MODULE 25 - LECTURE 20

Revision and Doubt Clarification Session 1

So, we begin with the revision,

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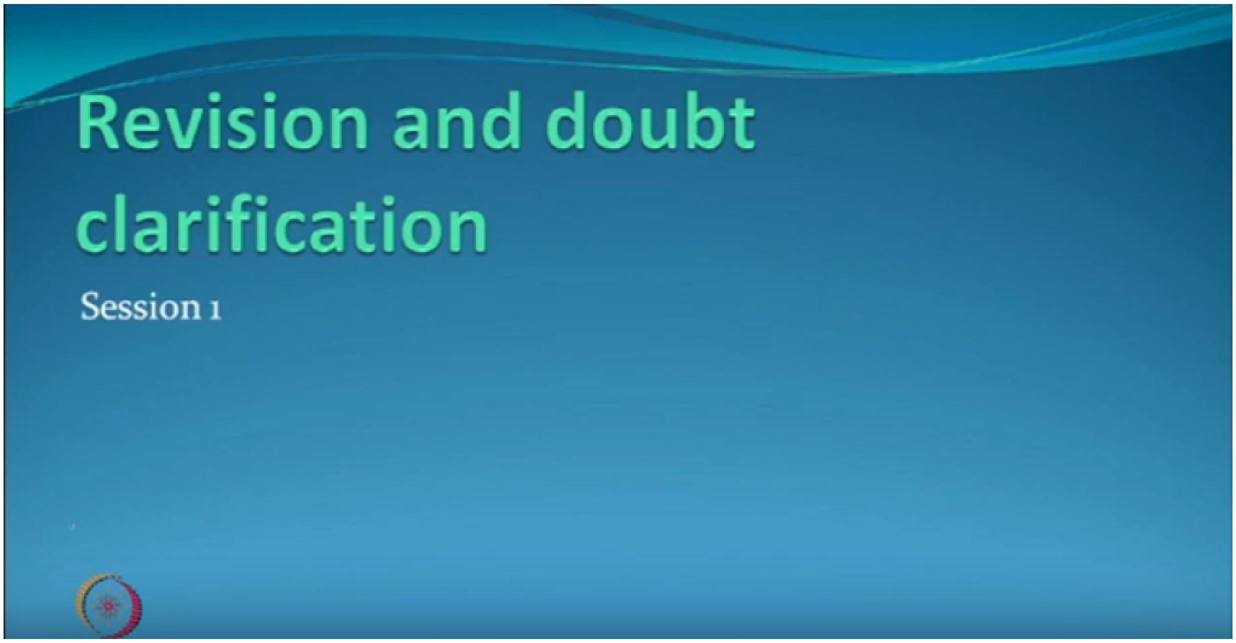

Revision and doubt clarification

Session 1

session today and also some, points which, were raised, I'll try to go through them.

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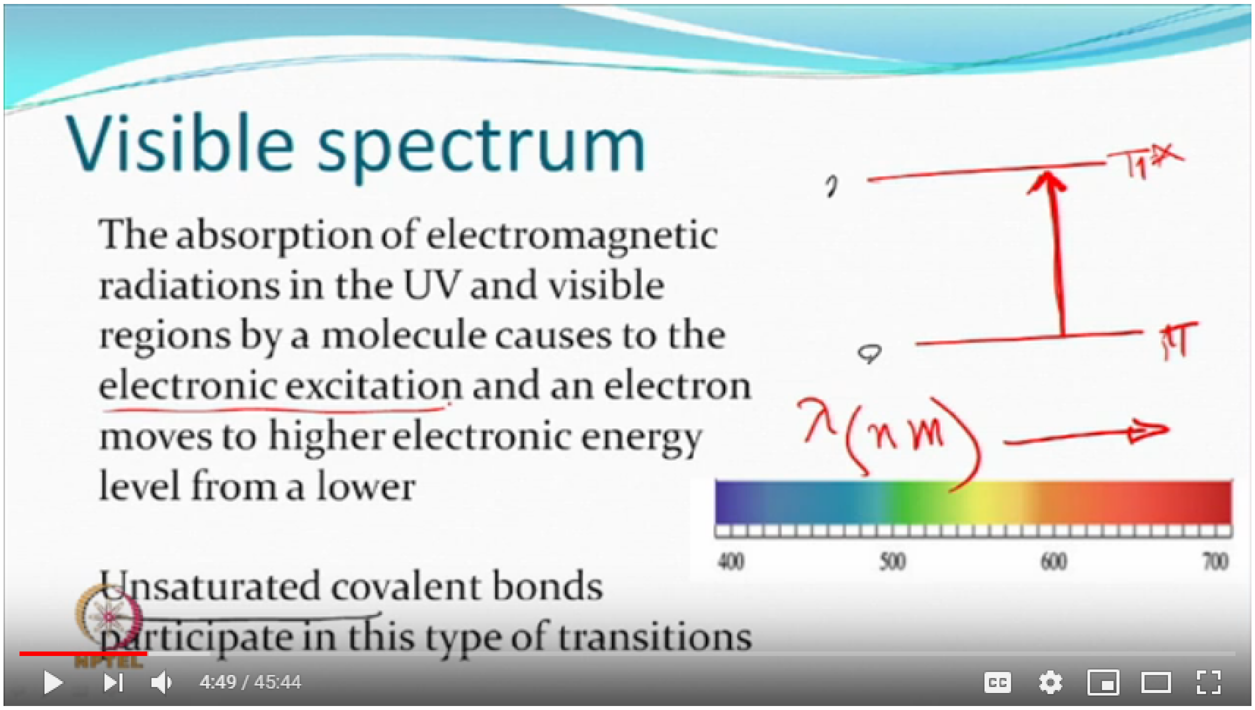

Visible spectrum

The absorption of electromagnetic radiations in the UV and visible regions by a molecule causes to the electronic excitation and an electron moves to higher electronic energy level from a lower

Unsaturated covalent bonds participate in this type of transitions

So, one of the thing which was raised at some point was, by some people, as to how an ox a chrome, works and why does anything change. So, one thing you must understand is that whenever radiation falls, on any material, depending upon the energy, of the radiation. So, gamma rays are more ready energy compared to the visible range and so, based on that energy, there is going to be some electronic transition.

So, electrons will move from, one energy level which is stable in a level to an excited state, let's say you have double bonded structure, the PI bonds are relatively, more susceptible, to this chain, that means they will absorb energy electrons, will go to a higher state and, and what will be absorbed, absorption will be at a certain frequency. So, energy is related to frequency and the wavelength in one way or the other and so, the shift takes place and if you do any change, in molecular configuration, then this shift could be enhanced, eased out, if it is eased out then, less energy or higher wavelength, radiation can also do the same job. So, there can be some compound which look very similar, which may not be giving any color, but if you add something to them, they will start giving you color. So, one important thing is that there is a transition, which takes place Alright? From one level to the another level and then obviously, it's a transition therefore it is not going to stay, there only electrons, will come back and whatever they can do they do sometimes this can happen, that some groups have responded, to near ultraviolet range, but when, the electrons come back, because of various reasons, energy loss here and there the final radiation, which comes out, is in the visible range, one of the thing which you probably understand is the optical whitening agents, they are colorless, but they absorb in the ultraviolet region, but while the electron comes back to a stable state, the energy released, is in the visible range and therefore, the brightness and so, on so, forth that you see. So, one interesting thing is that unsaturation helps. Okay? And so, most of these so called croma foods would have unsaturation so, there is a transition which will be made easy. So, so what you are looking at is electronic excitation, transition, changing from a lower energy to a higher energy, level and of course that’s an absorption of energy if the energy is very, high that this could actually go to such a state that you never come back to the same state you can actually a bond breaking, but if the absorption or energy, is in the range where, it is able to come back to the state, then you have compounds, which will be in the dyes and pigments wrench.

