

Lecture – 06

Discharge and resist printing

AlRight?. We start today with a new topic. But, let's say before what have you done

Refer Slide Time :(0: 30)

A step back..

- We have learnt
 - Rheology of printing pastes
 - Determination of viscosity of printing pastes by
 - Rotational viscometers
 - Ball fall method

Last time we talked about the rheology of printing pastes, which means they are shear thinning and they have a texture tropic, property that which the viscosity reduces, with shear but, is the reversible process and can come back, when the shear forces are removed and some methods of measuring viscosity of printing paste, rotational viscometer, is like blue field or a ball fall method and the principles, involved in the ball fall method, we will just spend some time, today on discharge and resist printing principles; we're not going to be going into recipes and so on. So, forth just some of the principles so, that helps you to, formulate, the strategy for doing a discharge printing or a resist bending.

Refer Slide Time :(1: 35)

Principle

- Direct printing with discharge paste on pre-dyed fabric
- White discharge
- Colour discharge with illuminating colours
- Oxidize or reduce ?

Let's take the charge first. So, the principle is direct printing with discharge paste on a pre dyed fabric. So, the color on the fabric, is called the, 'Ground Color' and the ground color is to be discharged, the dyeing can be done, in any method, by any method whether it's an exhaust process

or a pad dry process whatever, you can use any method for dyeing is concerned. So, you can have white discharge, in which case your discharge paste has, obviously discharging agent and maybe it is, supported by some other, inorganic systems compounds like zinc oxide, EIU or what have you, you can add them, if you look at, the color discharge is also possible. But, then you have two different types of dyes, one which is dischargeable dye, which is on the fabric and another color, which is called the illuminating color, can be added, to the discharge bed which is more resistant, to discharge. Right? The other principle. So, the discharging agent, should it be, an oxidizing agent or should it be a reducing agent, because we are quite, familiar with bleaching agents, which can in any different, different conditions can remove colors, that is how we work it out and reducing agents are the one which will act on a chromophore, also to, do the reduction.

Refer Slide Time :(3: 42)

Vat dischargeable

- Oxidation of indigo dye by nitric acid and chromic acid can give isatin, an indole derivative.

Indigo → oxidation → Isatin

- Difficulties?

So, let us see, if suppose we have dye, which is dischargeable, what it means is? That a dye for example, like an indigo, can get converted to, the compound with called, 'Isatin' which is an indole derivative. Now you can see that, the dye is now, not exactly, the way it looked before and there is very difficult, chance of it to going back, to the indigo, structure. So, if you can do that? You have no issues but, there may be some difficulties, he like it says that you're going to be using something like nitric acid and chromic acid, which can give this compound or suppose tomorrow, you decide to use another bleaching, agent like, hydrogen peroxide or nitrite, it's possible, that you can get this. So, what are the difficulties? The difficulties will be that you cannot guarantee that the fabric is not going to be damaged. So, that is one major problem, if you want to do, go by the oxidation route. So, although if we logically, look oxidation could have been a better route, because when you after discharge printing you leave the garments in whichever way they want, the general environment is an oxidizing environment. So, you don't have any danger, of it getting back to its original color. But if you go by a reduction route and let's say, some interesting things happen, then they can go back to the oxidized state, because there is an oxidization, possible in this environment and you

know that the red dyes, are generally oxidized in air also, you can oxidize chemically also, but you oxidize in air as well and so, theoretically speaking, by reducing a dye, there may be a possibility, of it's coming back, during use, may not be exactly in the same quantities, but a white starts becoming greenish, yellowish, with time you may not like it. Alright? So, but still, we prefer reduction of the process.

Refer Slide Time :(6: 50)

Leucoindigo

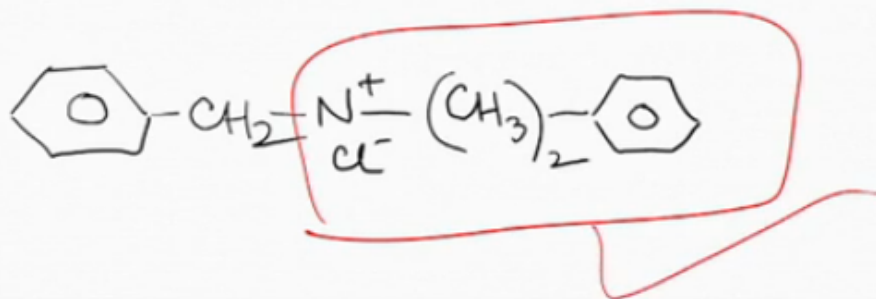
- Reduction of indigo gives Leucoindigo
- It can get oxidized
- So?

The diagram illustrates the chemical transformation of indigo into leucoindigo. On the left is the structure of indigo, a blue dye consisting of two indole rings connected at their 2-positions. On the right is the structure of leucoindigo, where the two carbonyl groups of indigo have been reduced to secondary amine groups. A red arrow labeled 'reduction' points from the indigo structure to the leucoindigo structure. In the leucoindigo structure, the oxygen atoms of the former carbonyl groups are circled in red. A red arrow points from these circled oxygen atoms back towards the indigo structure, suggesting the potential for oxidation back to the original dye.

