

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**NPTEL**

**NPTEL PROGRAMME ON  
TECHNOLOGY ENHANCED LEARNING**

**Video Course on  
Advanced Textile Printing Technology**

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**Lecture # 3  
Dyes and pigments**

Alright, so we meet again for this course,  
(Refer Slide Time: 00:30)

## A step back.....

- Glanced through the auxiliaries for printing
- Understood Langmuir, Freundlich and Nernst isotherms applicable to different classes of dyes
- Learnt that Vat dyes and solubilized vat dyes are good for printing
- Learnt that Reactive dyes are good for printing cellulosic and protein fibre fabrics



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and let's see what we did in the last meeting, we did glance through the auxiliaries that are essential for printing. We also understood various isotherms which are applicable to different class of dyes like Langmuir, Freundlich and Nernst.

And also learned that vat dyes and solubilized vat dyes are good for printing and actually solubilized vat dyes can print protein fibres as well. And also learnt the reactive dyes are good

not only for cellulosic but also protein fibres in fact we can spend a little more time here again just to recollect, just to what can be done with reactive dyes.

So we continue with our journey, and we will consider more dyes and pigment which are used in the conventional printing system which are likely to give good fastness properties after printing, so reactive dyes we did talk about, (Refer Slide Time: 01:47)

# Reactive Dyes

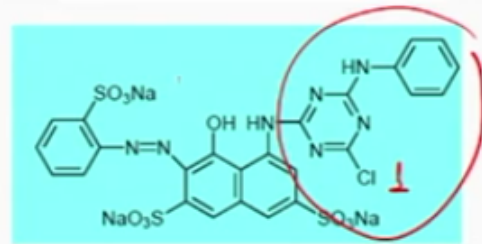
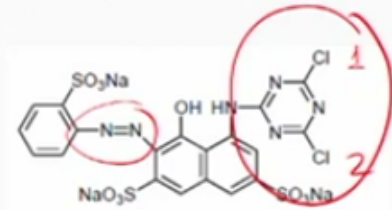
The slide displays two chemical structures of reactive dyes. The top structure is a dichlorotriazine dye, where the triazine ring has two chlorine atoms (Cl) attached. This structure is circled in red. The bottom structure is a monochlorotriazine dye, where the triazine ring has only one chlorine atom (Cl) attached. Both structures feature a chromophore with a hydroxyl group (OH) and a sulfonate group (SO<sub>3</sub>Na). The slide also includes the NPTEL logo and the text 'kushalsen iitd'.

so we said this is one reactive group where you have two chlorine, and so this is called the dichlorotriazine type of reactive dye, but the chromophore is somewhere here, alright, and this type of dye we thought is not good for printing because it is more reactive and you would prefer such dyes which would not react at all at least at room temperature, you have to take it to 60 degrees to 80 degrees before they fix.

And so one of the ways the same group was modified is that you have only one chlorine and so you have monochlorotriazine group, similar dye but this is the chain that you make and so this is sometimes known as hot brand dye as well, and so they are the ones which will be preferred for dyeing compared to the one which is on the top. (Refer Slide Time: 03:00)

# Reactive Dyes

- Water soluble

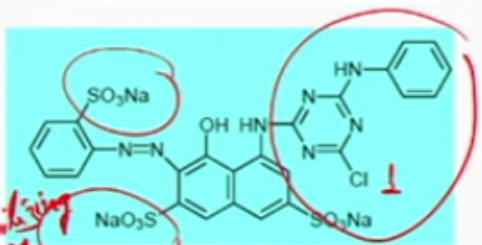
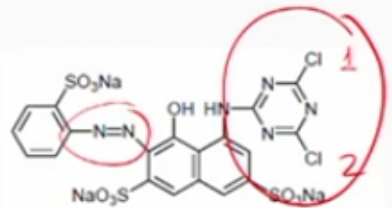


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All the dyes are water soluble as we know because of some groups like this, so this is the solubilizing group,  
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# Reactive Dyes

- Water soluble



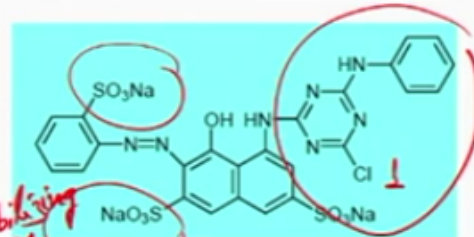
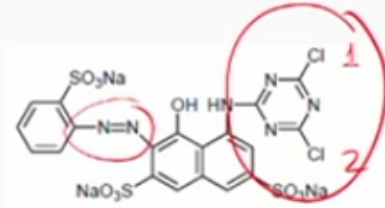
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and so they are water soluble, and so we'll make paste in aqueous medium.

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# Reactive Dyes

- Water soluble
- Diffusion followed by chemical bonding



*Solubilising group*

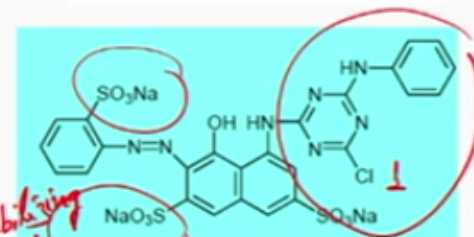
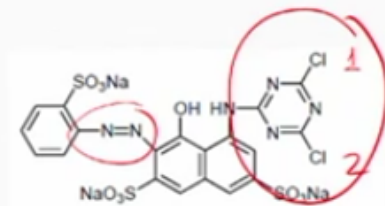


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So initially whether in dyeing or printing we would like first the diffusion to take place inside the fibre and then chemical bonding which obviously we believe is a covalent bonding that will take place, so this is true that we must make sure that this happens, so there are other types of reactive groups also like vinyl sulfone and their conditions that also different of fixation, so there are possibilities of using different reactive groups, (Refer Slide Time: 04:15)

# Reactive Dyes

- Water soluble
- Diffusion followed by chemical bonding
- Reactive system; triazinyl, vinyl sulfone, etc.
- Any specific requirements for printing?



*Solubilising group*



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where all of them should be such which give you an advantage in terms of reactivity being little low, so if we again recall the specific requirement for printing is that the temperature of printing or fixation should be high.

(Refer Slide Time: 04:31)

# Reactive Dyes

- Water soluble
- Diffusion followed by chemical bonding
- Reactive system; triazinyl, vinyl sulfone, etc.
- Any specific requirements for printing?
- Fastness

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Fastness would be said if everything has reacted covalently the fastness will be the excellent fastness, there is no issue on that as far as the word fastness is concerned, light fastness depend on the chemical structure and not on the reaction alone, so if most of us have found it difficult to believe that the reactive dyed and reactive printed fabrics actually give fastness less than 5 is because some of the dye does not react, but stays back.