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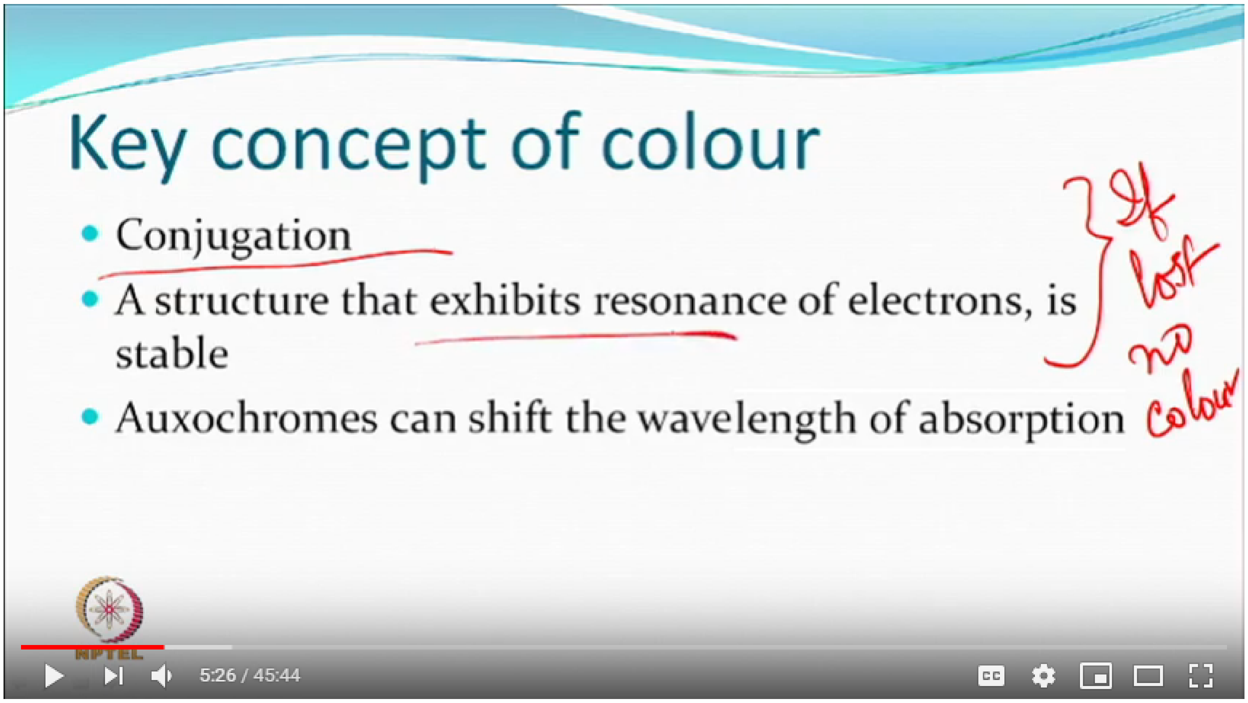

Key concept of colour

- Conjugation
- A structure that exhibits resonance of electrons, is stable
- Auxochromes can shift the wavelength of absorption

If lost no colour

So, one important thing is other than an un saturation, in the molecules there should be, conjugation, conjugation means alternate double and single bond, availability, in the molecule, if this is very nicely, done easily available transitions become easy, it also is important the molecule also, exhibits resonance, that is it has got one resonating structure, versus the other resonance occur both if the resonance is possible, that also means n as the absorption, of some type going one state to another state, but they are stable States. So, this also helps in making the dye or the pigment a stable, chromospheres, you may be aware, like alien black have you heard of this color. So, what happens is the aniline keeps on polymerizing, molecules keep getting added and you have conjugation, being increased, as this conjugation, keeps on increasing, it becomes a different color, you know pale blue to a green, to a blue, to black, this is how the colors change. So, conjugation if it is more, you are going towards a deeper, depth of shade auxochromes are such groups, which do not by themselves, give any color that is they do not absorb in the visible range, they do absorb they will absorb infrared. So, there they will absorb, but it is not visible to you, but if you have infrared spectroscopy you will see every functional group absorb something or the other, but what we are interested, in what can be visible to the eyes and that's what become color, it is as far the absorption is concerned, every molecule will go through this process, of excitation of electron and vibrations etcetera, which also means, absorbed some energy, that's why you have a start vibration, but only at a particular frequency, that's the important part.

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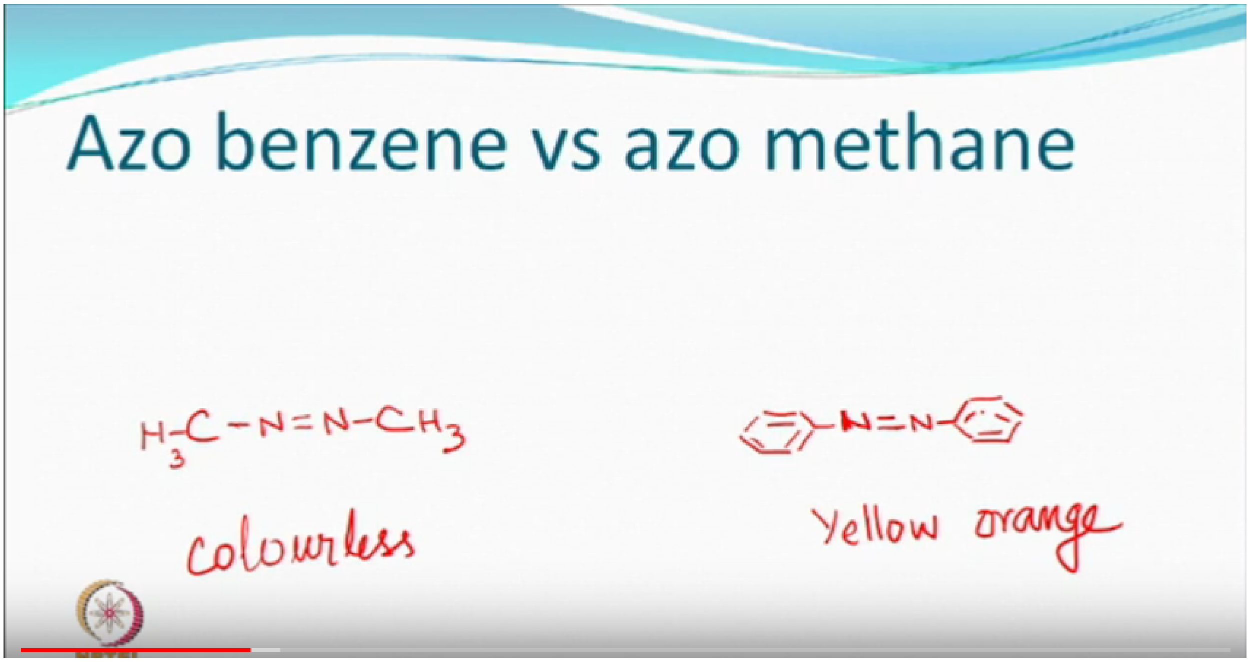

Azo benzene vs azo methane

$H_3C-N=N-CH_3$

colourless

Yellow orange

So, there is this compound, which you can see, is a so, group has it has but it's a methane no time, the methyl group is there, on the other hand you, have as a benzene type of a structure and so, in one case, in both the cases you have as a group, but enough conjugation is not there. And so, you see it absorbs radiation, but also in a region, which is not in a visible range. So, just having another group does not mean that it's going to give you color, it has to be supported and one of the interesting thing of support, is this conjugation if you see this. So, you have this group double bond, single bond, then you go there then you have a double bond, then single bond, double bond, single bond, double bond, single bond and things like, that one can always, if you can provide some of this type of structure, then suddenly you will feel you will get some color.

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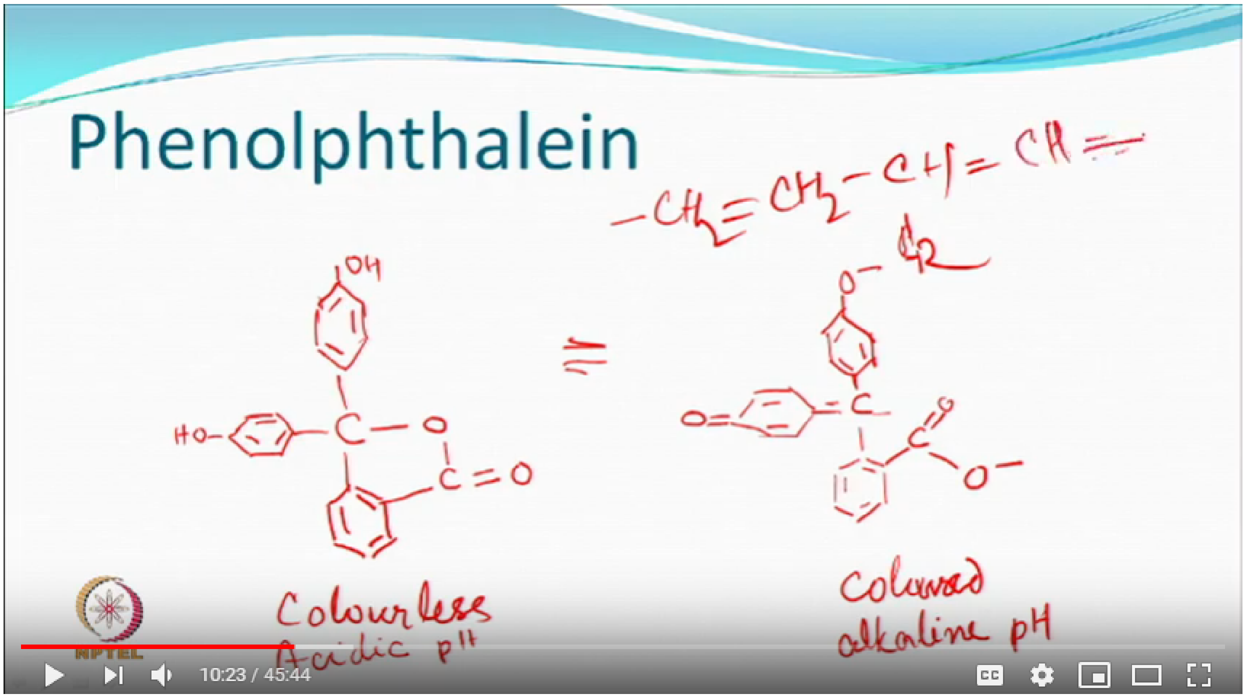
Phenolphthalein