Let's see, if the same died that means the indigo, is reduced. So, we know that, you can make a leuco die. Now, this Luco die, theoretically has every, at every opportunity, it can, go back to this structure. So, this difficulty remains. So, what do we do? Some suggestions could be that if this thing can be oxidized, then what can we do? So that's one important part.

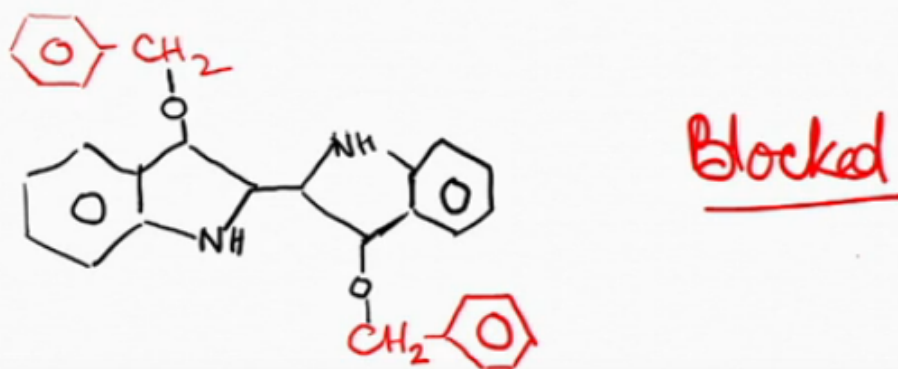
Refer Slide Time :(7: 31)

Blocking agent



So, we can have, application of something called a, 'Blocking Agent' and this blocking agent has got two part, it's a nitrogenous compound. So, you can say it got a plus charge here and another part which is the cs_2 Phenylene compound. So, in some ways, if you can break this type of a compound, which is in some sense ionic and can, break and react and if it reacts with, if it is, if it react with, some of these groups. Then it will be difficult for this die to get oxidized and go back to this.

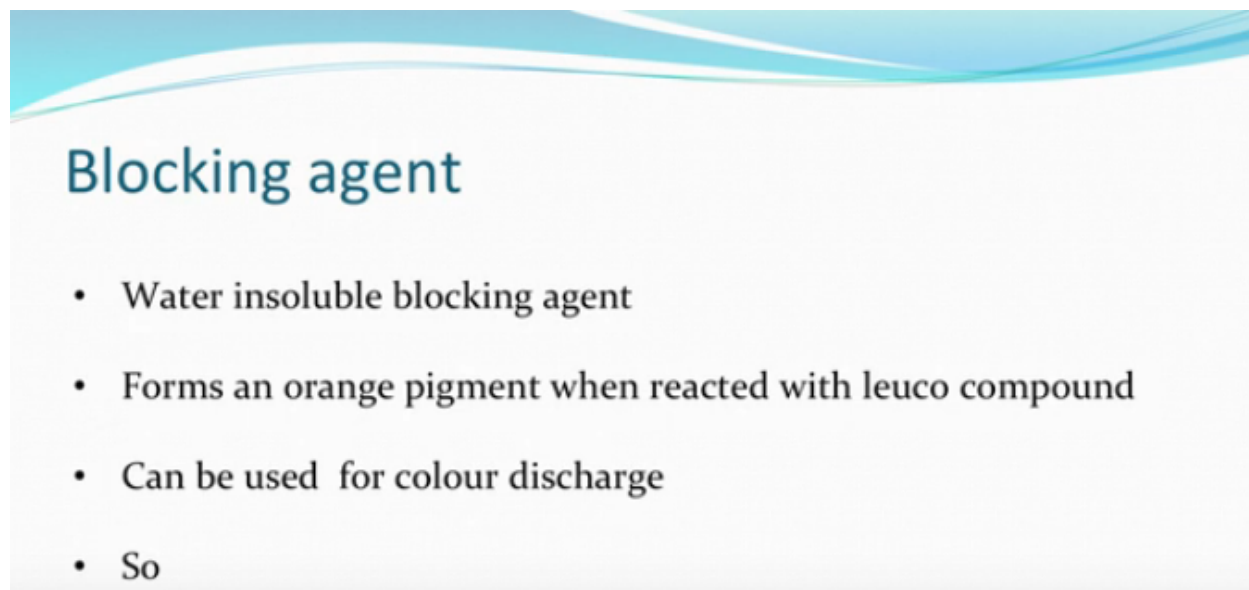
Refer Slide Time :(8: 24)



So, a reaction of this type is possible and so, the other part of the compound would go out. Right? So, you can go by a reduction route, on a wet kind of a molecule, which could be indigoid or Anthraquinoned, possible but then, you have to block, one important thing which also, one has to realize is, that the compound that you are getting, does it have a color or does not have a color.

Al right? So, if we say that we, first of all you must remember also, that this indigo dye, when it is reduced, becomes a very pale color. But some of the Anthraquinoned dyes, will be also deeply colored, they may not be that pale. So, one thing remains is, does it go back to its original position or it also has a color left out, at the end reduction, in such a case you would be more interested in removing the dye. Right?