(Refer Slide Time: 05:05)

# Reactive Dyes

- Water soluble
- Diffusion followed by chemical bonding
- Reactive system; triazinyl, vinyl sulfone, etc.
- Any specific requirements for printing?
- Fastness
- Substantivity vs reactivity

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We did talk about substantivity versus reactivity, so moderate reactivity is a good idea not very high reactivity, so all the molecules that you make will have moderate reactivity, substantivity also towards the fibre should not be very high, because in case particularly in the cellulosic case if there are hydrolyze dye which are formed because we are looking at reaction with the hydroxyl group of cellulose, and water also has the same situation, so this can cause hydrolyze dye if the conditions are as good as for reaction with cellulose, (Refer Slide Time: 05:53)

**Reactive Dyes**

- Water soluble
- Diffusion followed by chemical bonding
- Reactive system; triazinyl, vinyl sulfone, etc.
- Any specific requirements for printing?
- Fastness
- Substantivity vs reactivity

Use less reactive dyes

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and therefore, alright the problem is not of fixation alone, the problem is storage of the printing paste, the printing paste is made sometimes or almost a week, the main paste and the dye is added maybe for the whole day and so we keep printing but we must make sure that while it is in the paste it does not react, that's one of the important thing, and obviously we'll be storing the paste at room temperature, so highly reactive dye which will require less temperature to get fixed, temperature is one of the important parameters which can be fixed to vary the time of fixation etcetera, and so that's not a good idea.

As far as the dyeing is concerned we do cold pad batch method where the dye solution is prepared very quickly, alright, and then you pad then you pad within alkali and then you batch, alright, so one has to take precautions, once it is on the fibre and there is no water, not much water then slowly it can get fixed at room temperature, but printing the paste duration is large so we don't prefer that kind of thing.

Substantivity as we said would be low, relatively low, is not that there should not be substantivity all then you should not go to the fibre, although it is not exhaust process, you take a screen or a block or whatever you actually put it there wherever you want the dye to be there, and so dye cannot run away and the concentrations are also high, and so it is going to diffuse but it should not be repelling, you know, it should not be something like hydrophobic fibre versus hydrophilic dye, so that's not a good idea, but affinity should be there but not very high

substantivity like every time we wanted to do good fastness properties we always wanted high substantivity so that goes more towards the fibre, but here the mechanism fixation is chemical bonding, so even if it is, once it goes in and then gets fixed, then the wash fastness does not depend on whether it is substantive or it is not substantive, it will be fixed, that's the advantage in reactive dyes.

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# Reactive Dyes

- Water soluble
- Diffusion followed by chemical bonding
- Reactive system; triazinyl, vinyl sulfone, etc.
- Any specific requirements for printing?
- Fastness
- Substantivity vs reactivity
- Substrate?

Cell-OA H-OH

Solubilising group

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Substrate that would be set cellulosic, cotton, viscous, rayon no doubt that's for basically reactive dyes initially were synthesized for these, but all this reactive dyes can die very easily, all protein fibres and also nylon. And amino groups is good enough to be reacted and don't require alkaline medium, and if you don't require alkaline medium hydroxyl group will not react that is water will not react, and therefore you will have less hydrolyze dye and so for the protein fibre PH being different is a much better option and the reaction takes place.

(Refer Slide Time: 09:48)

# Reactive Dyes

- Water soluble
- Diffusion followed by chemical bonding
- Reactive system; triazinyl, vinyl sulfone, etc.
- Any specific requirements for printing?
- Fastness
- Substantivity vs reactivity
- Substrate?

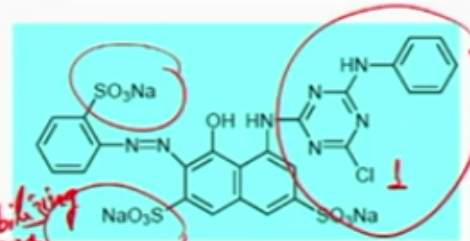
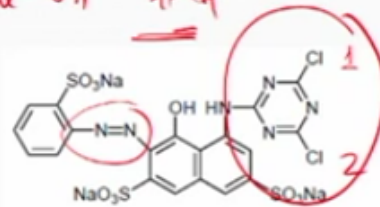
- Hydrolyzed dye?



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Cell-OH H-OH

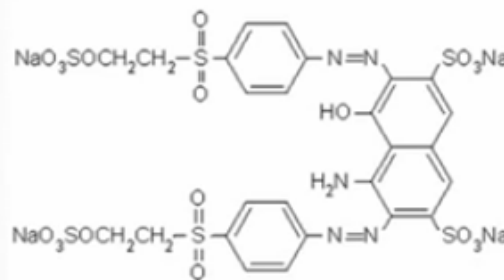


And if anything, any dye which is not reacted is not hydrolyzed also, so this is what we just talked about that PH for the protein and nylon are going to be neutral and little acidic and so no hydrolyzed dye is going to form, so that's the biggest advantage.

So we do have other type of dye which are called bifunctional, they are from the dyeing purposes they are known as high exhaust dyeing, (Refer Slide Time: 10:06)

# Bifunctional reactive dyes

- High exhaust dyes
- Homo- Bifunctional
- Hetero- Bifunctional



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so they have two reactive groups, this reactive group is called vinyl sulfone, right, so there are two reactive groups instead of one and therefore they are called bifunctional reactive dyes, see



you must appreciate here also there are two chlorine but this is not called bifunctional dye, this chlorines are on the same reactive group, so bi-functional dyes are the ones which have two different reactive groups they can be homo-bifunctional like this both are vinyl sulfone or they can be hetero-bifunctional which could be, one could be triazinyl, the other could be vinyl sulfone or any other reactive groups which anyway so those will be called the bifunctional reactive dyes.

And as a percentage if you look at fixation, they get exhausted well and in the dye bath printing doesn't have that issue and they also require higher temperature because you're choosing such type of reactive group is required high temperature so they are stable, so they are pretty good for the printing, all this fibre so bifunctional dyes are good.

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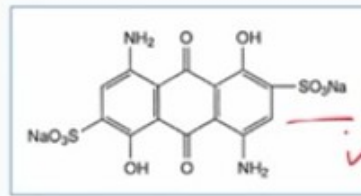
The slide is titled "Acid dyes" in a large, blue, sans-serif font. Below the title, there are two chemical structures. The first structure is for CI Acid Blue 45, which is an anthraquinone derivative with two amino groups (NH<sub>2</sub>) and two hydroxyl groups (OH) on the central ring, and two sodium sulfonate groups (SO<sub>3</sub>Na) on the outer rings. The second structure is for CI Acid Red 138, which is a disazo dye with a central benzene ring substituted with a hydroxyl group (OH) and an acetamido group (NHCOCH<sub>3</sub>), and two sodium sulfonate groups (SO<sub>3</sub>Na). It is connected via azo groups (-N=N-) to a phenyl ring substituted with a C<sub>12</sub>H<sub>25</sub> alkyl chain. In the bottom left corner, there is a logo for NPTEL (National Programme on Technology Enhanced Learning) and the text "kushalsen iitd".

Then the acid dyes, so common like anthraquinone based dyes and also acid based dyes, so you have this group and the anthraquinone by itself as the reactive group, sometimes people do ask they also have solubilizing group, direct dyes also has solubilizing group, they are also an ionic in nature, these are also an ionic in nature, but sometimes people want to know what is the difference between direct dye and an acid dye, so that difference I think you will recall whenever you go back, try to understand what is the difference between the two types of dyes, both are an ionic okay.

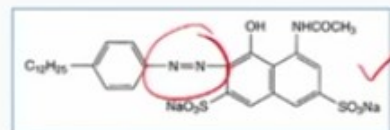
And theoretically the kind of fibre that we used these for they will have positive charge,  
(Refer Slide Time: 12:53)

# Acid dyes

- Organic acids



CI Acid Blue 45



CI Acid Red  
138



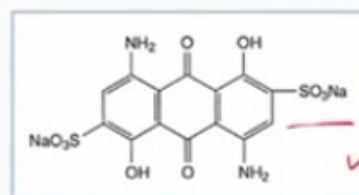
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and they have negative charge so they can go there as well, make ionic bond, so there acid dyes they are generally organic acids and therefore they are the acid dyes, so they are basically acid so you can actually react them with alkali and you will make sodium salts, right, other than also we, other than the solubilizing group as well.

