Textile Finishing
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Lecture-07
Non-nitrogenous agents

Welcome back to this lecture series on textile finishing, so before we go further let us see what we had done till now.

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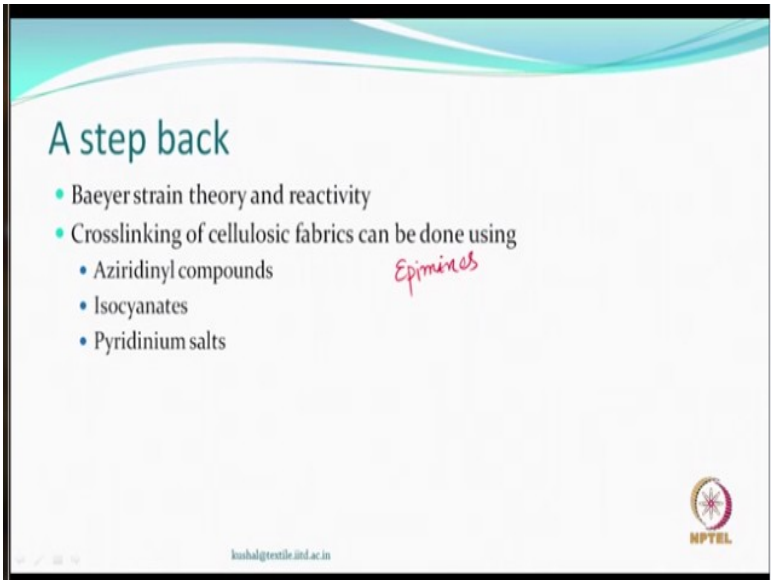

In the last lecture we try to understand what is the Baeyer strain theory that whenever there are cyclic compounds the 3 membered, 4 membered ring there is a strain on the bonds. And because of that those compounds or those systems become more reactive and so we have unstable relatively less stable structure and so it becomes more reactive. Because there is a strain and everything in this world would like to release the strain.

So, one of the ways of releasing straining just break the bond whenever the conditions are suitable, that is what we learnt. And the Aziridinyl compounds were some of those compounds which were 3 membered rings and could react with let us say the hydroxyl group of cellulose.

So, in the last lecture we did learn about various compound which were non urea based compounds which can be used for cross linking on cellulosic fabrics like cotton and viscose.

So, one of them as we just mention Aziridinyl compounds which sometimes they are also known as epimines and others were the isocyanates which can react as we know with alcohols which is like cellulose, hydroxyl groups of cellulose. And also pyridinium salts which reacted as if they were chloro-alkyl compounds, what was the byproduct at the end of there was a pyridine and acid like HCl.

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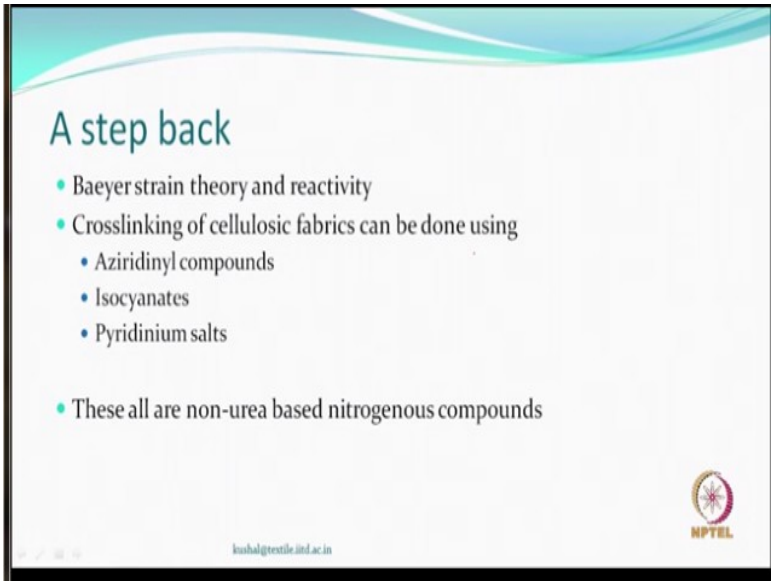

So, all of these were non-urea based nitrogenous compounds alright. So, they had nitrogen whether it through the pyridine part of it or through the isocyanate part of it or the aziridinyl group.

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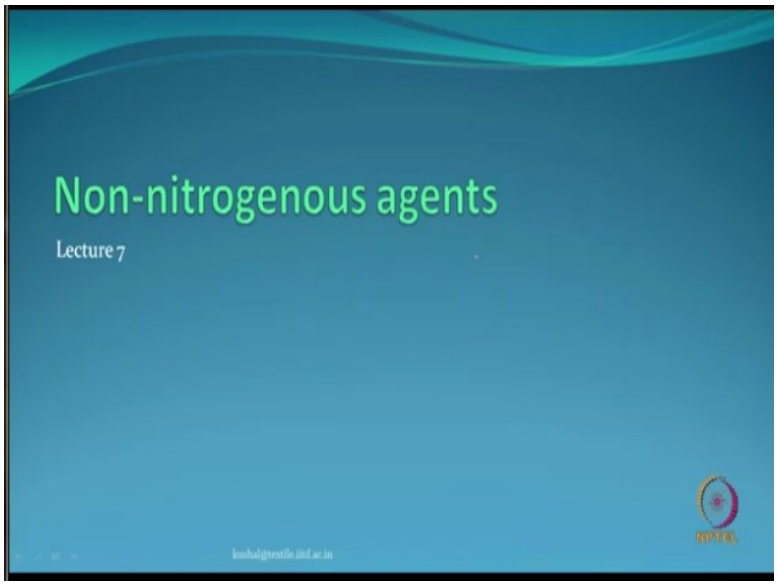

