### MODULE 25 – Lecture 21

## **Revision and Doubt Clarification Session 2**

So, we will just take up some of the questions which were raised. Let us say, one of the questions was, How off-set printing produces photographic prints?

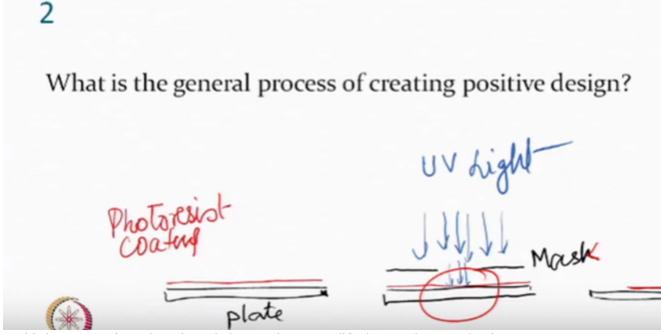
So this is very clear that, if a photographic print has to be print has to be produced, then you should be able to generate large number of shades, very large number of shades, alright? So, the minimum thing that we can expect is that it is going to be called a four colour process. And the plates that have to be made, will be one for the yellow, one for the sin and one for the magenta, one for black, so you will basically separate the colours digitally first, so that you have separation in four colour scheme and then make four plates and just overlay, one or the other. That is the way you can produce.

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So, four different rollers, for four different colours, but basically what you have to do is, first segregate, so that is the way photographic prints are produced. So it could be inkjet, it could be any other method but you have to do the same thing.

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So this is one question, I have just tried to you know, modify the question, weather it covers one or two responses from different people. What is the general process of creation positive design? Weather it is a Roller printing, Rotary printing, Lithographic printing or any other printing, that you think, so what has to be seen is, finally what is happening? Finally, if suppose there is a thing that finally it is a, like a stamp, the stamp is being printed, so whatever design is to be printed has to be exactly the same has to be printed, alright? Or if it is the Screen, then you are going to do the screen design in a manner that the colour does not flow, from the areas which you don't want. So, it based on the technology that you will be generating, a positive and negative, like you make a tracing paper, either by hand or by any other process. So you have to decide, which technology you are thinking of. If the technology says that, well, this is going to be used to produce a design, which is going to be positively use for thing, then you will ensure that this particular area, if it is a photo resist is hardened, on the plate. if it was a screen, then you would say the other area should be hardened and therefore weather you would make a positive or negative before let say exposing it to a altar violet light, your technology will decide, weather the tracing is going to be positive and after that was it going to be negative. And this is although you know, what you wanted to do, but this is what is going to be. For example, if this is a plate for an offset printing, and then you have a photo resist coating which has been put on the plate and then you put a mask, okay? So this is a mask, so you put a mask which could be a tracing paper or whatever and so light cannot come from some areas and the light can come from some areas. So where ever the light comes, that portion is going to be hardened, let us say it is a photo resist and it is sticking and when you wash it off, other portions will go and only this will remain. If this happens, to be an offset printing, then this is a oil attracting portion. So the oily ink will be attracted here, other is acquass where the ink will not go, when you clean, so this is a in a way you have made a positive, which is going to be actually be transferred, as it is. Where ever there is a design, this hardened portion is there. It was a screen printing, then it would be reveres of it. The screen roller would have a reveres of this. This is also a general question. Refer slide time :( 05:30)

Structural features of disperse dyes suitable for sublimation transfer printing?

Structural features of disperse dyes suitable for sublimation transfer printing. So, basically the question is for the sublimation and therefore what can sublime. Sublimation obviously means, without melting going directly to vapour, because if it melts then we don't know what exactly can happen. Then the transfer of the dye in a molten form will go by different mechanism, right around is a different story, good or bad is not a question. But here we are expecting it is going to vaporize. So there are some type of organic material, this is also one of the thing generally organic. So organic material which can sublime, have to have some of these characteristics,

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Structural features of disperse dyes suitable for sublimation transfer printing?