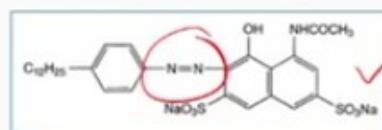
So one important thing is they are applied through acidic media,  
(Refer Slide Time: 13:21)

# Acid dyes

- Organic acids
- Applied through acidic media



CI Acid Blue 45



CI Acid Red  
138

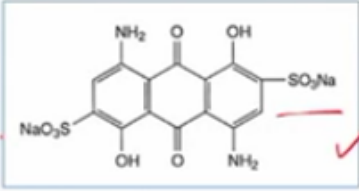


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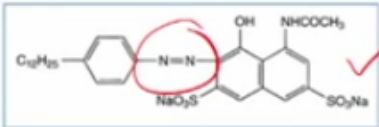
so when you have acidic medium so they would not have so much of a problem, but the fibre which is the substrate wool, silk, and nylon can also be,  
 (Refer Slide Time: 13:42)

# Acid dyes

- Organic acids
- Applied through acidic media
- Substrate? *Wool, Silk, Nylon*




CI Acid Blue 45



CI Acid Red 138

*Handwritten notes: A red circle highlights the azo group (-N=N-) in the CI Acid Red 138 structure, and a red checkmark is next to it. Another red checkmark is next to the CI Acid Blue 45 structure.*

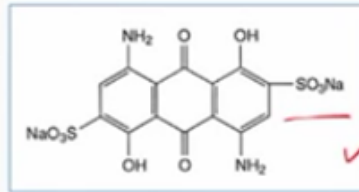
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any kind of nylon, so you have wool, silk, nylon, all of them will assume a positive charge and so anything which is negatively charge will get attracted and so we'll have various controlling mechanisms to make sure the right kind of bondings are formed.

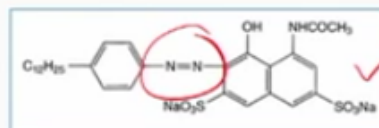
So dye fibre interaction is ionic,  
 (Refer Slide Time: 14:18)

# Acid dyes

- Organic acids
- Applied through acidic media
- Substrate? *Wool, Silk, Nylon*
- Dye fibre interaction? *ionic.*
- Fastness; Wash? *Light?*




CI Acid Blue 45



CI Acid Red 138

*Handwritten notes: A red circle highlights the azo group (-N=N-) in the CI Acid Red 138 structure, and a red checkmark is next to it. Another red checkmark is next to the CI Acid Blue 45 structure.*

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wash fastness is can be an issue because they are smaller molecules and ionic bonds in aqueous medium they dissociate ions are dissociate very easily, and so although they are good dyes, they go very nicely and get printed also very nicely, but wash fastness can be an issue, so for dyeing anywhere we use them, for printing you may like to say well little larger molecule, more molecular weight maybe a good idea, so that the wash fastness also improve, because there is no other mechanism of fixation except making ionic bond, alright, unlike reactive dyes, so they are water soluble and they make only ionic bonds and therefore they can come, okay.

So if the molecular weight becomes high then obviously wash fastness can improve and that's what people will like to do,  
(Refer Slide Time: 15:30)

The slide features a decorative header with blue and green wavy lines. The main title is 'Acid mordant / metal-complex dyes' in a blue font. Below the title are two bullet points: '• What are these?' and '• What is the advantage?'. The text 'Wash fastness.' is centered in red. At the bottom left is the NPTEL logo, and at the bottom center is the text 'kushalsen iitd'.

and because of that you may get some advantage by using mordant dyes, okay, so metal complex dyes which are already there either the complex is pre-metalized, so you already made the complex, so you said hydro molecule or you make the complex later in some way or the other in printing you may like to have metal complex dyes or than just a, or you have to print with a mordant first or a pad with a mordant first and then print the mordant dye and so you can get the complex formation there, so one of those things will have to be done, and then the advantage definitely comes the word wash fastness.

So for printing you may like to use metallized, pre-metalized or metal complex dyes also in whichever manner that you want to use, so this you should try to get the information from wherever, from your previous classes that you have learnt,  
(Refer Slide Time: 16:30)

## Acid mordant / metal-complex dyes

- What are these?
- What is the advantage?

Wash fastness.

What is the chemistry of the dye that helps in complex formation? What are the essential features of a mordant dye? How are metal complex dyes different from mordant dyes?

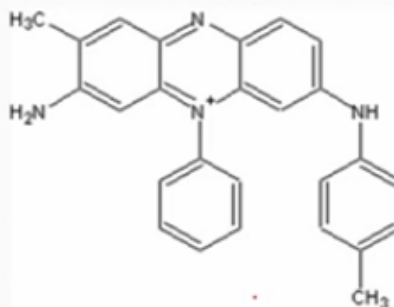


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what is the chemistry that helps the dye in complex formation, why any dye forms are complex, and we're looking at metalized complexes here, so what are the essential features of a mordant dye, and how are the metal complex dye is different from mordant dyes, so mordant dyes are there and how the metal comes, and mordant dyes can have different models also, complex formation so you may like to check these out, and keep the note with you.

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## Basic Dyes



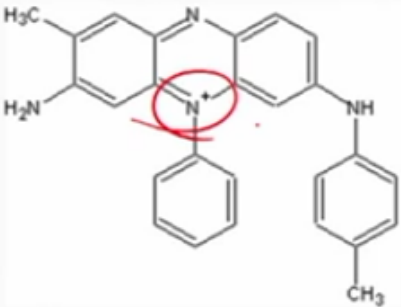
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The next dye which obviously are very interesting dyes and these dyes called basic dyes or sometimes cationic dyes, where the dye has a positive charge and the conditions that we use

them, and so they are called cationic dyes, initially these dyes were used for cotton cellulosic fabrics as well, using a different kind of a mordant, but mostly they are going to be used for printing acrylic fibres or fabrics, so they are called basic dyes because they are bases, the acid dyes are called acid dyes because they are acids,  
(Refer Slide Time: 18:30)

**Basic Dyes**      *Cationic Dyes*

- Organic bases



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because they are bases therefore they can interact with an acid, alright, that's an important part.

Interestingly because of their structures this one which is been shown then you have triphenyl methane based cationic dyes, high tinctorial value, when tinctorial value high generally means is they can actually absorb radiation from the ultraviolet region, and also radiate out in the visible region, so actually they appear more brilliant than other dye, so that's the way the structure is, and so you love those colours in general, very nice.

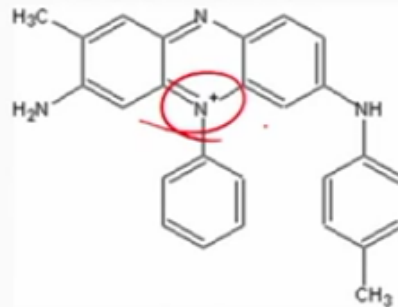
So the similar looking dye which is similar structure which is an acid dye after some change it becomes a basic dye, next, the other structure obviously looks more brighter, it's counterpart in acid dye looks not so bright, little duller than compared to the bright, so high tinctorial value, so these are also dyed from aqueous medium,

(Refer Slide Time: 19:32)

# Basic Dyes

# Cationic Dyes

- Organic bases
- High tinctorial value
- Dyed from ??? Medium?, Ph?