If by any action, your conjugation, is somehow stopped or restricted or diminished, or reduced, then also you may not be able to get color, for example the phenolphthalein line, which you must have used an indicator, in an acidic medium, is colorless, in alkaline medium, it is pink. So, if you see here there's a double bond and a single bond, then double bond, double bond, double bond, then doubles and from here it, it goes there. so, there is a possibility here double bond, double bond here it starts breaking it's all single and there's no conjugation, very easily available and in this range there is no conjugation, available and so this becomes a problem, so, if it is a continuous, conjugation it'll help, I mean even, if it is CH 2 CH 2 or CH R the key. So, this type of a single bond conjugations, if you can create then also you will be getting within a linear molecule or an aromatic molecule does not matter.

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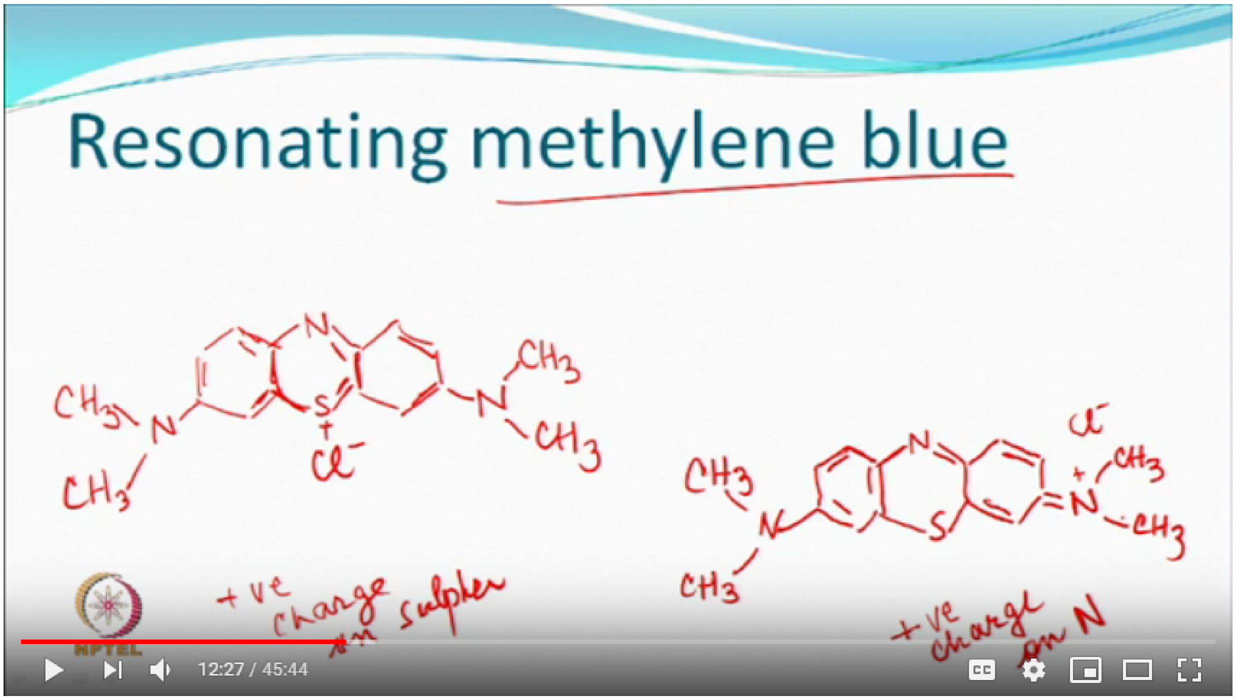

Resonating methylene blue

The other thing which we said is the resonance. So, you see there is this methylene blue; you have a good from here onwards, conjugation. there is a conjugation and the, there is a positive charge on sulfur. This compound is stable, because it resonates, another structure is where this positive charge is on, nitrogen. So, it has shifted, this chloride and can be anywhere, so some if you have this type of structure, which also resonates and also remains somehow conjugated, here there was a conjugation because of sulfur, here you have through this, any link that you can make and so, the color remains stable, it does not change, if you have a resonating structure, so there is a conjugation approximately the number of groups, that are available are similar ,the number of conjugations ,remain same and the chromospheres whichever for example ,you know, diameter nitrogen or two methyl groups, here they remain the same and so, the color does not change, but it becomes, a much more stable structure.

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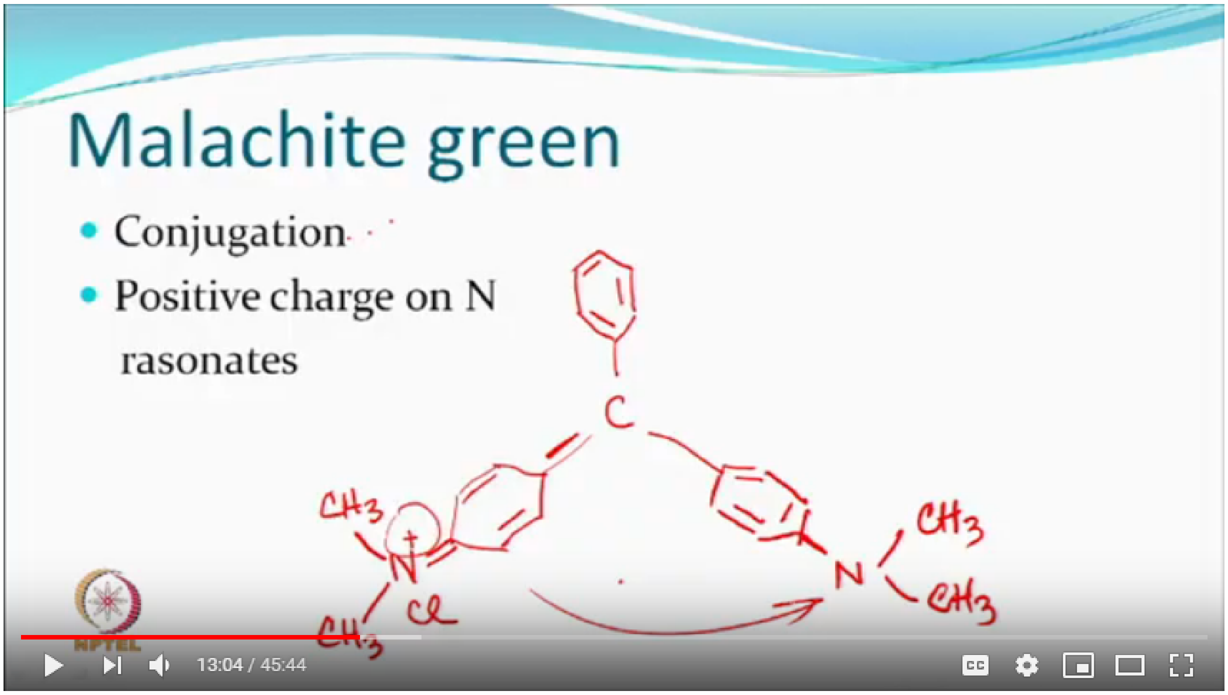

Malachite green

- Conjugation
- Positive charge on N rasonates

A malachite green, for examples, can have this nitrogen the plus charge here, which can be, which can in another resonating structure can go there also. And so, if it is possible, to have conjugation, if it is possible, to have resonance, then you will have a more stable, structure, which will give color, all right. so as a simple tri phenyl methane structure.