Refer Slide Time :(9: 46)



Blocking agent

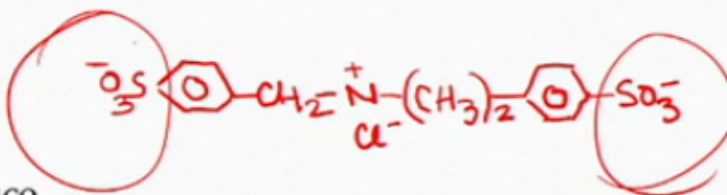
- Water insoluble blocking agent
- Forms an orange pigment when reacted with leuco compound
- Can be used for colour discharge
- So

So, this particular blocking agent was a water insoluble compound. Right? By itself also, it makes some kind of an orange pigment, when it reacts with the leuco part of the dye, the leuco dye. So, you have a issue, unless and until, you say well, we are actually going for a color discharge. So, not too much of a problem. But, if you want a white discharge, then there can be a problem. So, original color maybe whatever, let's say it was a blue in the case of indigo, but after reacting with this kind of a blocking agent, you may get some, yellowish, orange compound which may also be sticking there and so, if you are going in, for a color discharge then you can say well, this is the kind of color I'll get. But if not and if you are interested in white,

Refer Slide Time :(10: 51)

Blocking agent

- One can design a water soluble blocking agent
- Reacts with the leuco compound to form an alkali soluble orange pigment.



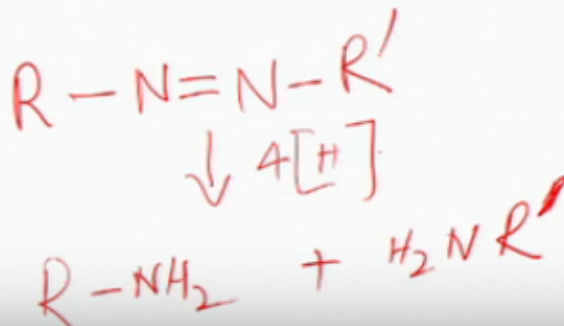
Zinc oxide, if present,
can give better whites

Then we can probably use the same compound. But also, add some group like this, which we'll be able to solubilize, the pigment. So, it is the same compound but, if you had a solubilizing group, then whatever forms, can be washed off. So, this is an alkali soluble pigment and so it can be then, washed in alkaline conditions and you can, remove this and if you add other inorganic compounds, like zinc oxide, in the discharge paste, they can get better whites, which normally people may be doing. All right? So, you have a blocking agent required. So, that the chances of the dye, if it remains going back, to its original form, is restricted, if you add a solubilizing group, you can wash it off also. So, that's one part, that is it otherwise it was a water insoluble compound which is difficult to do.

Refer Slide Time : (12: 18)

General wisdom..

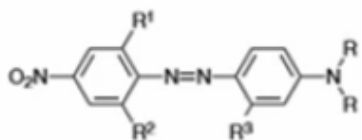
Use azo based dyes



So, what is the general wisdom? General wisdom, when people talk about discharge printing, that use azo, based dyes rather than indigo, ID or Anthraquinone based dyes for discharging. So, that's general it's not that they're they cannot be used, you can use it, but that making life more difficult. Because if this type, if this type of a azo dye. Is with us, then this can be reduced, let's say, in a reduction environment and you will get a means and you can appreciate that combining, these two amines back and making this, is a very difficult process. All right? So, if you are using azo based dyes and using a reduction environment, then it will be very, difficult for somebody, to just oxidize it, in a manner that it actually goes and makes and as a group, for making it as a group, what you require? Is a whole desertization and then coupling with an apple, then only you can get back to that? So, if you haven't azo dyes, you have easy, way to discharge and absolutely a confident way of looking that it's not going to go back to its own structure and so, you will never get back the original color. So, it we just think, if it can be washed very good, even if it cannot be washed it would still not give you a problem. Right? That means the basic chromophore has been destroyed, if it's a mono azo dye, then one will be destroyed if is, a you know? This is mono or multiple you know? As the groups are there, all of them get destroyed there is nothing like it and it becomes a smaller molecule converted off also. And the discharging or discharge ability, of this group is, much higher and that means, if you want to use, a color discharge, then you can use the other groups, which are not easily dischargeable and then together, they'll get you. So, as our base dyes are the best, as far as the, discharge printing is concerned,

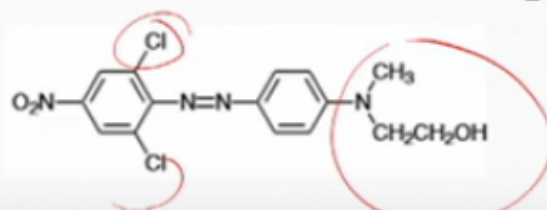
Refer Slide Time :(15: 27)

Azo based.....