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and what is the PH? What is the PH of dyeing according to you? Acidic PH, so acidic PH is required only in the acidic PH this group gets generated, otherwise you will not be able to dye.

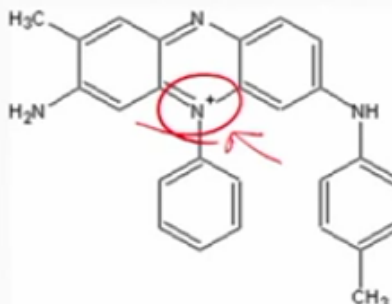
And because they are cationic the anion comes from substrate which is acrylic. If somebody ask you what is the anionic part in the acrylic fibre, what is the anion in the acrylic fibre? Alright, so during the manufacture you can either have a copolymerization which will be acidic or based on the polymerization method your initiators which could be sulfides, bisulfides and so on and so forth they remain attached at the end of the chain, and so that is how the negative group is there in the acrylic fibres.

(Refer Slide Time: 20:57)

# Basic Dyes

## Cationic Dyes

- Organic bases
- High tinctorial value
- Dyed from ??? Medium?, ~~PH?~~ pH
- Substrate? *Acrylic*.
- Fastness ?



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The fastness generally is good as I mentioned sometime back also, if the molecular size is high the wash fastness will be good as such acrylic fabrics if they are used, they themselves are hydrophobic in nature and therefore the interaction with the water is not as nice as with the hydrophilic fibres, and so once the dye goes in, that the dye goes in, of course the temperature etcetera are important, PH of course is important, as far as printing is concerned you have to be careful, acrylic fibres are sensitive to heat and so they can get yellow, and so you have to optimize the fixation conditions carefully.

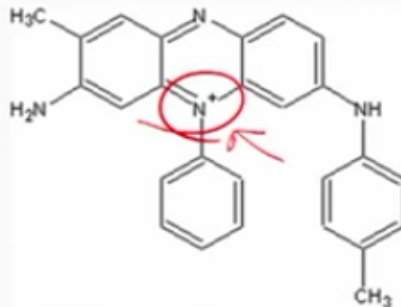
Light fastness of these dyes is also good, acrylic fibres being hydrophobic they have less of moisture but the bond is ionic and so the radiation energy which is absorbed by the dye and the chromophore is the dye, actually is able to transfer the energy to the fibre and remain safe, and so light fastness of these dyes on cationic dyes on acrylic fibres is also pretty good. So you may note down from somewhere what is called the tinctorial value,  
(Refer Slide Time: 22:22)



# Basic Dyes

## Cationic Dyes

- Organic bases
- High tinctorial value
- Dyed from ??? Medium?, ~~pH~~ pH
- Substrate? *Acrylic*
- Fastness ?



What is tinctorial value? Why do basic dyes have high tinctorial value?

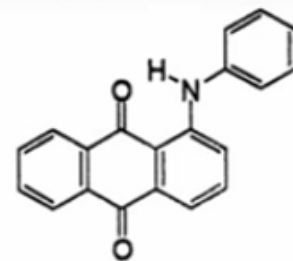


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why the basic dyes have high tinctorial value, learn little more about it and keep it in your notes.

(Refer Slide Time: 22:33)

# Disperse dyes



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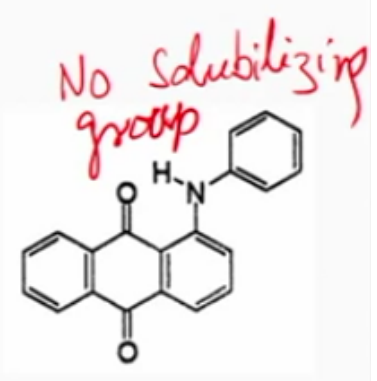
Disperse dyes, as the name suggest they are dispersed in solution and so they are not water soluble, so compare to the previous one this is the major difference that we see, and you can see in a dye molecule or example that is there, there is no solubilizing group, but there could be smaller molecules, but not water soluble, so they remain in particulate form, whenever a situation comes when there is not water soluble, it's not soluble then the molecules like to come

together and that's the way thermodynamic works, so they like each other and you get particulates matter.

But it's not a zero solubility, you know, it's a limited solubility, because they are called dyes, (Refer Slide Time: 23:44)

# Disperse dyes

- Very limited water solubility



The image shows a slide titled "Disperse dyes" with a bullet point stating "Very limited water solubility". To the right is a chemical structure of a disperse dye, which is a naphthoquinone derivative with a phenylamino group. A handwritten note in red ink above the structure says "No Solubilizing group". The slide also features the NPTEL logo and the text "kushalsen iitd" at the bottom.

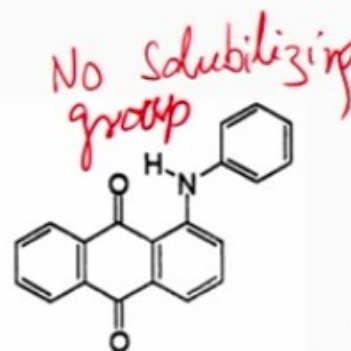
if they were absolutely insoluble, then they would be pigments, right, so in water they have solubility but very less solubility, and this is the whole trick that the most dye remains in particulate form, small amount of dye get dissolved like in a printing with the total amount of water available is also very less, but it gets dissolved of course, temperature and solubility are related, so if you have higher temperature solubility will be more of a disperse dye even within the, in the aqueous medium also, and so once it is in molecular form, but then diffuses in, and they have to be applied on substrates which are hydrophobic, (Refer Slide Time: 24:32)

# Disperse dyes

- Very limited water solubility
- Substrate?



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relatively more hydrophobic, and so the name comes polyester, so the textile people are concerned, so these dyes originally were made synthesized much before the polyester came into the market, because we had acetate fibres which was not able to take, and could not be dyed in printed with the conventional dye that were available, so they had to think about so the structure, architecture of the molecular change with over the period.

But when the polyester came these were the dyes just made for them, polyester hydrophobic, the dye hydrophobic, the bond is pretty nice, the wash fastness should not have any problem and so it was good, they can be dyed and printed onto acrylic, they can also be printed on nylon, alright, but generally we find that if the polyester which is this major substrate for printing with dispersed dyes, with nylon there has been one issue that the glass transition temperature of a nylon fibre or fabric in water goes down and goes below room temperature, in a dry state the glass transition temperature is close to 70 or 80 degrees, but when you put it in water with glass transition temperature goes down, and what it means is there is lot of mobility at room temperature and many wash, and so the wash fastness of the same dye on a nylon is not good, although it's supposed to be not water soluble, but that's one.

It can be dyed and printed onto acrylic, but not very popular because the tinctorial value of these dyes is not as bright as the cationic dyes on acrylic, and so the preference obviously is towards the cationic dye rather than the dispersed dye, difficult to dye but polypropylene can also be dyed with, and printed with also dispersed dyes, but you have to adjust.

