increase the visible blue light emissions significantly. Brighteners can also be quenched. Too much use of brightener will often cause a greening effect as emissions start to show above the blue region in the visible spectrum. Besides the formation of the cis isomer in stiblene-containing brighteners only the trans isomer is optically active, continued exposure to UV containing light will actually cleave the molecule and start the process of degradation.

So, you see that why boosters are required because if stilbene type of brighteners have been used they get converted into cis type because of the energy transfer, and then finally, they get degraded or there will be too much of light that will be emitted, and this too much of light can shift now the blueness to the greenness of the visible region. And that will not be acceptable, because the whole purpose is to make it more bright not look greener or yellower and so on.

(Refer Slide Time: 27:52)



The total use of fluorescent brightening agents: If one takes an evolution, in 2006, textiles still accounted for 25 percent of the worldwide use a fluorescent brightening agent. Synthetics and plastics accounted for additional 5 percent of the total use. The fluorescent brighteners are typically incorporated into the fabric and plastic via dying during manufacture to enhance aesthetics and consumer appeal once incorporated these brighteners improve coloration and also disguise fading. So, you see it also kind of retards fading. So, there are two advantages not only does the fabric look brighter, but it also kind of slows down the fading process.

A wide of colored fabric that can be treated to appear brighter optimally each fabric and shade is treated with the fluorescence brightener that will best enhance the original fabrics hue or base dye making it vibrant. For example, some brighteners give off highly fluorescent greenish-yellow shades and would be appropriate for green fabric.

So, you see that they can even at as a color enhancer it is not only just giving a visible effect of brightening the material, but it can also brighten the or enhance the color. Suppose if brightening agent is used which has very high fluorescent greenish-yellow shades to contribute then this will act as an enhancer to a green dyed fabric also. So, even for dyed fabric not only for white fabric it acts as an optical brightener, but even for dyed fabric it has the contribution that is very important and is beneficial.

(Refer Slide Time: 30:06)

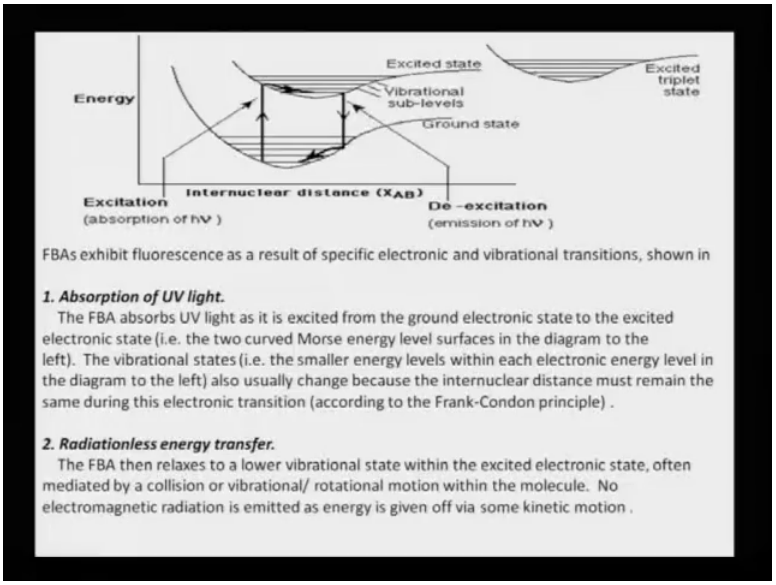
Usefulness of fluorescent brightening agent: For a fluorescent brightener to be considered particularly effective and useful for the use in textiles, it must possess the following three characteristic; that means, to be certified as an optical brightener. The fluorescent emission in the desired range - they give off the correct color; that means, it should not it should not be that is a white cloth and is giving greenish ting it should only give the light yellow bluish ting.

Second - fastness to washing, perspiration, and sunlight. They lost long because they bond or adhere well to the base material and should be nonhazardous properties; that means, it should be safe for the human use, because we saw that some of them had allergenic activity. So, such optical brighteners have been actually banned, but if fluorescent dye or optical brightener whatever you wish to call has the desire fluorescent emission; that means, it should only be a optical enhancer or it can enhance the color in case of dyed fabric.

Otherwise, it can have a detrimental effect the second thing is that the washing, the perspiration, and sunlight should not the fastness properties of a dyed material should not get affected on the contrary it should act as an enhancer.

And thirdly that it should be nonhazardous, because after all any chemical has its own reactivity towards human body and it should not be harmful because all along we have been talking about eco friendliness and about you know disposal problems of the dyes and so on and so forth. And you know how to come back these toxins from entering into the ecology, and it should not disturb the ecology and these toxins should not enter the environment, all these things we have been talking about. So, in that case these brighteners also should not have any kind of hazardous effect.