**General
structure**

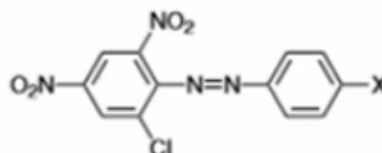
Dischargeability



Some example, so like the structure we make. So, what around the other group they are could be aromatic and if it is, an aromatic group, there can be many other, possibilities, at the orthopositions, on a paraposition, of combination, of various kinds of groups, which could be larger groups, like a group of this type, large group or a small group, here also you can have any type of group. But, for example, if a group like this where, you have two chlorines, at the orthopositions, it has been seen that the discharge ability of such nepeta is dye, high and so, that means people will talking about making a molecule of one type or the other and checkup which is dischargeable, more dischargeable or less dischargeable, the one which is discharge ability, of let's say, on a one to five scale five, that generally very good for the ground, maybe four to five also can work for the ground, but if the discharge ability is towards, two or one, then you can use, those type of dyes, as eliminating colors. Right?

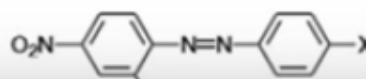
Refer Slide Time :(16: 52)

- Two nitro groups make it difficult to discharge



- These dyes belong to which class?

Dispers

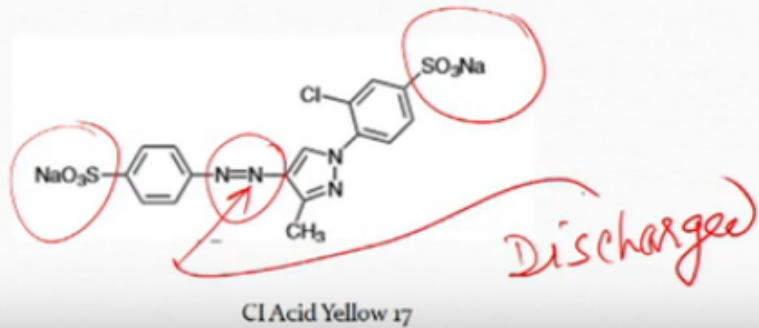


In this case the difference between, from the previous one is that there is, there are two nitro groups, in one and one nitro group in the other, there is one halogen, chlorine. So, between the two dyes, which one do you think is going to be more dischargeable, if there are two nitro groups, it becomes more difficult, to discharge despite one halogen? So, it's a relative, a bit of a steric, conditions also are created here? And so, this dye compared to this structure, will be more dischargeable, these dyes if somebody won't know, which kind class? They belong to, direct, reactive he said, disperse, there is no anionic group here, there is no reactive group here and so, if the X, is another nitro, another ch₂, another ch₃. So, this will be more, close to disperse dyes.

Refer Slide Time :(18: 20)

Azo - acid

Dischargeable acid dye

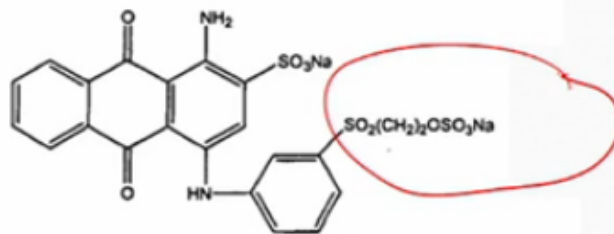


So, if a similar thing has to have you know? Has to be an AC die, for let's say, nylon or wool or silk, in this case, you would be adding, such groups. So, if you can add, such groups, then you can think, of and I said die. But it still has, the most important chromophore, as Oh which can be discharged.

Refer Slide Time :(19: 08)