Can we print polyester with dispersed dyes? Of course, any methods, all kinds of methods can be used, all you have to do is the fixation condition, the fixation condition could be dry heat, super-heated steam and such type of things, so at temperature which are higher, polyester is very responsive, very responsive and so the dye diffuses, you have thermosol methods also, so you can use different fixation techniques, but it will once it goes in it just goes in, and you will be happy, so dispersed polyester combination is one of the best combinations that you have.

The wash fastness, so the cationic dyeable polyester is different polyester, so your aim is to dye and a print with a different type of a dye and not dispersed, if you make it very ionic then there will be issues of affinities, okay, so we're looking at the normal polyester which is at 90% of the substrate that you see anywhere in the market, so that's the major thing.

The cationic dyeable percentage wise will be hardly any, you can make it and of course then you will take the cationic dye, that's a preference, but if you want to dye a cationic dyeable polyester with a dispersed dye you may be able to dye and print, but what's the point? Dispersed dye can just go very easily on polyester why do you want to modify the polyester and then dye with a dispersed dye, that's costly also.

So where wash fastness should not be a problem, light fastness depends on the molecular structure there are no other way, so it depends on which type of a molecule the fastness will be tendermint, perspiration fastness also doesn't have so much of a vat.

Rubbing is not an issue because it does not become particulate as such cosine unless and until there are something is, as a particulate get deposited on the surface, in case that happen then you'll have to do some post treatment to remove those particles, otherwise no problem, but new problem is there with these dye which is called the sublimation, which the other dyes did not have whether new sublimation issues are there so these dyes can sublime, (Refer Slide Time: 30:32)

The slide is titled "Disperse dyes" in a large, teal font. Below the title, there are three bullet points: "Very limited water solubility", "Substrate? Hydrophobic Polyester", and "Fastness; WF, LF, PF, RF, sublimation". The word "Hydrophobic" is written in red above "Substrate?". "Polyester" is written in red and circled in red below "Substrate?". To the right of the text, there is a chemical structure of a disperse dye, which is a triphenylmethane derivative. The structure consists of a central carbon atom bonded to three phenyl rings. One of the phenyl rings is attached to a nitrogen atom, which is also bonded to a hydrogen atom. The other two phenyl rings are attached to carbonyl groups (C=O). The text "No solubilizing group" is written in red above the chemical structure. In the bottom left corner, there is a logo for NPTEL (National Programme on Technology Enhanced Learning) and the text "kushalsen iitd".

so if temperatures are suitable you can say the shade is changing or does not even a problem dye from one gets migrated to some other portion where you didn't wanted even storage, high temperature storing if suppose they are, so that becomes a problem, sublimation fastness, the new fastness which has to be checked on the dispersed dyes.

So they define now the dyes with the based on the molecular weight, high energy, medium energy and low energy dyes, so if you actually are printing with the low energy dyes then you have a most sublimation issue, if you're really looking at fastness, better fastness then you are looking at high molecular weight which is high energy dyes, that you means you require higher energy for sublimation and so they will not sublime, so that selection has to be made.

So whenever you want to do printing the data sheet provided by the dye manufacture becomes your one of the first guidelines to choose the dye, because you don't want to have all problem that are related, so it would not have wash fastness, sublimation fastness can be an issue.

(Refer Slide Time: 32:00)



Azoic colours, well these are formed in situ that means on the substrate itself and one of the reason is these dyes are colour are also not water soluble, so you have two components one is called the base and the other you called the naaptol, and so you mix them in a right way, right conditions suddenly as a group it generates, okay, so chromophore is an azo group,  
(Refer Slide Time: 32:32)

# Azoic colours

- Formed in situ
- Chromophore ?

AZO



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this generates when the digitized you know base is reactive with a naaptol, alright, so affinity of a naaptol comes as an issue, so what kind of a naaptol you want, but this is a very interesting thing to learn and see the same naaptol can give different colour with different bases, and same base can give different colours with different naaptols and so one of the easiest way to synthesize the molecule, the azo group synthesis is easy, but how do we print? If you remember dyeing what you were doing in dyeing, you have to digitize the based to make it salt and the temperatures have to be kept around 5 degrees or below, and the whole process therefore is a tough process, and how do we print that?

So but they started you know modified diazonium salts which could be stabilized so that they can be stored as it is when you dissolve them in directly in water and use you don't have to digitize, so such type of things will have to be used for printing purposes, you can pad through a naaptol and then do the printing with stabilize salt and then go for a fixation.

(Refer Slide Time: 34:08)

# Azoic colours

- Formed in situ
- Chromophore ?  
*AZO*
- Substrate



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Cotton of course cellulose and of course the kind of substrate which generally will be used for this type of colours, because the reaction is so quick, is actually spontaneous, the colour development is so spontaneous, so much before you say I'm fixing the colour is there, right, you can dry it, you have to be very careful in washing of course because all the things that you have done, you have to remove but the colour develop, so people have used various kinds of technique like spray, you know, you use pad through a naaptol and then spray different basis, and you get all kinds of multi colour defects on the fabrics, because they are so quick, so without even a paste that's the interesting, you know you can have a paste and print the way you want to print, but you can have a solution and through which also you can spray and get some kind of design which you may like which are quite interesting.

Rubbing fastness is the only thing which we should be worried about that wet and dry both,  
(Refer Slide Time: 35:19)

# Azoic colours

- Formed in situ
- Chromophore ?  
**AZO**
- Substrate
- Fastness
- What is the difference between azo-dyes and azoic colours?



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otherwise they are water in soluble compounds, so if you've done nicely the padding is nice, the temperature is in conditions are good, the wash fastness should not have a problem, so what is the difference between azo dyes and Azoic colours? The Azoic colours are formed in C2, and azo dyes are formed somewhere else and azo dyes can be dispersed, reactive, direct, all classes you can have.

(Refer Slide Time: 36:12)

# ILLUMINATING colours

- Non-dischargeable colours
- Why do we need these?



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Within this printing one set of colours is called illuminating colours, illuminating colours are for the discharge style of printing, so you have a background which is the fabric has been dyed