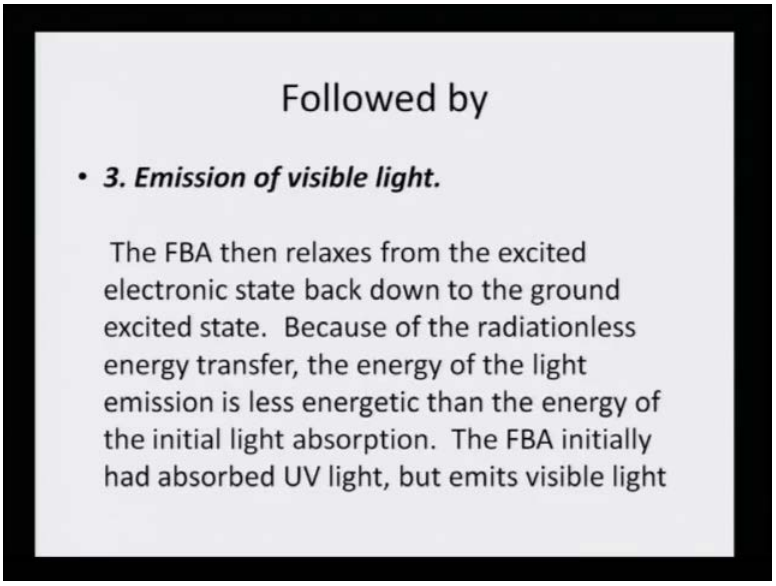
(Refer Slide Time: 32:34)



Now, the way they work is you know a very simple situation, and in order to exhibit the fluorescent brightening agents fluorescence effect; what is the electronic and the vibration transitions that actually take place in terms of energy. The fluorescent brightening agent absorbs UV light and it is excited from the ground electronic state to the excited electronic state - the two curves are showing that in the diagram. The vibrational state that is the smaller energy levels within each electronic energy level is also shown are usually change because of the inter nuclear distance must remain the same during this electronic transition.

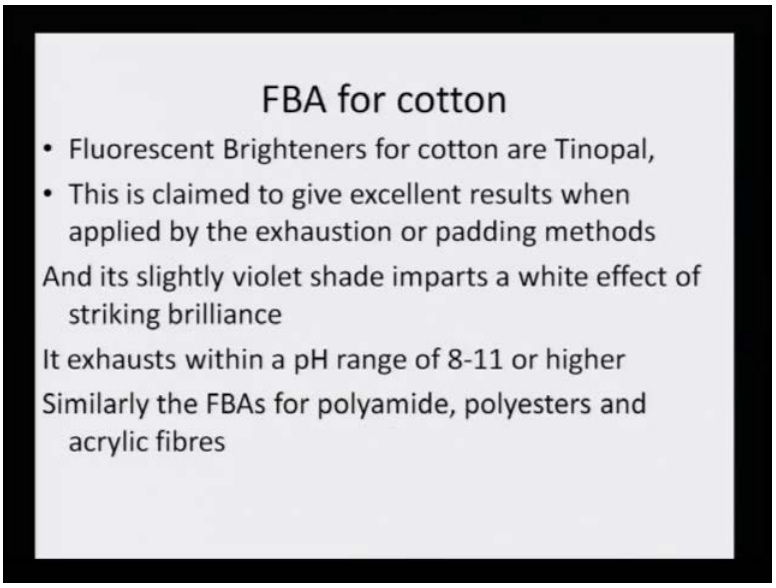
So, from the physico chemical point of view what exactly happens, when the UV light is absorbed, and then it is like a radiation less trans energy transfer. These agents then relaxes to a lower vibrational state within the excited electronic state often mediated by collision or vibration of rotational motion within the molecule, and therefore, there is no electromagnetic that is emitted at this stage, but there is a third stage where emission of the visible light actually occurs. So, it is happening in three phases first is the absorption second is the excitation and third is the emission.

(Refer Slide Time: 33:57)



So, emission of the visible light is what actually is causing the brightening effect or the fluorescent effect. So, if one has to understand the phenomena if the phenomena happens in three stages. The fluorescent brightening agent then relaxes from the excited electronic state back down to the ground excited state. Because of the radiationless energy transfer, the energy of the light emission is less energetic than the energy of the initial light that has been absorbed. The fluorescent brightening agent initially had absorbed UV light, but emits visible light. So, that is where the change occur it absorbed in the UV region, but emits in the visible region.

(Refer Slide Time: 35:03)



The fluorescent brightening agents that are used for cotton particularly, but of course, they are used for polyamide polyesters different agents are used fluorescent brighteners for cotton are the very famous tinopals, we have heard time and again people using it. Now earlier tinopal was added to the final rinsing of the washing, but now tinopals are added in the washing powder mixtures like ariel's and surf excel's and have tinopal in their combination.

This is claim to give excellent results when applied by the exhaustion or padding methods and it is slightly violet shade imparts a white effect on the striking brilliance. It exhaust within a pH range of 8 to 11 or higher. Similarly the fluorescent brightening agents are therefore, polyamide, polyesters, acrylic fibers.

So, you know it is there is no (( )) the companies and manufacturing tailor made fluorescent brightening agents for different types of material. In order to make it look appear and be a very white appearing material. So, you see that these agents are also a very much an integral part of dying system in the textile industry it is one cannot do without it. So, therefore, it is important to even know and learn and spend some time about these fluorescent dyes although ideally they are not dyes.

Why because according to the definition of dyes dyes are colored molecules. So, we can say, but according to another definition dyes have conjugated system and have a chromophore they these fluorescent dyes also have chromophoric groups and have

conjugation, but absorb light only in the UV region. And they give out light or re-emit light in the visible region, whereas dyes which are conventional dyes absorb in the visible region and emit also in the complementary visible region.

So, with this we have come to an end of this fluorescent brightening agent chapter because I thought that you should know about it.