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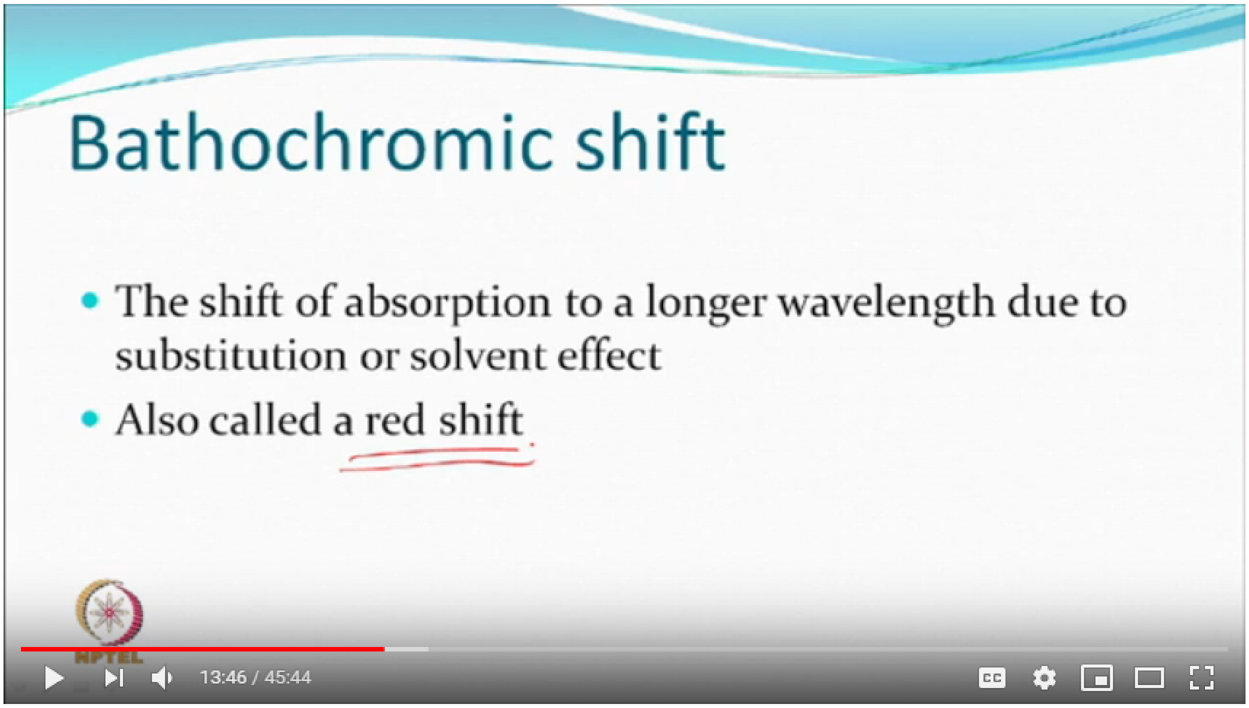

Bathochromic shift

- The shift of absorption to a longer wavelength due to substitution or solvent effect
- Also called a red shift

So there is a shift. Which we call as a better chromic shift, by adding some groups, you can change the wavelength to words, higher longer wavelength, which is towards the red, part of the spectrum and therefore, sometimes also called the red shift. So, either you add a substitution, which we are calling is an of the chrome. Or sometimes when you, when something dissolves it also has some effect. So bath shift.

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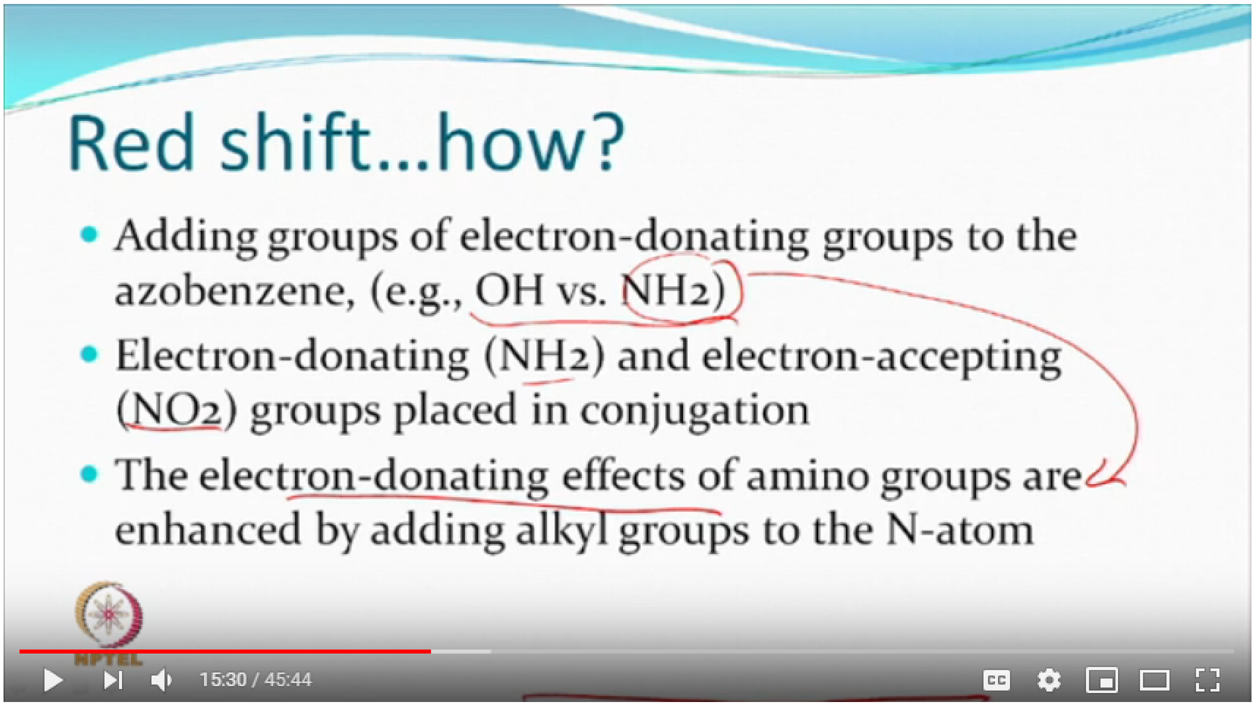

Red shift…how?

- Adding groups of electron-donating groups to the azobenzene, (e.g., OH vs. NH_2)
- Electron-donating (NH_2) and electron-accepting (NO_2) groups placed in conjugation
- The electron-donating effects of amino groups are enhanced by adding alkyl groups to the N-atom

How can it happen it can happen if you have electron donating groups the same as oh benzene which you have seen if you change add something like NS 2 or H things will be different if you also have a possibility in a molecule that there is an electron donating group like an NH to an electron accepting group like no.2 again placed in a manner that they've become part of some conjugation so like one is trying to take the other is ready to give if this happens in a conjugated area then also it helps or the electro donating group like this NH2 instead of H if you add alkyl groups instead of NS 2 you have two methyl groups for example on the nitrogen then also this will start changing so Oh H versus this we can see n h2 and no2placed in a manner that they help each other and the electron donating effect of NH 2 can be increased or any otheramino group could be increased by adding alkyl groups look at.

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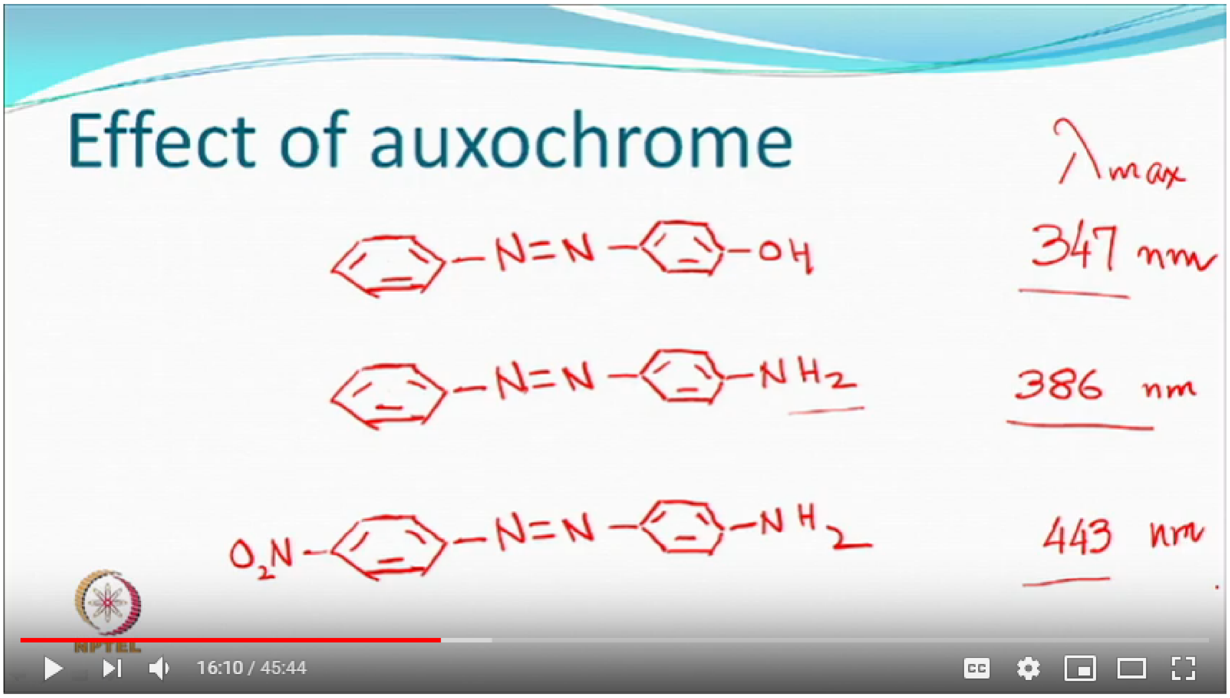