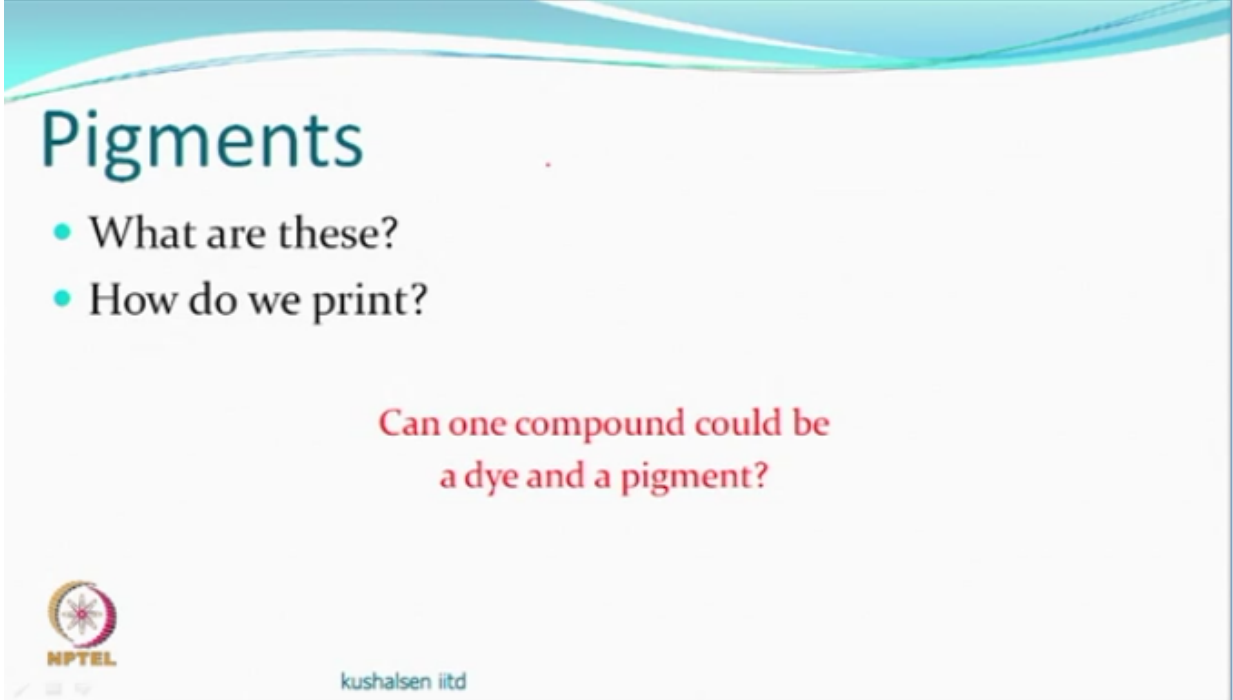
with some dye, and we want to discharge that dye so that is fine, so we use your reducing agents to discharge the dye from the portions that you have, so you can get a discharge area which would be hopefully white, but if you want coloured discharge in that case you got to choose some colours which are not dischargeable or difficult to discharge.

In the conditions that you use you know, a very strong condition everything can be discharged, but that time your fabric also may get damaged, but in a reducing environment that we actually want to discharge so there are colours for example cationic dye, anthraquinone based dyes they do not very easily get discharged, so triphenylmethane based dyes are highly non-dischargeable and so if you in your paste, discharge paste if you use them then you can get coloured discharge as well, alright, so you have this thing which normally we have not been talking in this condition, in the context of dyeing, but in the contractive printing we do have the illuminating colours.

Then there are pigments, in printing they're very helpful particularly if you have blends, dyeing of blends is also difficult, printing of blend is not less difficult, two different fibres wanting two different dyes and in case your fibres are not of the same chemical structure, then you got to have two different types of dyes, two different types of conditions to be used for fixation, just different, but if you have pigment they don't like any fibre, they have nothing to do with the fibre, so they can be printed on any kind of a blend, of course they can be printed on single fibre fabrics also.

So how do we print?

(Refer Slide Time: 38:47)



**Pigments**

- What are these?
- How do we print?

**Can one compound could be a dye and a pigment?**

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Obviously we have the same way, you have a paste and then you got to have some kind of a binding system, so film has to be formed and once you make a film, with the film and this fastness of the film which determines, how fast the pigments prints will be.

Can the same compound be call the dye or a pigment? Surely, anything which does not go at a molecular level can be pigment, and you can use them but of course there are specially designed pigments for doing certain things, because when you add something else on the surface of the fabric then the third component also has to be handled from the point of durability, so that's the only reason why somebody will still like to have dyes for printing rather than just pigment for printing, right, but these days and one of the reasons was also that the binder, then I'll makes a film manifest the stiff film then the handle etcetera issues can come, but these days lot of research has gone into making flexible films, very, very flexible films.

(Refer Slide Time: 40:19)

The slide features a title 'organic pigments ...examples' in a large, teal font. Below the title is a table with two columns: 'pigments' and 'Colour range'. The table is divided into three rows. The first row lists 'azo' pigments with a color range of 'yellows, oranges, reds'. The second row lists 'naphthalene, perylenetetracarboxylic acid, anthraquinone, dioxazine and quinacridone' pigments with a color range of 'very fast and brilliant oranges, reds and violets'. The third row lists 'halogenated copper phthalocyanine derivatives' pigments with a color range of 'blues and greens'. At the bottom left of the slide is the NPTEL logo, and at the bottom center is the text 'kushalsen iitd'.

pigments	Colour range
azo	yellows, oranges, reds
naphthalene, perylenetetracarboxylic acid, anthraquinone, dioxazine and quinacridone	very fast and brilliant oranges, reds and violets
halogenated copper phthalocyanine derivatives	blues and greens

Some of the chemistry of pigments like azo based pigments are there which could give you yellows, oranges, reds quite a lot that's the kind of range there you can get, the naphthalene based and anthraquinone based and there are two other interesting series which is perylene based pigments and quinacridone based pigments, they're very fast and very brilliant, they give oranges, reds and violets, so range is pretty good, then there are phthalocyanine derivatives which have got some metal like copper, so copper based phthalocyanine derivatives if you remember we had direct dyes also based on phthalocyanine derivatives, blues and greens can be obtained using phthalocyanine, so they are beautiful blues and so you have range of oranges and reds and violets also.

Just an example of one or two,  
(Refer Slide Time: 41:54)

# Perylenetetracarboxylic dianhydride



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so that you remember there was a molecule like this also, perylenetetracarboxylic dianhydride, so if it was a carboxylic acid it could be hydrophilic, anhydride is obviously less hydrophilic, so it's going towards saying a no effort is being made to increase substantivity.

(Refer Slide Time: 42:20)

# Perylenetetracarboxylic dianhydride



Pigment Red 224



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So this is the kind of a molecule that would be there, but of course you can keep changing, add a nitro or a chloro or all kinds of things can be added, we can see there is anhydride on this side, and there is anhydride on this side, so interesting type of a chemistry perylene, so you have

tetracarboxylic acid, carboxylic 1, carboxylic 2, one on hydride carboxylic 3, carboxylic 4, another anhydride.

(Refer Slide Time: 43:00)

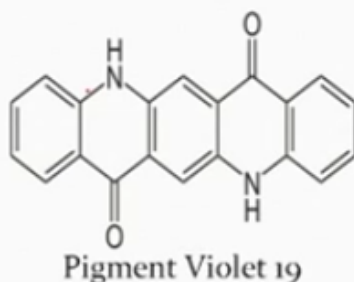
The slide features a decorative blue and white wavy header. The main title is "Quinacridone.....family" in a large, dark blue font. Below the title, the text "yellowish red to violet" is displayed in a smaller, dark grey font. At the bottom left, there is a circular logo for NPTEL (National Programme on Technology Enhanced Learning) with a star-like symbol inside. At the bottom center, the text "kushalsen iitd" is visible in a small, light blue font.

So quinacridone group of things gives generally yellowish red to violet kind of shades they can give, and this is an interesting molecule, you're quite a familiar anthraquinone and so on and so forth, but it's slightly different chemistry, so you have almost 5 aromatic rings connected together,

(Refer Slide Time: 43:25)

# Quinacridone.....family

yellowish red to violet



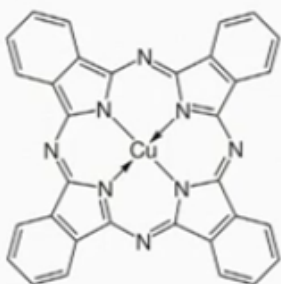
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and of course there is this own part of it, so you have a carbonyl group which makes this acridone, and so you have large number of pigments based on this as well.