- Low molecular weight
- More side groups
- Less polar groups

So if it is a low molecular weight compound it will help sublimation, if there are more side groups, then it will help sublimation. If there are less polar groups, then again it will help sublimation. So molecular weight may be responsible, the side groups will be responsible and less polar groups will also be responsible. That means any groups, any other things if they are less, then it will help in sublimation transfer, that is the approximately the thing.

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### 4

How do polar groups, ionic group and solubilizing groups affect volatility?

Higher is the intermolecular forces lower will be the volatility.

So it is the same question repeated again but in a different way, the polar, ionic, solubilising groups affect volatility. So something with sublimes obviously means, the inter molecular forces are weak. And the polar groups, ionic groups and the solubilising groups which means they love water, they love such kind of things and therefore, these groups will reduce the volatility. So higher is the inter molecular forces, lower will be the volatility. And so approximately is the answer is similar to what we had said as the suitability, of any molecule to be able to sublime.

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# How do inter and intra hydrogen bond affect vapour transfer?

# Intra-molecular bonding would help the sublimation transfer because the vapour pressure would be high at STP condition.

Again similar kind of a question, but specific to, inter and intra hydrogen bonding, that is if you have a molecule where inter molecular hand bonding is possible, verses intra molecular hand bonding is possible or shall we say, where the inter molecular hidden bonding is less, so in one the inter molecular hidden bonding is more, in the other case let's say the intra molecular hidden bonding is more and inter molecular bonding is less or not facilitated. That is the kind of question. So intra molecular bonding if it is more, it will help in sublimation transfer, because the molecules will be able to separate out from the solid and get into the vapour phase and under the standard temperature and pressure conditions, you can expect high vapour pressure. So we would expect high vapour pressure, would mean more relatively high rate of diffusion also, at the temperature that we are talking about.

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### 6

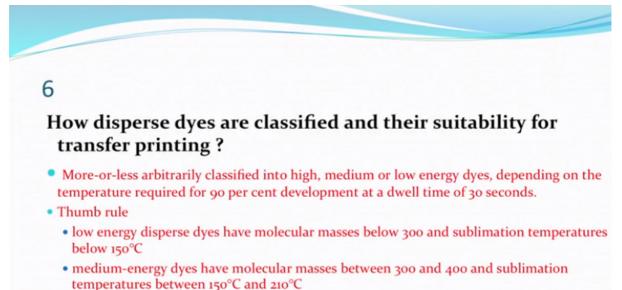
# How disperse dyes are classified and their suitability for transfer printing ?

• More-or-less arbitrarily classified into high, medium or low energy dyes, depending on the temperature required for 90 per cent development at a dwell time of 30 seconds.

General question again, "How disperse dyes are classified and their suitability to transfer printing? So this classification is on a group, this is not that, because every dye molecule is a different molecule, so you are talking about segments, that is a range and this range, is in somewhere an arbitrary range. We would classify them into very high energy, very low energy and things like that. So but approximately, roughly this may be that, classified into high, medium and low. Some people have classified into A, B, C, D also, so B and C would come into medium category, approximately. Depending upon the

temperature required for 90 percent of development diffusion in a time period of 30 second. So higher is the temperature required, will be higher is the energy of the dye. So 90 percent of it goes in 30 second, then you are quite efficient. Otherwise every dye, at almost all temperatures, which are higher enough, would keep on vaporizing and diffusing. And if you give more time, more diffusion will take place. But then hopefully we are looking at polyester, nylon, so and so forth, you would not like to keep such material for a very, very high temperature for a very long period because in oxidity of environment, everything could happen. So, it is not just a dye transfer, so this is standard. But you may still optimize at 45 second that is okay, because you may want more that 95%, that, that is fine, but general definitions.