Effect of auxochrome

λ_{max}

347 nm

386 nm

443 nm

the structure you have over h here there is a lambda max some 347 nanometers if this is changed to NH 2 it increases because this is more electron donating if you have here as in a thing at the end of a conjugated structure you have no.2and goes further so same structure same chroma for more or less chroma gene also is same except now the auxo chromes are being changed or added alright so there is a minor shift the red may appear a different red and a blue may appear a different blue those kind of things can happen and that’s what an organic chemist is going to be working on making a new molecule adding something some of these principles will be used.

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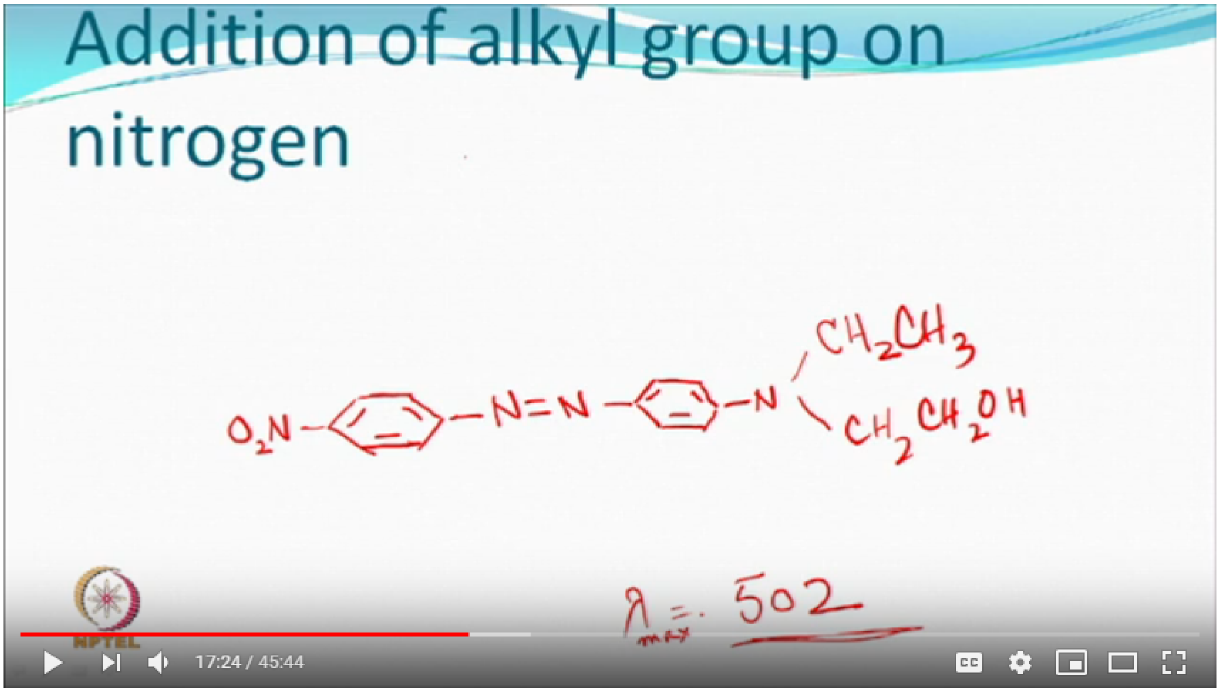

Addition of alkyl group on nitrogen

for example the same thing instead of NH 2 you have a group like alcohol cs2 cs3 or cs4 cs2 o-h also added and the wavelength of this EV length means lambda max you know you understand the beard Lambert's law you know that so we are wearing at the moment was the lambda max because if you take of a visible spectrum of any colored compound you will get absorption maximum so wherever a solution is possible we go for the absorption spectrum if you have a textile material fabric dyed printed then you will have to go for reflectance and so there is a relationship between absorption and reflection reflectance and that way you will be able to understand how much dye is there or how much shift is there these things become important sometimes these small changes can also happen in a solution also or on the fiber if there is a possibility of aggregation also so sometimes even when you do some aggregation there also there can be some shift it would appear as if there is a change in color happening but that also can be seen either by a change in the lambda max or appearance of a doublet so the, the wavelength or the waves the spectrum maybe having more than one peak if you have a mixture of dyes then also the spectrum can tell you that there are more than one peak lambda Max and therefore this can because the absorption spectra are additive in nature so if I have one molecule of a dye and the other molecule of other dye molecule and if you mix these products then based on their concentrations you will get the absorption peak and the height the intensity that's based on the concentration but the wavelength is based on some of these things if there are two of them in equal moles then you will get two peaks correctors from them add it together.

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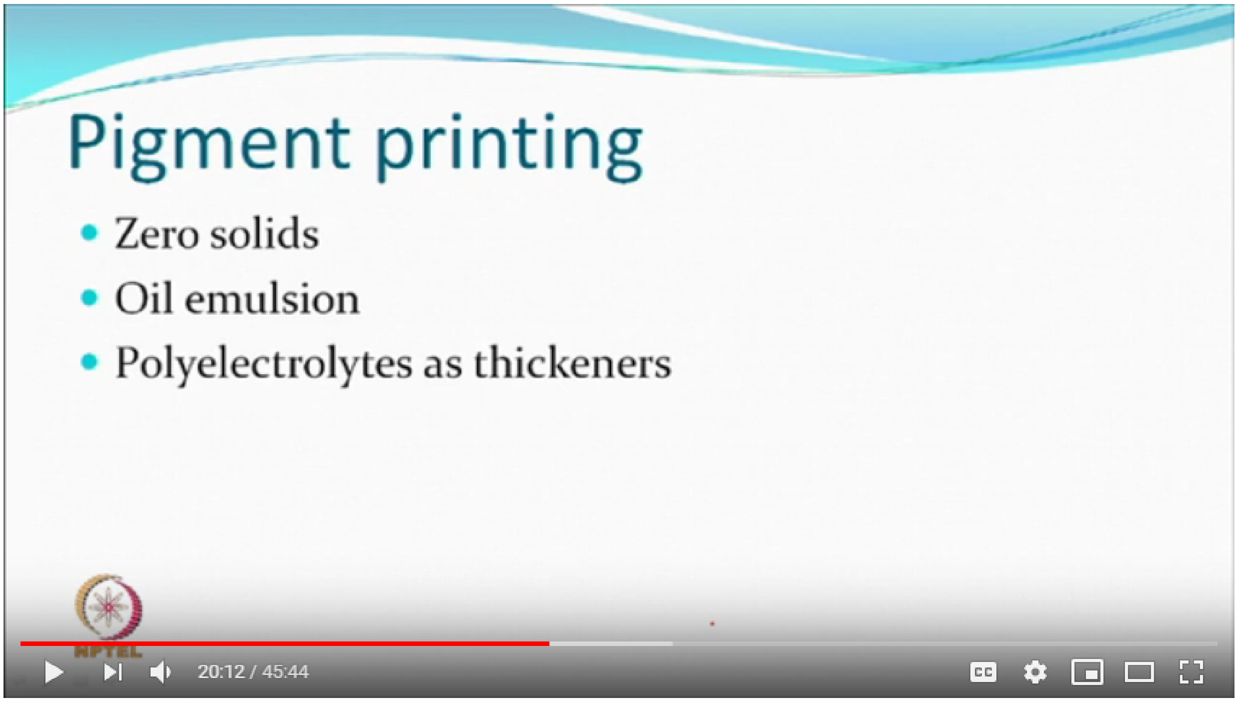