And you know pigments are not just use for textiles, they're used for paints, plastics, everything, so one of the advantage sometime is that you can go for little high temperature like a molten material and you can add it nothing will happen to this stability, if you have like a dispersed dye you want to use and let us say molten polyester, at that temperature you might find all subliming, you know, so it's not easy to get to that type of situation, so one always has to choose things, so pigments are from this kind of range as well.

(Refer Slide Time: 44:40)

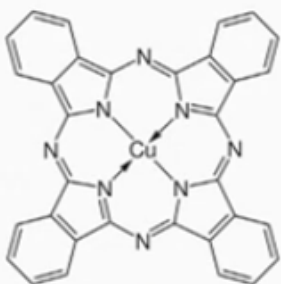
# Halogenated copper phthalocyanine



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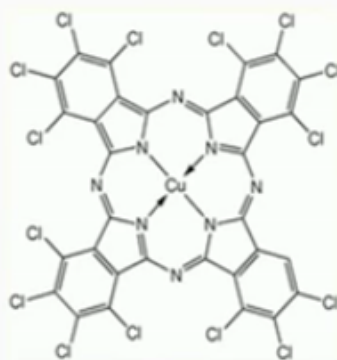
So this one interesting compound, this you must have seen this is the copper phthalocyanine alright, beautiful blue it gives, almost across and so this type of shade is not very easy to obtain, and so this can be used as a pigment, there are no solubilizing group here, there is nothing there you can use this as a pigment, but if you add chlorine all over, look how many chlorines have been added, so only at one portion it appears there is no chlorine, everywhere there is chlorine, (Refer Slide Time: 45:19)

# Halogenated copper phthalocyanine



Blue

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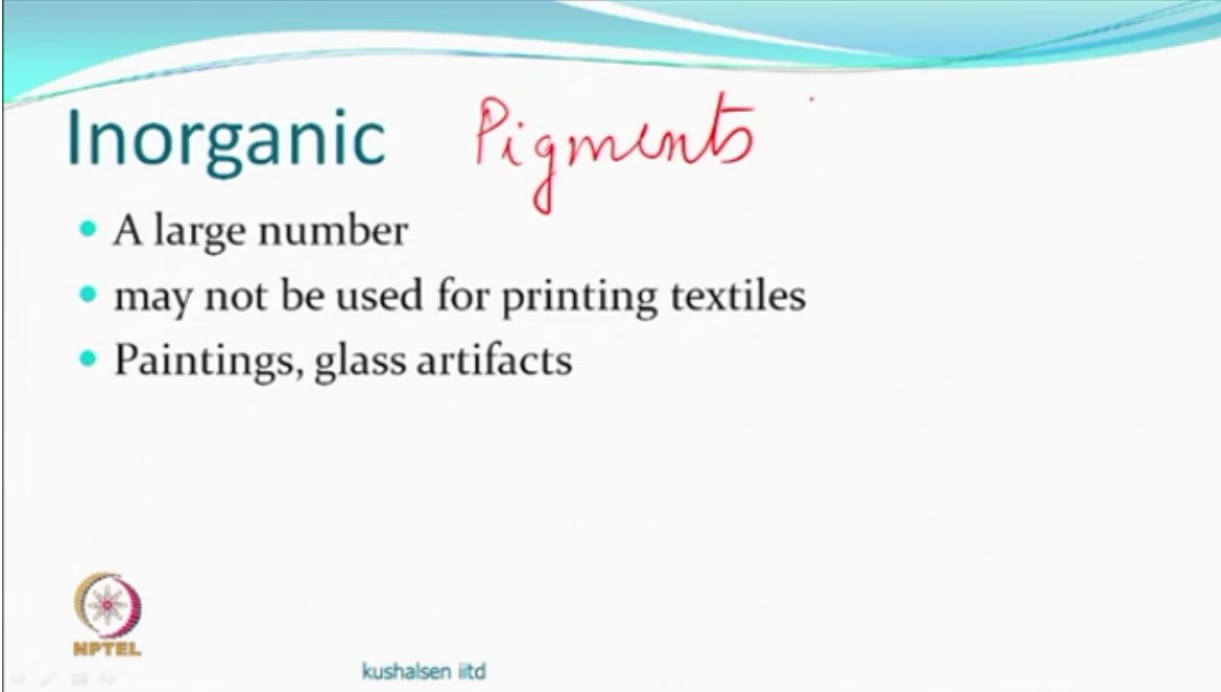


Pigment green 7

until somebody says you can't use chlorine compound because they are not environmental friendly, so you may not use it but it gives green you know from blue to green, similar


compound just a change in a beautiful green it gives, and there are large number of inorganic pigments also,


(Refer Slide Time: 45:51)



**Inorganic Pigments**

- A large number
- may not be used for printing textiles
- Paintings, glass artifacts

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some of them can be used for textile printing also, but generally they are used for paints, ceramics, glass, and high temperature resistant so we can confuse them melt the glass and insert them various techniques people use, all the churches, old churches that you see all the coloured glasses all over the place, so inorganic compounds are used the maximum and thing and ceramic until support.

(Refer Slide Time: 46:21)

# Pigment emulsions



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particle size 0.03–0.5  $\mu\text{m}$

So pigment are not generally sold as powders, dyes are available in powders, so example then you dissolve them with a wetting agent and make a paste and do everything else, and here because this process maybe little difficult, and so the chemical manufacturers are supplying emulsions.

The particle size we can see is quite small, right, 0.03 to 0.5 micrometers, okay, so it's the micron isn't it, what is the diameter of fibre? A normal textile fibre approximate, generally a polyester fibre available, approximate diameter, rough don't have to be exact because all diameters are different, in terms of microns, 50 microns quite course fibre like wool, but polyesters could be 10 microns and so on and so forth, so what is important is the size of this particle has to be less than you know that, although you don't looking at any diffusion, the particle filters diffuse, but this is the large particle, first of all the rubbing fastness will be a problem you will see something sticking on the fabric, this will or actually we seen as if something extra is there, naked eye will not be able to see the particle, and you don't want to see actually see there are lot of particles here, so it will look like this very uniformly printed system.

(Refer Slide Time: 48:25)



# Pigment emulsions

- Are aqueous pigment pastes, the dispersion medium is water.



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particle size 0.03–0.5  $\mu\text{m}$

So as I said aqueous pigment pastes, dispersion medium generally is obviously water, very easy to evaporate later after the whole process has been done. Surfactants which are used generally would have an HLB,  
(Refer Slide Time: 48:40)

# Pigment emulsions

- Are aqueous pigment pastes, the dispersion medium is water.
- The surfactants used must have an HLB value  $>10$



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particle size 0.03–0.5  $\mu\text{m}$

you understand HLB? Hydrophilic lipophilic balance of a molecule should be over 10, normally nonionic dispersing agents are used for making emulsion,  
(Refer Slide Time: 48:58)

# Pigment emulsions

- Are aqueous pigment pastes, the dispersion medium is water.
- The surfactants used must have an HLB value  $>10$
- Nonionic dispersing agents based on ethylene oxide condensates with C<sub>12</sub> to C<sub>20</sub> alcohols are commonly used.



particle size 0.03–0.5  $\mu\text{m}$

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they're based on ethylene oxide condensates with various alcohol series which could be there, so this is what actually makes it, you know the balance from this carbon and the oxygen or ethylene oxide groups, so their balancing has to be done.