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high-energy dyes have molecular masses greater than 400 and sublimation temperatures

so general thumb rule is a thumb rule, we already know that, generally the molecular weight may be less than 300 for low energy disburse dyes, alright? And sublimation temperature may be below 150, you know, there will be difficulty of this, because if your ironing temperature also was around the same when you had and this may also come out, so those are the things. Medium energy dyes have been classified roughly with the molecular masses, between 300 to 400 and sublimation between 150 to 200 which is this is a very large range. This is not something which is ever, this is it a naught. And high energy would definitely have more than 400 and sublimation temperature also more than 210 and so you are going for higher temperatures. And what it mean is may be, if you want to go for a transfer printing, then may be the temperature is to be kept, may be 210, 220 and so. You may not like to do that.

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What is the practical use of free mean path concept in disperse transfer printing?

This is related to size of molecules the dye and that of any other molecule present in the path. One would love if this path is less than the distance between the surface of the printed paper and the fabrics; the gap could be reduced by

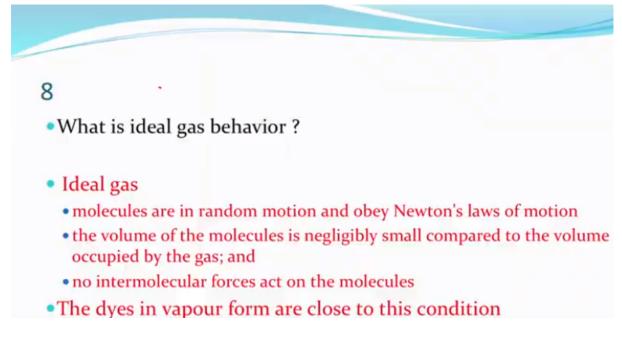
Applied Pressure

**Applied Vacuum** 

There was another question, "What is the practical use for the free mean path concept in disperse transfer printing?" Well, people who duly with molecules, they would like to characterise the behaviour of every molecule in any face that you want to test it out. So for a practical person who is only optimising the transfer efficiency of from a paper to a fabric, here she may optimise by time and temperature. But the people who design molecules and the people who say where this is going to be better than the other one, then they would like to consider this as well. Now if the molecular size is large, in a vapour form, it will collade faster. If molecular size is low, it may go more distance, if the molecular size is low, but can go more distance, but can come out also easily. So the decision, weather it is going to be good sublimation fastness, sublime is less, is also dependant on molecular size and everything that we are talking about is happening in the vapour phase. In a vapour phase, the transfer is by travelling, in the space and not, most of the time instead of, if it was a solution, then the dye was to travel in the solution, by interacting with almost everything, the moment you say there is a solution, the molecule is interacting with everything. But here when you add a gas, there is a space, where the molecule may go without touching anything and so you may be able to, if suppose, you happen to have a distance between the ink surface and fabric surface is very low, then it may immediately go there and if this is very large you have to decide what are you going to do? Apply more pressure. If you apply more pressure, some fabrics will tolerate, others may not tolerate, so this, whenever you do a theoretical study, so it is basically characterising a molecule which would behave or how will it behave in the practical thing when actually it is going to be used. In this case because it is going to be finally in the vapour form, so it is behaving like a gas and how much possible path is there before it contacts the other molecules, so related to the size of molecules the dye and that of any other molecule present in the path. Now you can appreciate that there will be other molecules also other than dye in the path. It is not a vacuum, so other molecules are there, it can strike them also. There molecular weight may be also different. So theoretically one would be interested in finding out, 'what kind of molecules are there?' and what are their sizes? Infact not only that you may have mixture of dyes because of which you have made a shade, so all the dye which may have a different molecular weight, approximate molecular weight may be same. They are available and they would hit each other and so mean path, which you actually wanted the direction to be always, in the direction of the fabric but in a kinetic energy straight at a high temperature in a gas form, the molecular may like to go anywhere. So if the path is very less, is very good but the distance or a gap at a molecular level is very high, even that. So you will say you will apply some pressure or apply a vacuum. Vacuum would mean that, you