Pigment printing

- Zero solids
- Oil emulsion
- Polyelectrolytes as thickeners

people have written some questions on pigment printing so I'm just trying to make sure that we all think in the same lines so pigment printing wanted zero solid thickener because you are making a film of a binder and if it can bind the pigment it can bind any other particle also and so if there is a zero solid that means during curing itself everything evaporates nothing is left behind then the film is more transparent and the print would appear brighter okay oil emulsions are therefore were always suggested for this reason and they still give the best results there is no doubt about that if at all one has a problem is because of the environment and fire these are the reasons why people would not like to use oil or they would like to replace the oil, oil emulsion and therefore there are many synthetic thickeners who are not which are not poly little lights okay every thick net is not a poly electrolyte so you can have so they their viscosities would depend on what is the concentration of that particular compound in any solution that you make so the concentration dependence of and the molecular weight dependence of the viscosity is done the more is the higher is the molecular weight higher with viscosity nobody will doubt about that higher is the concentration hand viscosity there is no thought about it but the polyelectrolyte's give an additional advantage that at a given ph know you could have acidic groups or amino groups whichever you can put in a polyli flight so the acrylic acid based polyester Kleist's when they get negative charge let us say they start repelling each other so even if the concentration is low the molecular repulsion itself is so high because you are still contained in a some environment which has some dimensions and therefore the viscosity increases this is a third dimension of it's costing one is concentration other is molecular weight and if you have a possibility of creating repulsion between the molecules by generating same charges any large numbers then also is costing us so this is the reason why for pigment printing some such type of thickeners also have been suggested because at a relatively lower concentration they can give printable viscosities which could be in the range of 15,000 18,000 see Peaks so if you can get this in point 5concentration compared to let's say a normal starts going to 6% 7% or alginate in 3% 4% 5% based on work of it when you say well it's not 0 solid but it's a very low solid and therefore it is not going to give you it will give you relatively brighter prints pigment prints and will not have the problem of environment fire and other issues.

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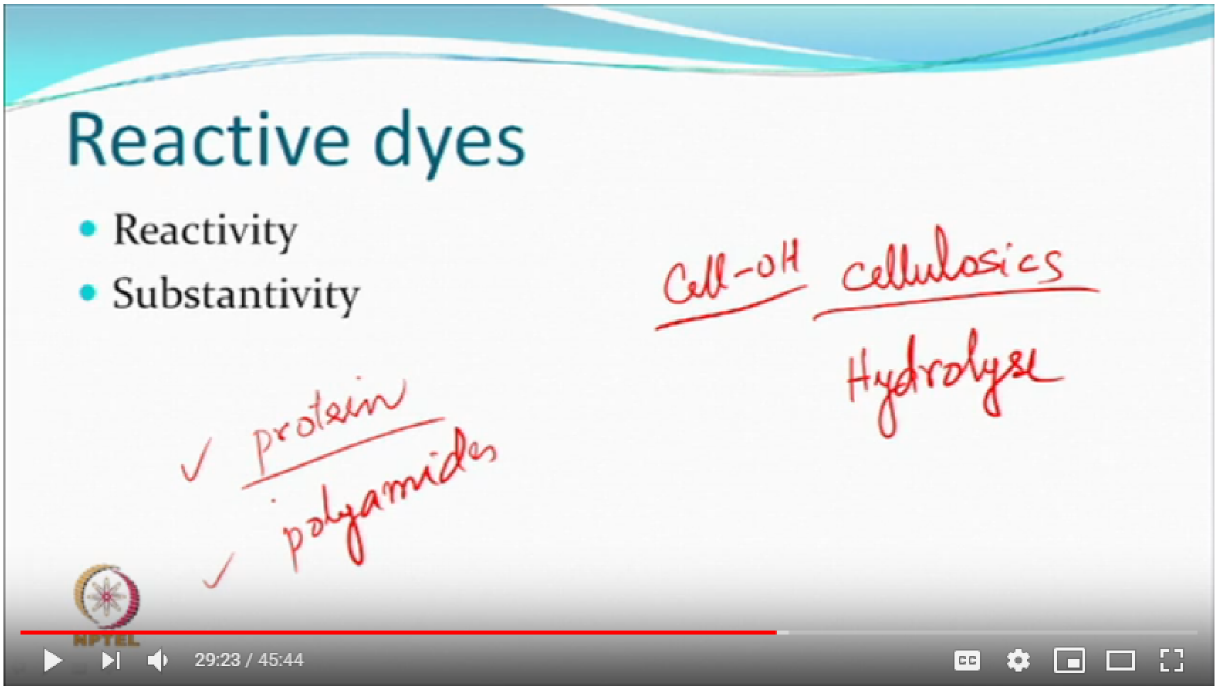

Reactive dyes

- Reactivity
- Substantivity

so reactive dyes which are the most popular dives forbid printing also they're obviously water soluble as you are quite aware they were initially synthesized for cellulosic cotton and others this question of reactivity and substantivity came only because they would hydrolyze when at the same condition where the reaction takes place with cellulose --ax so reaction takes place an alkaline medium water also has got enough hydroxyl groups and so in alkaline medium they would have the tendency to hydrolyze first rather than at a later stage because the excess accessibility of hydroxyl groups in water molecules is much easier compared to even a large polymeric molecule like the cellulose you still have to go at some place only the hydroxyl groups are not free in water they are just moving everything is mobile so from the probability point of view hydrolysis or hydrolyzed dye is more expected outcome so while if covalent bond has happened has, has been made with the cellulose after that the it is difficult relatively more difficult for this dye to come out of the substrate but if before this reaction has taken place hydrolysis is taking place then the hydrolyzed dye is just sitting there unreacted just like a direct dye but obviously its structure is not as large as a direct dye and so every wash it would like to come and so the wash fastness of reactive dyes has not been five they should have been just five there is no question of it being less than five but it is almost never five and that's because the hydrolyzed I always happen and therefore they in dying they improve the processes that first you exhaust so that most of the die is somewhere near the fiber and molecule and hydroxyl groups of the molecule of cellulose rather than in water so first you exhaust and then add alkali alright in printing also people can do all kinds of things we can always make alkalis which are latent only at the time of accession they will become active or add mild alkali or use dyes which are not so reactive alright that's the reactivity issue so you are not really looking at very high reactivity substantivity normally everyone would want there should be high substantivityof a dye molecule so that it goes to the fibre here the high substantivity also meant that the hydrolyzed dye if it is more substantive would not get washed off easily during your washing processes you know you have printed drying fixation washing and keep coming out at level different points of time and therefore they wanted the substantivity not to be too high because if it has reacted then substantivity is no problem no meaning at all it is only if it is not reacted then there is a problem because you are let's say trying to create conditions where reactivity will be moderated in a way and conditions will be created so that cellulose reacts more so less hydrolyzed die less hydrolyzed die having less lesser since stamp as a substantively would also mean that it will be washed off easily so in the customer side you will have more satisfaction if they had already died the interesting thing that obviously happened at a later stage was that it was found that they are all good for protein and polyamides so protein based fibers polyamides the reaction with these groups of the amino group and amino groups can take place in acidic or neutral medium covalent bonding also if this is true then obviously there is no hydrolyzed dye or the chance of any kind of hydrolysis of a dye is minimized because it requires alkaline medium to hydrolyze so in these cases you found that this, this the same kind of a dye has become much more acceptable because it would not hydrolyze because your phconditions are different and that was the maximum you know highlight the highlight of these reactive dyes now is that in the protein and polyamides type of material you can die with them print with them and you would have least chances of production of hydrolyzed dye so that is one point so this is somewhere it comes you can always.