(Refer Slide Time: 49:33)

# Pigment emulsions

- Are aqueous pigment pastes, the dispersion medium is water.
- The surfactants used must have an HLB value  $>10$
- Nonionic dispersing agents based on ethylene oxide condensates with C<sub>12</sub> to C<sub>20</sub> alcohols are commonly used.
- About 20% pigment dispersions.



particle size 0.03–0.5  $\mu\text{m}$

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Generally available as 20% solids, okay, so rest is whatever water many, so this HLB in some way or the other has to be balanced, so HLB value of nonionic surfactants,

(Refer Slide Time: 49:53)

## HLB value...

Griffin's scale for non-ionic surfactants is from 0-20



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Griffin had defined the range from 0 to 20, there are other ways of measuring HLB also, but this is one of the ways, so 0 to 20, 0 is more lipophilic obviously, and 20 is very hydrophilic, and what it means is Calvin calculated 20 multiplied by MH/M, (Refer Slide Time: 50:20)

## HLB value...

Griffin's scale for non-ionic surfactants is from 0-20

HLB value can be calculated as  
 $20 \times (M_h / M)$



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and what are these? MH is the molecular mass of the hydrophilic portion, (Refer Slide Time: 50:28)

## HLB value...

Griffin's scale for non-ionic surfactants is from 0-20

HLB value can be calculated as  $20 \times (M_h / M)$

where  $M_h$ , is the molecular mass of the hydrophilic portion of the molecule, and  $M$  is the molecular mass of the whole molecule



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and  $M$  is the molecular mass of the whole molecule, so the ratio of this multiplied by 20, so you ethylene oxide you will control, the hydrophobic part you will control as the mass is concerned and the balance you have to keep, so less than 10 if it is there, (Refer Slide Time: 50:55)

## HLB value...

Griffin's scale for non-ionic surfactants is from 0-20

HLB value can be calculated as  $20 \times (M_h / M)$

where  $M_h$ , is the molecular mass of the hydrophilic portion of the molecule, and  $M$  is the molecular mass of the whole molecule



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<10 : Lipid-soluble  
>10 : Water-soluble

they are lipid soluble that is they have soluble in oil and so on and so forth, more soluble and there is more than 10 they are more water soluble, so obviously you will be using for our purposes water soluble, surface active agents, okay.

(Refer Slide Time: 51:22)

## Binders role....

- Pigment printing



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So binder, it is required because pigment does not have any affinity for fibre, therefore we said blends also no problem, binary or ternary whichever blend that you want you can use them, and so required a binder, it is the binder which is more important as far as this is concerned, colour of course comes from there.

(Refer Slide Time: 51:44)

## Binders

Are addition polymers, preferably copolymers;

Synthesized using emulsion co-polymerisation,

Are sold as 40-45% binder dispersion in water

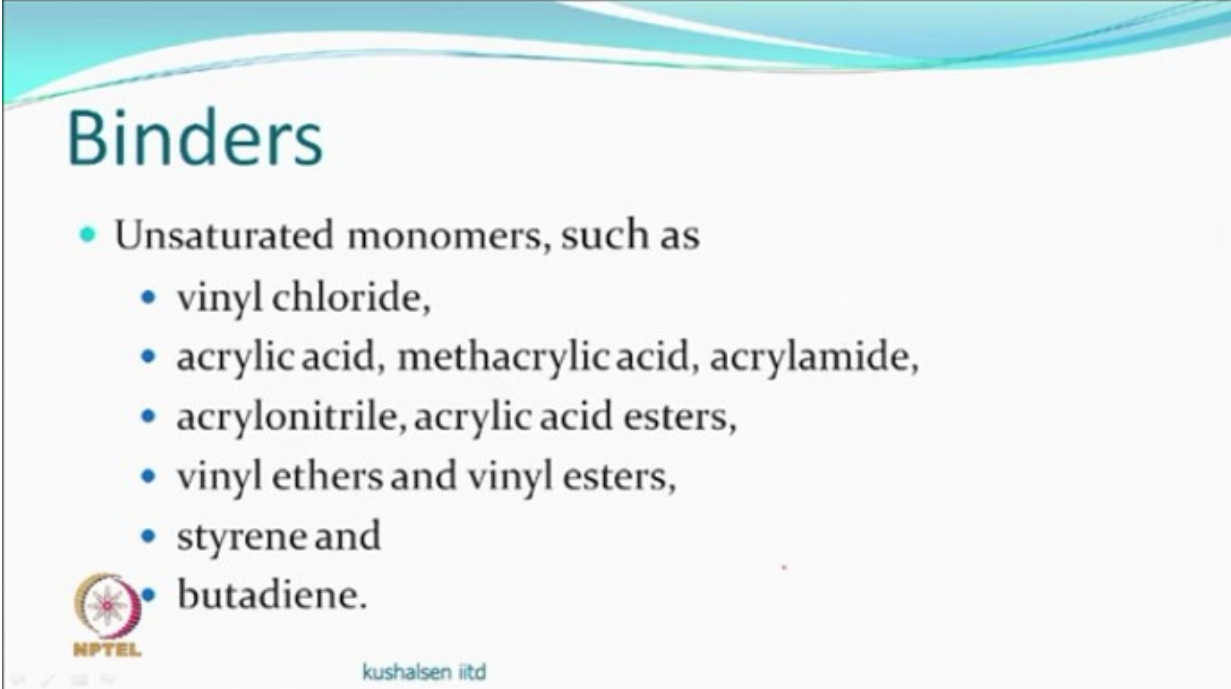


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And these binders are also polymeric substances or they are pre-polymer which can be polymerized during curing, so you have a pad dry cure sequence, pad print cure sequence, not pad actually sorry print dry and cure, so a print dry cure sequence so the curing, during curing

the reaction and polymerization will take place, so you will have obviously some catalyst there to help it out, and are also sold as dispersions, so you have a pigment dispersion, you have a binder dispersion they can all be mixed very easily and then you got to have a thickener, (Refer Slide Time: 52:39)



The slide features a light blue header with a wavy pattern. The title 'Binders' is in a large, dark blue font. Below it is a bulleted list of monomers. At the bottom left is the NPTEL logo, and at the bottom center is the text 'kushalsen iitd'.

## Binders

- Unsaturated monomers, such as
  - vinyl chloride,
  - acrylic acid, methacrylic acid, acrylamide,
  - acrylonitrile, acrylic acid esters,
  - vinyl ethers and vinyl esters,
  - styrene and
  - butadiene.

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so some of the monomers that are used for making binders are vinyl chloride, okay, so unsaturated acrylic based, acrylonitrile based and vinyl ether, styrene, butadiene, these kind of monomers can be used along with each other or otherwise to get to some binders which will give relatively more softer film, and be in the glass transition temperature of the binder film should be very low of the glass transition high, it will become stiffer if the glass transition temperature is low, so that's the calculations that you have to do, that's the manipulation that you have to do, the binder manufacturers, the printer doesn't do anything, we just uses them, that obviously there is a chemistry involved, so part of the chemistry is not bad idea to recall.

So today we stop here, we've learnt something about dyes and pigments that can be used for printing textiles, different kinds, (Refer Slide Time: 54:00)

# We have learnt about

- Dyes and pigments for printing



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next time we will see whether we talk more about thickening agents and things and before we take some other topic. Thank you.

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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