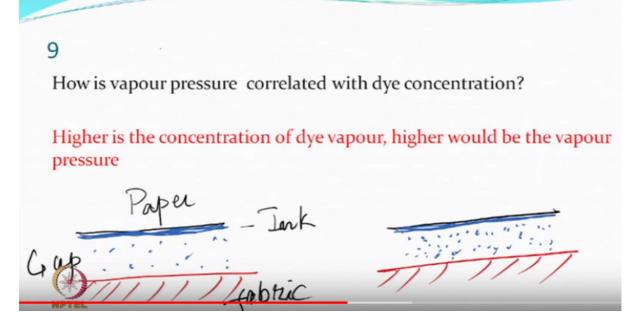
are reducing the other molecules which are other than dye you may be, also you are creating a direction in which the molecules may travel.

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Let's say I put it this way, 'What is ideal gas behaviour?' this also is one of the thing. So this is defined by three major properties, which is for the ideal gas. You must believe that there is no ideal gas in general. So an ideal gas would be that where the molecules are in random motion and they obey the Newton's laws of motion. Going in a straight line just keeps going in a straight line, unless selected acted upon by some external force. So, the random motion, if you put vacuum, if you put anything else then it is not random either. You are trying to push them, so you may create an environment which is not necessarily ideal gas but it may be on your favour that is what you will do. And the volume of the molecules is negligibly small, compared to the volume occupied by the gas that means there is enough space. Fact is, gas is meant to have lot of space. So volume occupied verses the number of molecules, number of molecules could be the size of the molecules is small, therefore it can travel distances and also respected that each molecule is independent and does not have inter molecular forces. You see whenever the inter molecular forces become strong, gas becomes a liquid, liquid becomes a solid. Now you are going in the reverse direction and so at a high temperature it is expected that the kinetic energy is going to be sufficiently high, that any of such thing called inter molecular forces are not going to be acting. Otherwise, one molecule moves the other will move along with it because of the interaction. Now it will only move because it collade, then it will have elastic collations for examples, this also could be one of the assumption that elastic collations, the shape of the molecule and particle does not change, it is just some kind of particle just goes like this. So this is ideal gas behaviour. So we expect that the dye, which are the dispersed dye, after sublimation are in the vapour form and would be closely governed by ideal gas law, that we already know that molecules do have attractions, but the condition is that you are at a higher temperatures, kinetic energy is so high, that the weak interactive forces do not affect.

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Other question was, 'How is vapour pressure is co-relate with dye concentration'? So I assume that what was meant is if the vapour pressure is high, does the dye concentration responsible for this? Is the dye concentration responsible for this? So, higher is the concentration of dye vapour, now vapour form. Higher would be the vapour pressure, because the molecule, the pressure is what? pressure means, if there is something called assumed container, the molecules and the kinetic energy, they are going and hitting one or the other and if they are more in number they would be obviously having less space and they will be hitting more often, statistically and so more pressure is getting created. So if higher vapour pressure is recorded or given to you that mean concentration is lightly to be higher in that area, alright? there is a gap, there is a paper, there is a fabric and a link layer and so in one case you see there are more number of molecules in the gas form, the other case, there are less and so pressure in one case is going to be less and pressure, vapour pressure in the other case is going to more. And how will it affect the dye? Obviously diffusion characteristics are going to be there, the probability of every such molecule conducting the fibre surface, where once it touches the surface hopefully because of the affinity reasons and then starts diffusing inside. So it is a transfer of a different type, so one would obviously expect high rate of diffusion as well. "Sir, it is depend on the molecular weight also?" It depends, in that we said all the properties, the molecular weight, the bulky groups, the polar groups, all of them will decide, so if the vapour pressure is low of a molecule then you know, this should not be used in mixing to get another shade, with another dye, so all the dyes which we use together, to get a shade, must have similar vapour pressure development at a same temperature. If that doesn't happen, obviously rate of transfer will be different, so your shades will change, what you expected will not be there, other than the fasteners properties.