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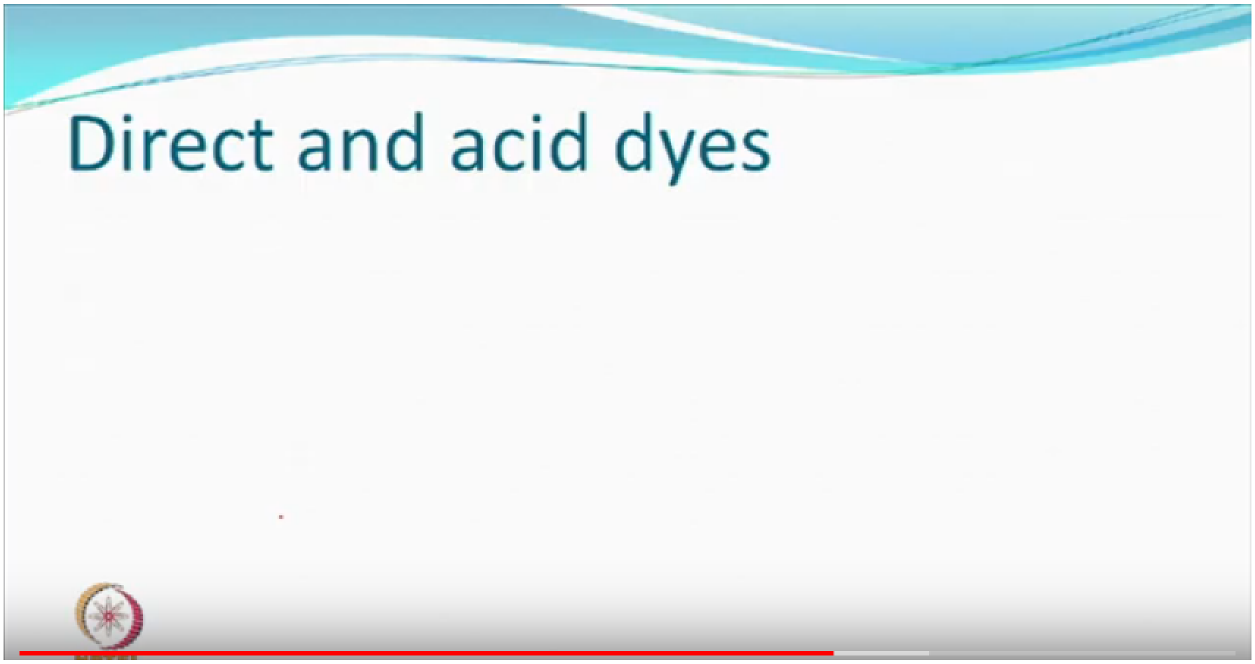

Direct and acid dyes

Some people, also always have some kind of an issue with direct and acid dyes. I saw some questions, in some answers quite simple answers, like direct dye can have more than one as a group, I said I will have only one as a group, that's not true, one of the important thing is an AC dyes are basically organic acids, then they are generally smaller molecules, both of them are anionic, because they have water solubilizing group, but direct dyes are large molecules approximately linear also. So, that they're substantivity towards, cellulose is higher, although they do not make, ionic bond, they do not make covalent bond, they make only hydrogen bond but the lengths are such that they almost go and fit so, so affinity substantivity of a direct eye towards cellulose is high, it does not mean that you cannot die wool with direct eyes because, they are also ionic only thing is a large, molecule anak a seed either smaller molecules that is one thing but a seed dies if you die in the same pH environment the wash fastness will be low because they are not substantive right as o and X I'm just

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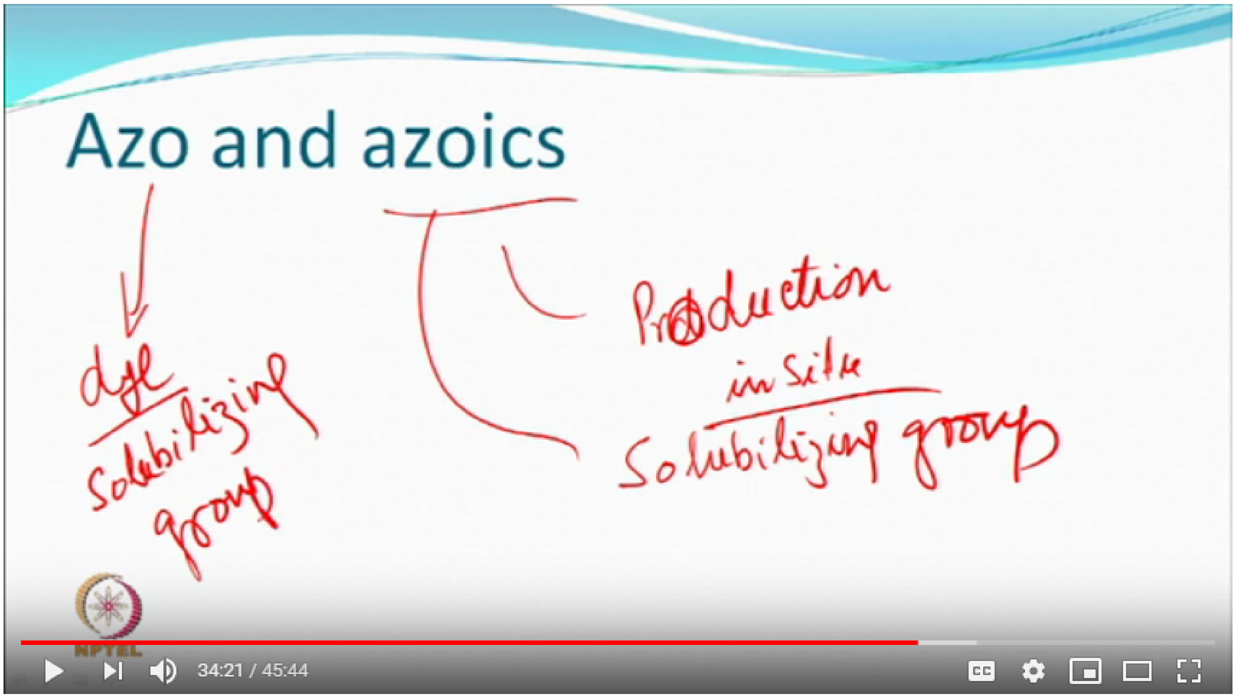

Azo and azoics

Repeating, this here because some of the answers, that I read we're not very clear, the manufacture of azo dyes, is also done exactly, in the same manner as a zoiks are produced. Right? The only thing that is being done, in an industry, the chemical industry they also have to if you make, an acyl group, the only way to make an as a group, is desertization and coupling, diazotization and coupling there is nothing else, the azoic means that the desertization and coupling, is being done in see to on the fabric, that's all and other thing is as far as the production, is concerned you 'reproducing in the same manner indifferent places, that's all the only difference here also is that you are in this case, you do not have a solubilizing group, we're here based on, a dye you may have solubilizing group, if you don't have then it is going to become like a pigment or a dispersed dye dispersed dye also may have some ionic groups I mean the you know

Oh H or some such groups, which would make solubility less, but not zero so, that's one difference and therefore wash fastness of Essex, because, they are synthesized, in situ is high and they don't have solubilizing group, but in case you have more particles, being generated which of course will be, there then you can have rubbing, fastness but fast less rubbing particularly could become poorer.

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Light fastness of basic dyes

- Cotton
- Acrylics

There was one question, also people trying, to answer this in one way or the other related to basic dyes, basic dyes, in obviously. Now you know and most of you whoever is answered this correctly, that they have positive charge and that positive charge is generated in acidic medium. Alright? In alkaline medium there is no positive charge. So, you don't we can't dye or print in alkaline medium, dye will not get destroyed but the mechanism is not available for that attraction fixation, like in cotton, cotton has no affinity, for such dyes but they can be attached through a mordant. Alright? Basic dyes can be dyed onto cotton via a mordant. So, what we had talked about, it the light fastness of the same dye, when it is linked, to the cotton through, a mordant which makes hydrogen bonds and so on so, forth and so some fastness increase, is not dependent on the ionic nature versus a clicks which have negative charges and a positive charge automatically has affinity in that electronic, way and goes there and gets fixed in the first case, the same die, shows no lesser light fastness prepared, to an acrylic, one of the reason was, the cotton is hydrophilic. So, there is enough moisture available so, based on the temperature you have chances of proxy radicals, being formed with radiations and if it is that also, leads to a reduction, in the fastness property, also the energy transfer, the absorption energy like, we said that whenever something is interacting with electromagnetic wave, there is going to be an absorption, at a certain frequency and therefore you see the color. if it absorbs more, for whatever reason because, when you actually talk about light fastness your electromagnetic, radiations, are obviously not limited to visible region, their ultraviolet strong ultraviolet, which obviously can break. Now this energy and when the electron, get excited goes there and becomes so, high then you can actually break the bonds so instead of that if the immediate absorption, of energy can also have a mechanism, of getting transferring, this absorption through a link, in this case an ionic link to a fiber then you can damage, the fiber hope not. So, much but the dye itself can be saved so, if there is a channel, of transfer of energy absorbed, to the fiber efficient, way then fiber being a larger, molecule and things like that and it can absorb, also maybe some changes, can occur in terms of some vibrations, happening maybe somewhere a bond may break, as well but you will be seeing that light, fast is high and it is more hydrophobic. So, less water available at any given point, of time and so that parody radical formation probability reduces, you can't say never nothing, will happen because we have oxygen all around a radiation, coming any polymer molecule, will also degrade but the relative, basis if you can have channel like, this then the same dye, shows you better results, in terms of fastness.