Dischargeable - Reactive

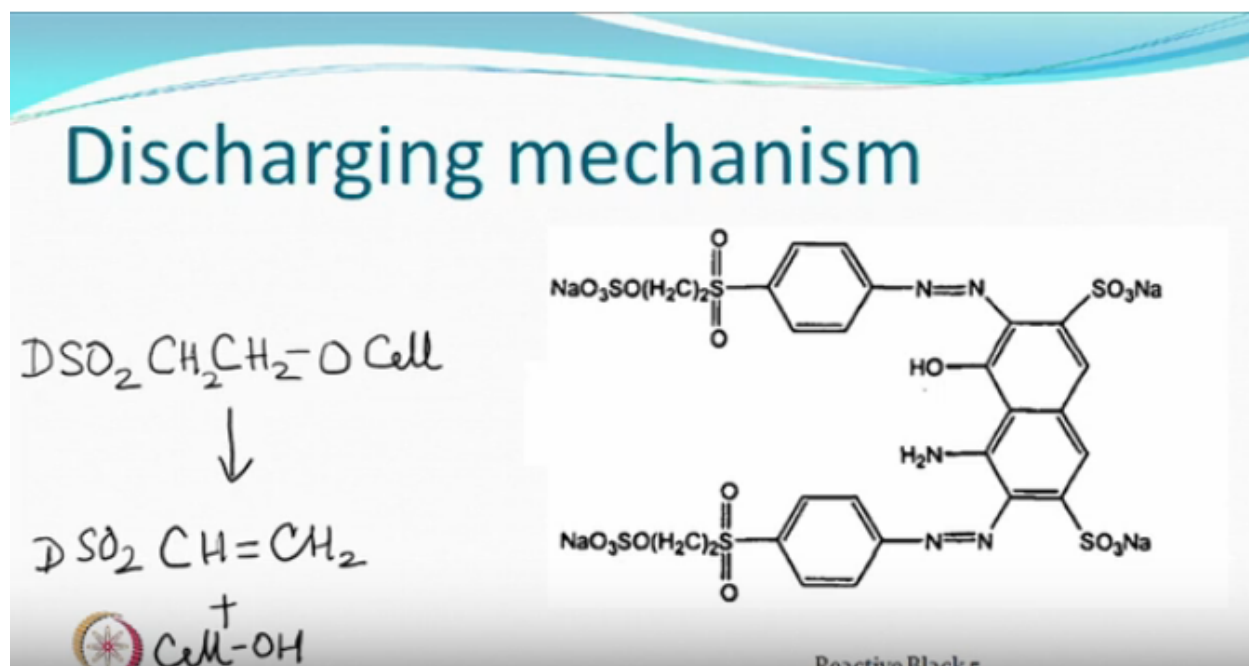
- Vinyl sulphone based



So, this is some, interesting lesson that we have when we talk about, dischargeable reactives, generally, as a groups may not be found in most of the reactor dies. But, if there is an as a Groupaz, you can break that but, from the reactive group point of view, people prefer vinyl, cell phone based reactive dyes. Because if, there is no, Azogroup like in this type, there is no Azogroup, it's a reactive blue, if suppose

this group reactive group was Procyon, you had difficulty, but if it is a vinyl cell phone, this reactive group linkage with the cellulose can be broken. So, that I can just be washed off. Right? And therefore on the ground people will like to use vinyl, cell phone based dyes, because the dye otherwise reactive, tomorrow if somebody wants to know, a reactive dye, dyed fabric is there with you, but you don't know, whether it's an azo group, or it's a, Anthroconannoyed group and somebody wants to do a simple example experiment, to determine, which died, which group, which chromophore, is present, then what you do? It's a reactive group, reactive die and you are looking at, which whether Anthraquinoned based or an Azo based, dies there think about it.

Refer Slide Time :(21: 07)

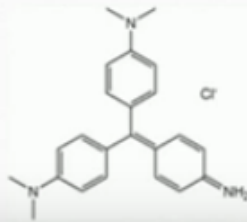


So, this is an example, of the reactive die, with an azo group and this is also by functional, reactive die. So, theoretically, it is possible, that you can have a breakdown here. So, in case instead of Vinyl cell phone group, you had, a tri chlorotriazine, dichloro or a mono chlorotriazine, it can still be reduced. Right? But, if this is the type of a die, then this type of mechanism is available with you. Okay? So, people will prefer Vinyl cell phone based crime. So, there's a bi functional die, but again bi functional when I cell phone die, it may have as a group, may not have as a group. So, if it has another group it's. Okay? So, the both the mechanisms are available. So, that I can be destroyed, in the other case the reactive group can be broken and then you can still have, clear discharging possibilities.

Refer Slide Time :(22: 18)

Discharge-resistant dyes

- Are not azo dyes ✗
- Could be based on
 - Anthraquinonoid
 - Phthalocyanine
 - Triphenylmethane



On the other hand, if you look at the discharge resistant dyes, they definitely should not be Azo, do not be Azo, that's one. But, they can be Anthraquinonoid, phthalocyanine, triphenylmethane which are could be cationic dyes, based on what fabric, by combination we are using, some of the structures, can be of this type. So, they'll be discharge resistant, that's.

Refer Slide Time :(22: 57)