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10 What is the necessity of vacuum assisted transfer printing and what are the difficulties associated with it? Thickness of fabric, if more, would need such assistance, say pile fabrics.

So there is so many of them, but what I say is it is related to the transfer printing anyway but related to the gas being directed in one way or the other. So vacuum assisted, nobody would like to create vacuum, is costly, alright? But like scanning in a electron microscope, and a transmission electron microscope you create vacuum because you want to remove all other particles from there, alright? Creating a vacuum in a almost in a pour of substances is difficult, that means it is costly. But what it means is that you are taking out other molecules, which may interact, collade and you may like to give some type of a direction, for example, there is one paper here, vacuum is applied on this side, so chances are that either from the sides or from somewhere else the air is going to be sucked in one direction and so molecule is also going to go there, air may pass through, because you don't have affinity for the fibre, but the dye may strike and so once it strikes it strikes. So thickness is the fabric, is the one reason you may wanted particularly if it is a pilled structure, like a carpet, rugges and even non ovens for that matter. So if you have such type of material, then the difficulty is that there are more open spaces, and you don't have a flat surface and since in such cases you require some assistance. So you have a piled structure, you apply vacuum on the side, so you expect the direction of all the things to be in this direction more, so otherwise some of them because of space may like to go out as well because and you can't put so much of a pressure on a pile structure. That is also a difficulty, because if you put at a high temperature, good amount of pressure the way you the amount of pressure that you put it on a flat fabric, you may damage this texture, fibre may not get damaged but the texture can get damaged. So then you are losing the thing. So you would not apply so much of a pressure and if you don't apply so much of a pressure there are more gaps, if there are more gaps then you would like to have some mechanism to guide the molecules in some other direction, which is your direction. So difficulty, basically is, the cost because to the leak, you know and so that is the basic difficulty, if you can have that there is no problem, other of course is that you are also forcing some amount of air from the sides, so dye doesn't go outside, everything comes in, it is like creating vacuum within the system. But you are sucking, it is basically sucking.

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Can we use a pigment instead of disperse dye?

# The pigments have no affinity for the substrate so binder would be needed?

Pigments may not sublime at required temperatures for transfer printing

I think it is also the question that doesn't look the way, but it still I believe is connected with the sublimation transfer printing. So what it is meant is a pigment is also like a dispersed dye, alright? So, can we use pigment, through dispersed dye? As long as it behaviour is like a dispersed dye. And what is the behaviour at the temperatures that you're looking at? It sublimes. A large number of pigments may not be organic; they would have nothing to do with the supplimation. Large number of pigments may be metal complexes, organic organo metallic dyes, they may not like to sublime and if they do not sublime, then you can't do and other thing is generally pigments some, affinity are normally you require a binder, so if they had affinity then they would be dyed, they would be called dyes. Then there is no pigment problem. So they would be called dyes. So they may not sublime at the temperatures required atleast the organic pigments, so you may not be able to do that. Even disposed dyes don't have affinity for every fibre that is one. Affinity is important, as far as the dye or dying or printings are concerned.

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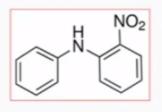
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2-Nitrodiphenylamine is not suitable for sublimation transfer printing. Why?

This was probably a different kind of question. I just tried to pick one up. This has a colour, this compound has a colour, 2-Nitrodiphenylamine is has a colour but still it is not a right dye. I mean you may not even use it for dying. So why would you use it for printing? Alright? so normally we believe that transfer of dye for printing or dying may have a different mechanism, but at the end of the day you would expect that this is going to last the washing cycle, wash everything else and so and so forth, actually by itself molecule is a very nice molecule, but it is not a dye, for the textile purpose.