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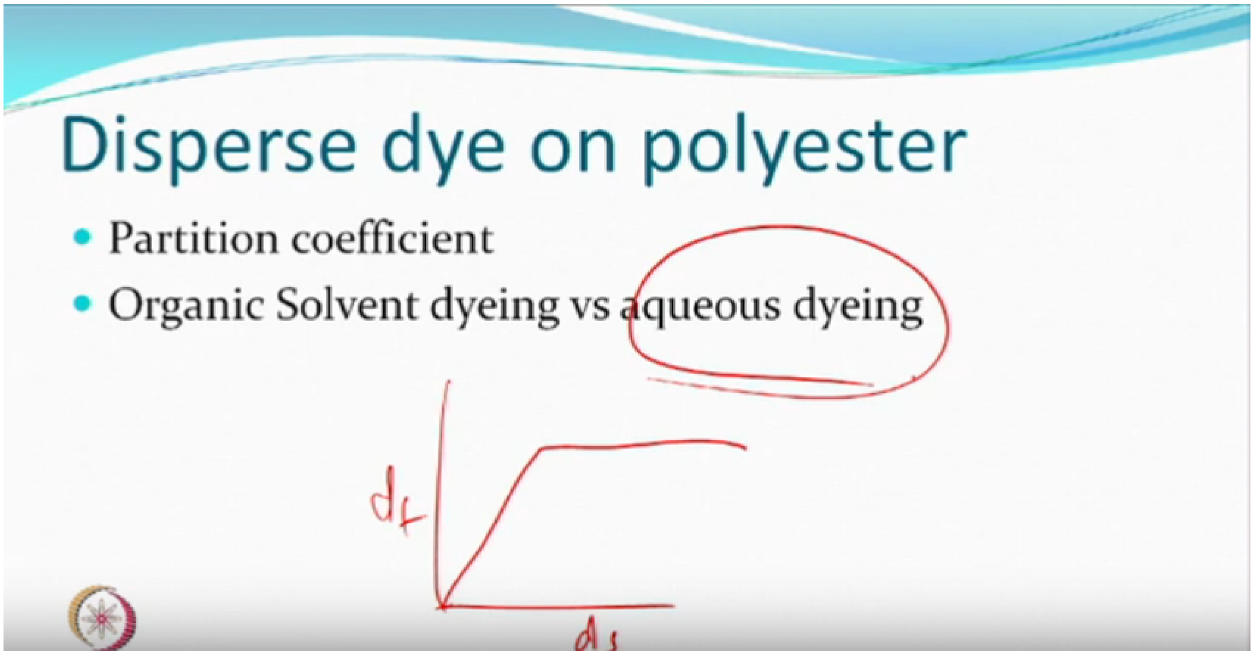

Disperse dye on polyester

- Partition coefficient
- Organic Solvent dyeing vs aqueous dyeing

There are some questions and answers written on, this topic as well the dispersed dye on polyester dispersed, yes, also more hydrophobic polyester is also more hydrophobic and therefore, this is the suitable die for this fiber for printing, as well as diamond. So, there was a question which will you answer so, as far as absorption part is concerned. So, you have solid state, dying isotherm, so, wherever the space it goes affinity of course, is because both are hydrophobic and of course whenever, there is a possibility of such type of molecules come, in together they would like to come together, in preference to water, because they are not water-soluble and they're dispersed and therefore, it is clear they don't like whatever.

So, whenever there is a chance they would like to go to that particular material which is other than water, between hydrophobic and that is one reason that equus dying, of polyester or even printing or polyester through equis paced, paste is a preferred process because theoretically, dye does not like, this it wants to go somewhere else. Okay? so, that is the advantage you get if you take an organic, solvent then means the dissolution takes place, when the whole game of getting, a hydrophilic dye on a hydrophilic fiber is being played between, the water which is a solvent dye likes the solvent also and the dye likes, the fiber also therefore you say let's increase affinity let's increase affinity do something. So, it goes more toward the Fiber in this case it's almost, built in it just likes fiber but if you make it organic solvent, then this equilibrium will shift towards the solvent, all right. And therefore excess medium good, for the dispersed. the pH is also approximately, acidic you note in the alkaline.

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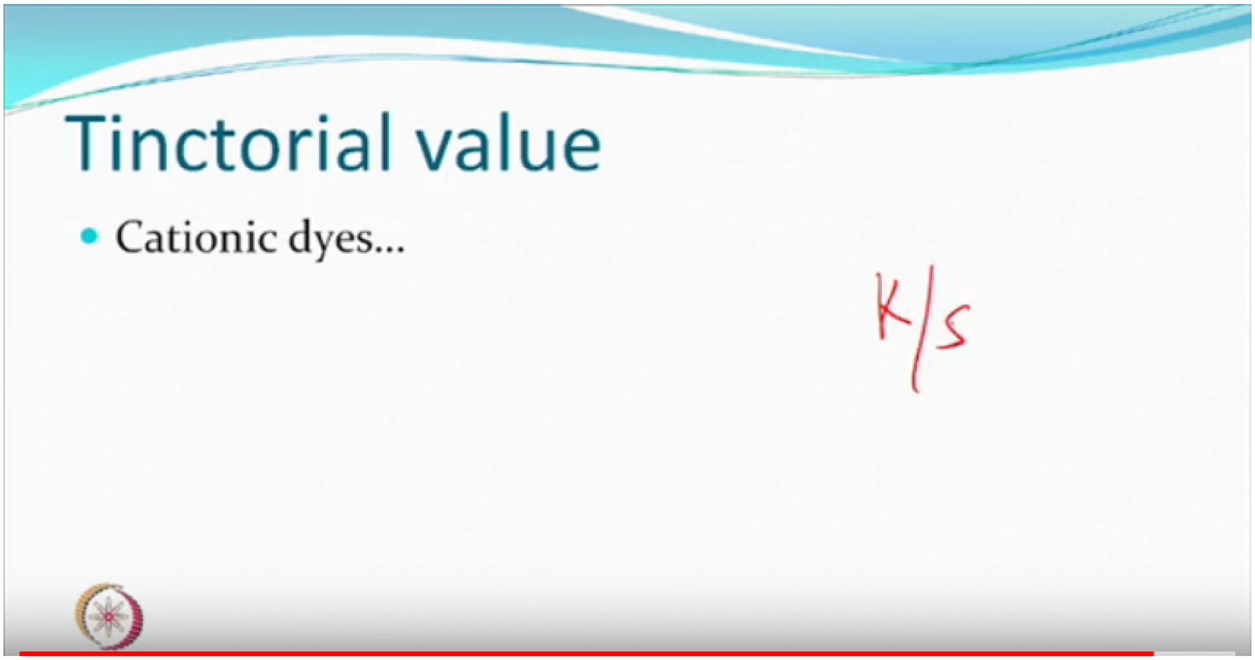

Tinctorial value

- Cationic dyes...

K/S

Some people have talked about this, saying that this, stink to riel value is K by s. which is not a good way to express this. So, this is based on the reflectance values, you get a value, which is proportional to they die on a surface, which is seen, die which is inside obviously he doesn't see, but this value can change, based on the substrate itself. and therefore, saying that well, it may get related with the tincture value, waiting tour the value is the amount, the kind of a color perception that you get, at a given let's say, mole of a dye. Right? K by s is measuring a perception based on how did I die. So this, is while it is okay, that whatever I see is reflected, through the K bias value, I'm happier sad, but if you do a bad job. Let's say, same amount of dye, if it is on the half of the fiber cross section, on one side, will appear dark, darker. Compared to the one, which is completely absorbed, therefore it is not reflecting the property of a dye. Right? The thick to riel value is a property of a dye. And not, die fiber combination. So, just saying that it is basically k by s, is not a right, wave looking at it the exactly, same thing should be there let’s say, white surface is there, which actually just makes a mono molecular layer, on that white surface is a standard white. And you know exactly how many moles are there and then you compare two dyes, 3, 4 dies. Then you can talk about this value also. And this also is based on; to start with, we always measure this in lambda max. You know, it is not the area under the curve of the spectrum. If you do that, kind of energy thing, that it's a different value. Right? So, while it may be related, but it is not this, all right. So. I think we can, stop here for today; this is the kind of revisions we thought we'll do, before we take the final exam, alright. Thank you.