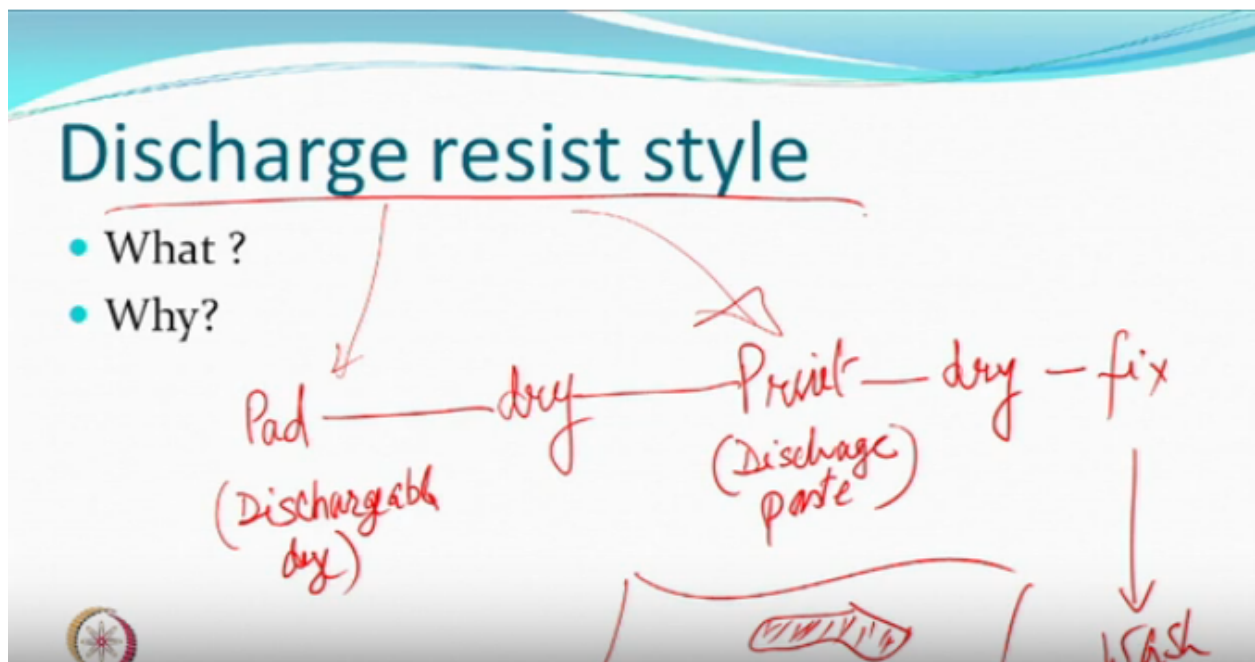
Reducing agents

- Sulphoxylate formaldehyde based (stabilized)
- Thiourea dioxide
- Stannous chloride

Among the reducing agents, we've been using for the we're dyeing for example, self oxalate formerly hide based, raging, reactivation reducing agents. But, they have to be for printing, they have to be stabilized. So, they could be instead of sodium salt,

they could be zinc salt, some people talked about calcium salt, salt or Birds zinc is, popular. So, therefore we some stabilized, because during this paste which is going to be stored for a long time, the reaction should not take place, this reaction should take place only, when you are doing fixation, I'm going for steaming or baking, where this, must act, in steaming conditions, an important thing also happens is, that the whole environment, around that can also become the reducing environment. So, the ground where you do not want the discharge to take place around that also something can happen. So, people sometimes use, mild reducing, mild oxidizing agent. Al right? A resist salt, have you heard of that? So, you may use a resist salt to, counter the general reducing environment and make sure the other colors are not affected, in some cases people use diarrhea dioxide also, in some protein, silk discharge printing you may, like to use tennis chloride, also. So, one has to do, the discharge printing with little more care, whenever you're using protein fibers. But you can do, this synthetic fibers also, like polyester for example, you want to discharge, it's not easy to discharge, the most of our agents are working in Equsmedium and polyester, being polyester and I goes, inside and then reducing agent can work on the surface, but difficult for it to penetrate so much and so, the results, normally are not so good, you can't compare them and generally, be all hydrophilic fibers cotton viscose, silk nylon, their results are better and polyester is difficult.

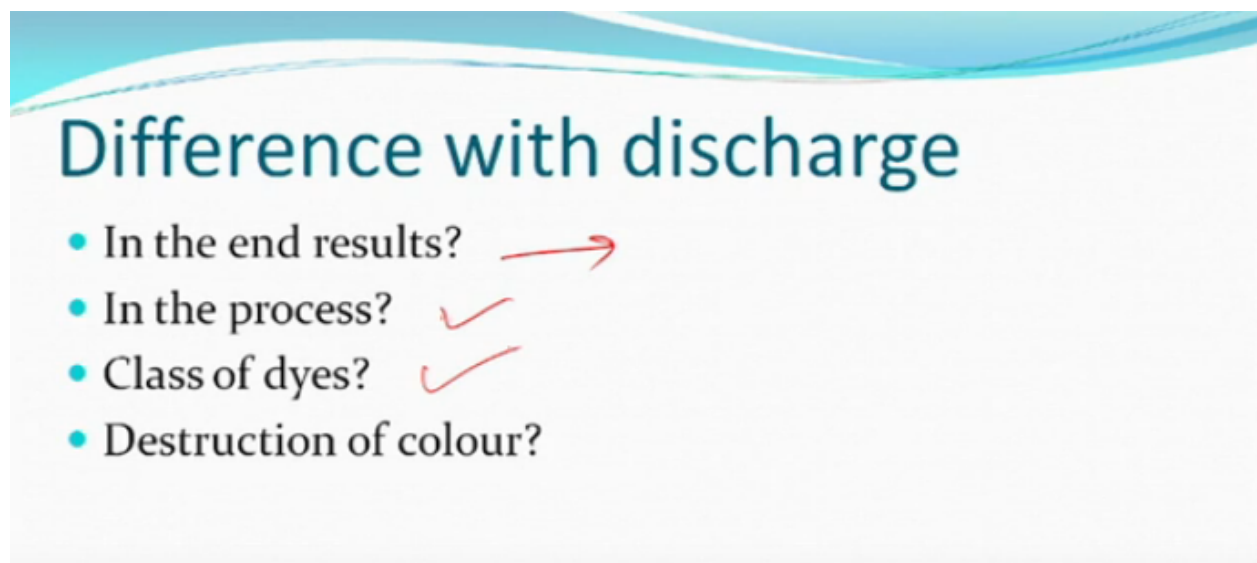
Refer Slide Time :(25: 41)