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2-Nitrodiphenylamine is not suitable for sublimation transfer printing. Why?



Melts at 74-76 °C

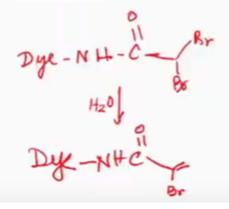
This is the molecule. And For sublimation it melts also, so sublimation transfer printing obviously by itself otherwise this is just a molecule which gives some colour, very nice colour, but very small molecule by itself that appears to be very nice.



So this is regarding the wet transfer printing of wool. Even if you do not do any transfer printing, Lanasol dyes are good for wool. Specifically designed for wool and silk and so the reaction mechanism obviously depends more on the, with the amino and groups. So wool and silk have and amino groups, a large number of them acidyes also do the same things, so Lanasol reactive dye, okay? We are talking about. So a suggested mechanism could be something like this

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What is the reaction mechanism of Lanasol dyes with wool?

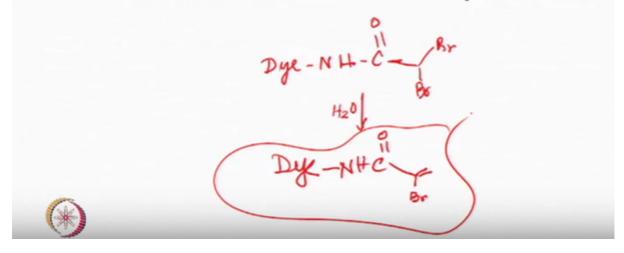


So you have a dye which obviously has a possibility of reacting anywhere, let us say, even water also at certain temperature you can expect one of the bromine goes off possible and so you create some groups which are ready to react, alright?

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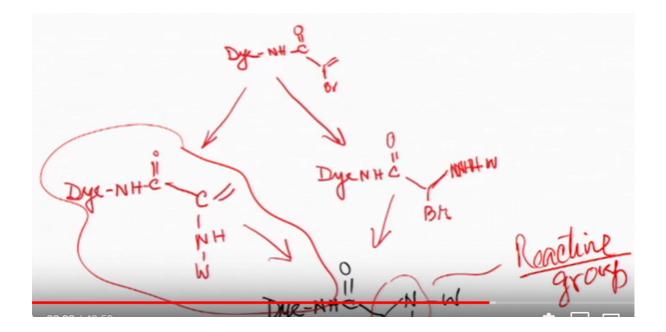
# 13

What is the reaction mechanism of Lanasol dyes with wool?



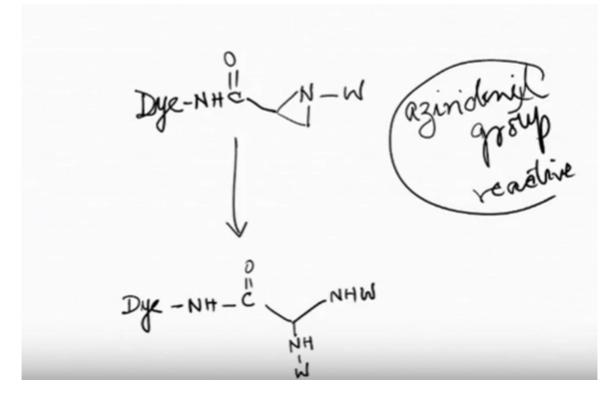
so when the dye is in this form which is this form then it can react in two ways, with the wool or amino acids.

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One that it can react and make a compound of this type of this portion still remains free and the other could be this. So both are different type of reactions, because in one the carbon has a possibility of freed two bonds and therefore it is more reactive it goes there and make some kind of additional reaction. It was basically bromine, so there was a CHBR, so one is showing that there is a possibility of H and there is a BR was gone. So there are two points which are available. Which are reactive sites and so one can become CH2, in this case H may be here and this, there is N, which is from the wool, which is come and the H of the NH2 also is here H. So that is one, So there are two ways of doing the reaction and then this compound also can go further and react and make both of them, finally would be more comfortable making a group which is a azeredine. Weather you come from there or you come from the other side you will still be able to form this type of a group, which itself is a reactive group, three membered rings.