So, there's another style which is, typical for hydrophobic fibers, which is called a, 'Discharge Resist Style'. What it means basically is that, the fabric has not been dyed and fixed. So, in the earlier case what we said, that you can die, either by exhaust method or you can die

by pad cure method, pad thermo soul method and then want to do this, let's say you do pad thermo sole for polyester and wanted to discharge, it is tough. So, one of the things with people I said is, do not fix the die, that you can pad, the fabric, with whatever dye that you want on the ground, dry it and then print dry fix. So, you pad, with dischargeable, paired with dischargeable dye, then dry, just dry, not fix, then print, discharge paste, then dry and then fix and of course you will wash. Now, what happens is? That because it has not been fixed and there is a discharged paste which means is about discharging agent. So, it is like a resist, not allowing it the dye to be there, but they resist, because of this and the discharge because the color is all over, which is being discharged. Al right? So, even if there is a color, here at this point, where you have put a paste, this is the design, where there is a discharge paste, here the dye, is going to be discharged, before it has been fixed. So, that is how people have handled, the difficulty levels in the polyester. So, you don't allow, the dye to diffuse at all so much, before the dye is diffuse it has not diffused here. So, during the fixation process the one, which is here, will get discharged anyway and will become a different kind of product, maybe and then it will not be, more it can be washed and you can remove that and so, we call this as a, 'Discharge Resist Style of Printing'. Right? So, it's an interesting style, they've got combination both. So, something on resist printing, gained just little principles.

Refer Slide Time :(29: 17)



Difference with discharge

- In the end results? →
- In the process? ✓
- Class of dyes? ✓
- Destruction of colour?

How, is it different is it in the end results? The end results in some cases may be different. But, most of it, it may be similar. Because in this case the advantage that you have, that you are not allowing the fixation, to take place. So, that way a finer prints, fine lines etcetera, you can do, with the resist printing, in the process of course there is the difference? You have printing and then you know? Putting the dye all over, some advantage people may think here is, because if you have a discharge printing in a very dark color, the discharge paste, almost is colorless and if you have a color discharge kind of

environment or otherwise you're trying to make different designs and different portions sometimes very, difficult to locate where the actual print is and if the machine is running at a fast speed, if there is some fault cycling somewhere, it difficult to say whether. Right? Printing has occurred or not, in this case that is not there, it's just like, first you are printing, on a white ground, if you are printing on a white ground, even a light pale thing is visible, then a light pale color is not visible on a diagram. So, sometimes they have difficulty in putting one design over the top the other, well that's it the process obviously is different, first print and then, put the whole thing called, 'Dye' dischargeable dyed. Is it different in the class of dyes, actually no, all the dyes can be used for discharge, printing can be used for resist printing as well, some of things which resist can do, discharge could not have done, here also whether you will like, destruction of color or not would depend on what method you are using? In the other case you had to, do something, to destroy the color, here you can have some possibilities or without destroying the color, you can get the effect.

Refer Slide Time :(31: 50)



Resisting agent

- Mechanical
 - Waxes, fats, fillers / pigments (china clay, TiO₂)
- Chemical
 - Acids, alkalis, oxidizing and reducing agents
- Both

And that's what basically we are looking so, there is a possibility, of a mechanical resist, process where you are not allowing, it to penetrate and therefore it will, not go to the fiber, other obviously is chemical where, if discharge is required, it can be done or you may not allow it to get fixed, if a particular dye, requires alkaline medium, then in a discharge paste you can have an acid and so, you've done nothing, to the dye. But, still cannot go in, if it requires, a reducing environment, to get diffused and finally put an oxidizing environment there and why super self. Al right? And theoretically therefore in this sense, this will be differently without, destroying the dye also you can get a color or a design, of one kind or the other. But, if it is required to be, the storage they will destroy it also, some things that you are, quite familiar with, happen to be tie-,dye and but a kind of things, which have mechanical resist and beautiful effects, are obtained by these processes.

Refer Slide Time :(33: 13)

Fundamentally

Ground	Chemical resist*
Reactive	Acids
Vats	Oxidizing agents
Oxidation colours	Reducing agents
Azoics	?



* Often mechanical resist may be a part for example TiO_2 , ZnO_2 , clay

So, If the ground is reactive, then you can use acid, in the discharge, if you have that, type of environment, then you have oxidizing agent, if oxidation colors, then you have reducing agents, if you have Azo's not Azo, then what you do? So, it's slightly more complex, because you may have, padded your fabric, with Nepal and then added digitizing, diazonium salt or a stabilized diazonium salt. Al right? So, what we do? Not so difficult, think about it. Al right? Think about it. So, if you want, to use mechanical resist along with it, no problem, it'll also particularly when you want to get more white, then you may actually have the work whitening agents of this kind also, as part of the resist paste.

Refer Slide Time :(34: 30)

Thickener

- High solids , e.g. British gum

Again, in case of let's say a pigment printing you wanted low solids,

very low solids. So, that you know? It doesn't get retained in the film. But, here we want this material also, to be acting like a resist, in some way. So, because the dye is going to be on top of this, diffusion should be made as difficult as possible. So, people say well high solid type of thickeners, could be good of better results on the, resist printing.

Refer Slide Time :(35: 09)

Dyeing –ground colouration

- Exhaust dyeing? X
- Dip-nip padding? X
- Nip padding? ✓
- Over printing?

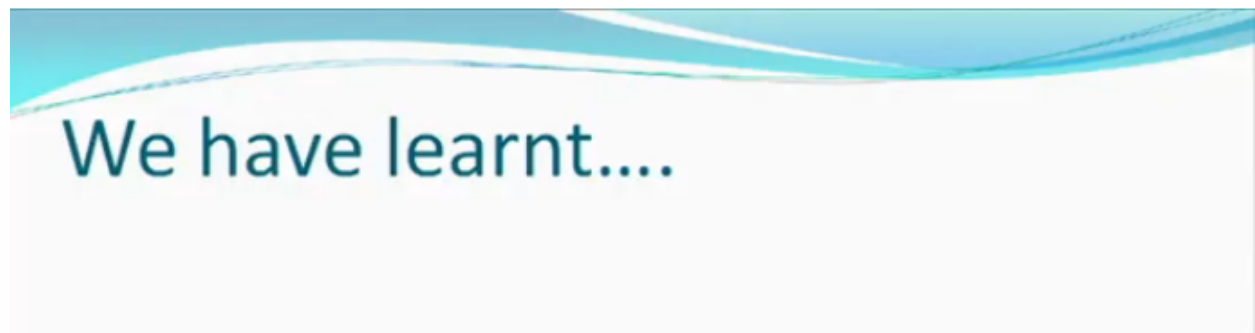
After Printing

Print → drying → dry → fix

Finally, we have done the printing and after that we have to do the dyeing, which dyeing method, would we like to use, after printing. Right? This is after printing. So, we have done the printing, drying and then, we have to put the dye, first of all do you understand all these methods. Right? Exhaust dyeing you understand? So, would you like to do exhaust dyeing, after printing. So, this is not the method which can be used, dip nip padding can use? No so, this also cannot be used, nip padding, what is the nip padding? So, the fabric is not dipping. But, it's just in the nip for example, you can have one roller, another roller and the roller may be dipping, you can have a, it's like, kiss roll technique and then the fabric goes like this, a printed fabric and then, whatever dye that you want to put, is goes onto the fabric and then you for dry and fix that's, nip padding. So, dye is still in solution. Right? So, you can use whatever you want to use? The other method is over printing. So, this can be used, deep loose over printing is, that means if you have a roller printing machine, then after printing, the final color, which is a dischargeable paste, is being put, on the surface, by a roller which has engraving all over or if you are going for a screen printing, then you have a blank screen, with which you can print and this would mean, that the first print, will not be destroyed, that means theoretically, you print, the design, follow it in a rotary print by a blank, print and then just go through and you will get something interesting, after drying and fixing. So, to get the best results, over printing is the technique, in the resist system,

exhaust means there is going to be agitation in solution, while you have just printed and you just dried in you're hoping that the print whichever the print remains in the position, in which the design is and if you, find that this leaves its place and goes everywhere else, then there is a problem. Similarly you're talking about dip. So, you actually go through the solution, in the dip situation you have, padding Mangle kind of a process. So, the fabric which has been printed, can go like this or any threading sequins. Now, in such case the dipping in a solution, you may not like it, because we are too much of solution and it becomes softer the printed portion also becomes softer and wet, then in this squeezing, many things can happen, which you may not like. So, if, you do resist, the printed portion has to be protected, the design has to be predicted and that is what is the more difficult part of it and therefore people may say well, I'll go for a discharge is easy atleast, the don't have to, do too much of a thought except selection of a dye, you just select the right kind dye, dyed the way you want to dye and then go for a discharge printing, relatively easy. In this case it is slightly difficult. But, you can get best results. Now, how do you choose with your economy and your method and your way of looking at it, not anything else because nowadays we are using, the bed sheets are there, backside is become white. Right? So, if that's the best part you can have. So, if you die, the back die means all the sides, all the fibers, all the yarn have been uniformly died and you are trying to remove now, from one side, no in other cases, that the you have printed everything, but in a different way, theoretically somebody could say well, that's very nice thing I'll directly do a direct printing also, a big blotch, the small blotch, everything else I will print. But, compared to that the resist, will be a better idea, you know? It can be done continuously also.

Refer Slide Time :(41: 36)



So, I think we stop here and what we have, learnt is that Azo, based dyes are better for the ground. In case of reactive dyes, you may like to go for when I'll cell phone base style, if you want to go for discharge printing of polyester then it is the discharge resist, style is a better one and in the resist printing, if you are looking at a chemical resist, it will be better, that we go for over printing, that would probably give the sharper, designs at the end of day. Thank you.