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So this ring can break and if this ring breaks that there is another possibility that this ring could combing with another molecule. But depending upon where the amino end group is, obviously static hindrances will always come into picture. So it can make and break another group which is NH and CH2 or OH and things like that but this also is possible. So either one molecule, with one dye or two molecules groups with one dye may react, so which one will be first which is second is not so important. So this is how approximately reactions can take place.

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### 14

Can we use Lanasol Reactive dye for Wet Transfer Printing of cotton?

There is another question which is related to this. Can we use Lanasol Reactive dye for Wet Transfer Printing of cotton? Because it comes from being use a wet transfer printing of wool. Idea is that wool, it was developed for wool because wool was not, doesn't get much time in transfer printing and you need something which can very easily react with the amino groups, and this particular thing was designed in manner that it would be reactive enough, in the acidic medium that is the way it was looked at. And it will be more stable also in acidic medium, otherwise with water, temperature and alkaline both the groups were immediately get converted to something else If it is alkaline medium.

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Can we use Lanasol Reactive dye for Wet Transfer Printing of cotton?

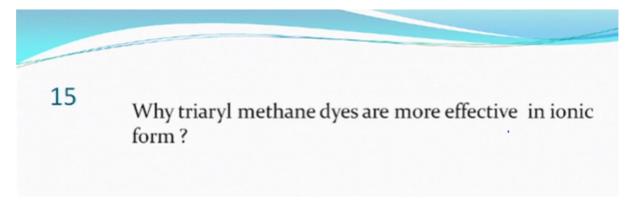
Lanasol dyes are used at a mildly acidic pH, like acid dyes, where these are able to react with amino end groups.

Not a good idea for cellulosic which would need alkaline conditions

Cell-0

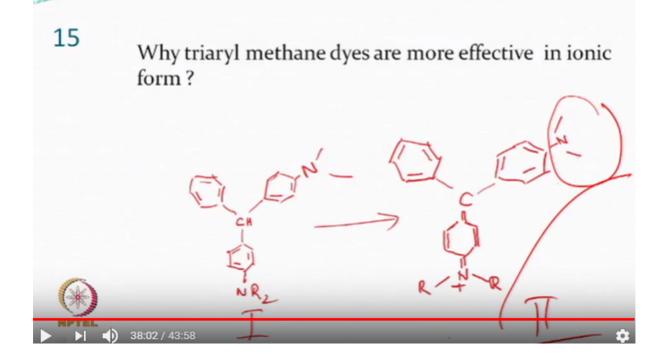
So they work in the acidic pH where they are able to react with amino end groups. So theoretically it can happen. But it is a alkaline condition the chances of dye remaining reactive are going to be less efficiency is going to be less, so we have other reactive dyes, which can be used because cotton would require alkaline conditions to make it om C, cell O minus type of a situation and so you require alkaline conditions. So theoretically, why not? But the chances of, it is like for example if you do not use, dichlorotriazine, because it would react too fast, and have more wastage, here also the 2 bromines they would immediately react here and there, so acidic reactivity being controlled wool is readily available around the time and so amino groups can react and so I don't think it is a good idea to use them, something you will get definitely.

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Question which is, just been modified in a way that, Triaryl Methane, type of dyes. They are brilliant, they have good colour, when in ionic form. Other than, that they, because they become Cationic, so certain fibres are preferred, that's one part.

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But if we look at the dye, which is the first structure and versus the second structure, so you can see that if cations are not there, in any condition, then the conjugation, is also not very good. So, the moment you create conditions where, cation is created, so you can appreciate, that from here, to here, the conjugation is there and there is a resonance possible that this particular nitrogen can also have a double bond like this and get a plus charge and this one. So two structures, alternatively are possible, so they have better resonance and also, better conjugation. And so, whenever such situations will be created, obviously, you know, deeper, better brighter colours are going to be produced. So, you have seen, I've given you, probably an example of phenolphthalein also. If it is not ionic, then it is a colourless material. So if you want colour, you go to the ionic state. So it doesn't matter, which type of a thing. You can have, you create a condition, where ion is going to be created. Should one print, polyester acrylic blended fabric, by sublimation transfer printing method? So, first of all, these two fabrics, two fibres, from thermal stability point of view, are very different in character. Polyester you can take it to, 220 degree centigrades and also feel good about it and lot of things can happen. Acrylics at higher temperature start getting yellow, so thermal stability is always an issue. And if you do, Sublimation transfer, that means you obviously have to have, some high temperature. So what are you compromising? Either temperature are going to be low? If temperatures are going to be low, maybe transfer to polyester may not be, that good. If temperature is high, acrylic may suffer. So, it would be better that we go by the different printing route, than the sublimation. You can always print polyester acrylic, using the normal printing techniques. Alright? Sublimation may not be the best method.

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- Should one print PET/Acrylic blend fabrics by sublimation transfer printing method?
- Acrylics are sensitive to thermal treatments, one can choose lower temperature for transfer
- Polyester requires higher temperature for fixation
- Not a good idea.
- However, low energy disperse dyes could be used.

So as I said, Acrylics are sensitive to thermal treatments, one can choose lower temperature for transfer. Polyester, not require higher temperature, so generally not a good idea, but if you still believe, that you need to do it, low energy, disperse dyes could be used, you can dye both of them and but wash fastness, may not be so much of a problem, but sublimation fastness would be an issue.

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# 17

### What is the advantage of coating chrome based material on paper?

So this was something on the release paper, very specific question which, we had chrome based, stearic acid etc, being used. So stearic acid by itself is a hydrophobic material, so hydrophobic printing etc, could be done very easily, compared to, you know, oil waste and then release can be done. So it was only a coating on a paper. There is a question, which is there, 'Why do you use that?

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## 17

What is the advantage of coating chrome based material on paper?

- Chrome complexes of myristic or stearic acid are cationic and positively charged moiety is attracted to the naturally negatively charged paper surface
- Becomes oriented with the hydrophobic moiety pointing away from the surface.
- Provide a surface printable by litho, gravure or screen printing

So, comb, core, chrome complexes of myristic or stearic acid have been used, they're cationic, because of the chromium. And so, positively charged moiety is attracted towards generally, negatively charged paper surface. Almost everything that we see here, chances are that, it is more negative. And so, when you coat, instead of going away, it would have some tendency to be there. So you can coat easily, but it's not a very, isle, high energy bond or something, but it is still there. So you can easily coat, so it can release also. But interestingly, the molecule, in some sense, becomes oriented. It's like, you have surface active agents, hydrophilic versus hydrophobic. So something which goes in one direction, the other goes the out direction. So, the hydrophobic moiety maybe pointing away from the surface of the paper. This makes printing of this, easy. It's against, for example, if somebody had a nice paper, you coat a silicon on this and try to print. The release can be good, but even coating is difficult. You see, normally what happens is, you have those stickers, which you remove and put somewhere else. So they may be based on thing that, mild sticking takes place, but you want to remove, you should be able to remove, that is one aspect. So, there is a milder kind of a arrangement, at the paper film, surface and hydrophobic moiety on the outside, because of just, some orientation automatically occur. And so, easy printing, of any, any technology, any technique that you can use method and print. And then of course, later on maybe it will be easy to, remove also. So I think, these are some of the questions that I have taken, from your responses. So hopefully, it will help you. See you, later.