So, today we will discuss some of the non nitrogenous agents which can be used for crosslinking.

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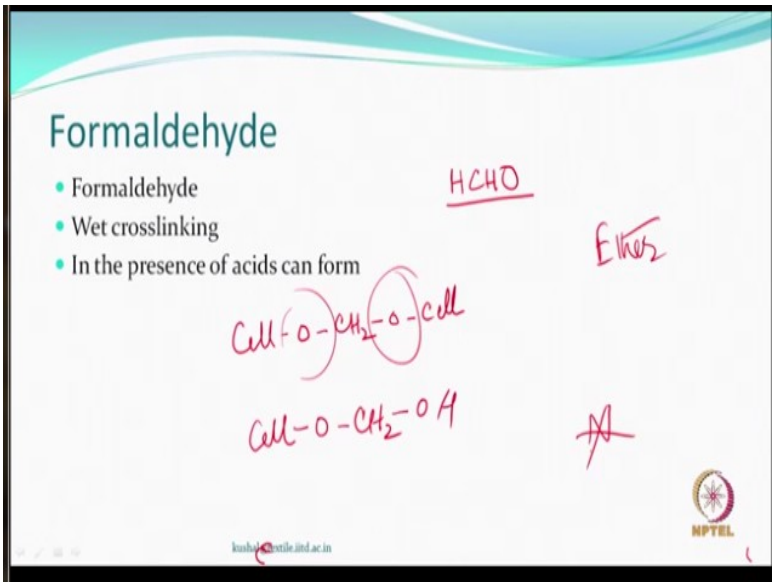

Interestingly the formaldehyde which has been used to prepare N-methylol compounds you remember itself can be used for crosslinking. This compound in acidic solute form from acidic solutions can react with cellulose hydroxyl groups. And also at temperature lower temperatures we may not like to go in for a pad-dry-cure process because formaldehyde may get evaporated for various reasons you may not like it.

But people have used it in wet crosslinking while the fabric is wet the formaldehyde is in a solution and the crosslinking can be affected in acid medium. And you may get a crosslink of

this type right which type of link is this, this is also ether. Of course some byproducts can also be formed where only reaction of this type may take place. So it is not a crosslink but the formaldehyde has been attached, this type of reaction is also possible there can be other type of reaction possible also. But definitely this does not have nitrogen right does not have nitrogen, no nitrogen.

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But we for various reasons may not like to use today of formaldehyde directly onto the textile because as we know there can be some issues with the formaldehyde use directly on textiles.

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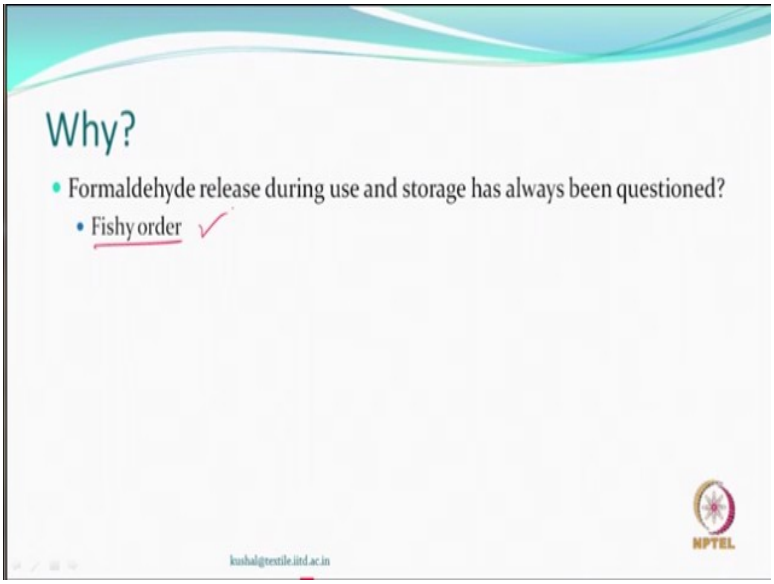

So, why should we not use let us say the formaldehyde or why formaldehyde always will be remain a part of discussion in various forums. Fishy order we already know, so one is the smell itself which people may obviously not like and that is why we shifted slowly from dimethylol urea to dimethylol ethylene urea dimethylol dihydroxy ethylene urea and there you know various products substitutes derivatives.

Because we wanted to reduce this compound did not want to go into the water, did not want to smell when fabric has stored.

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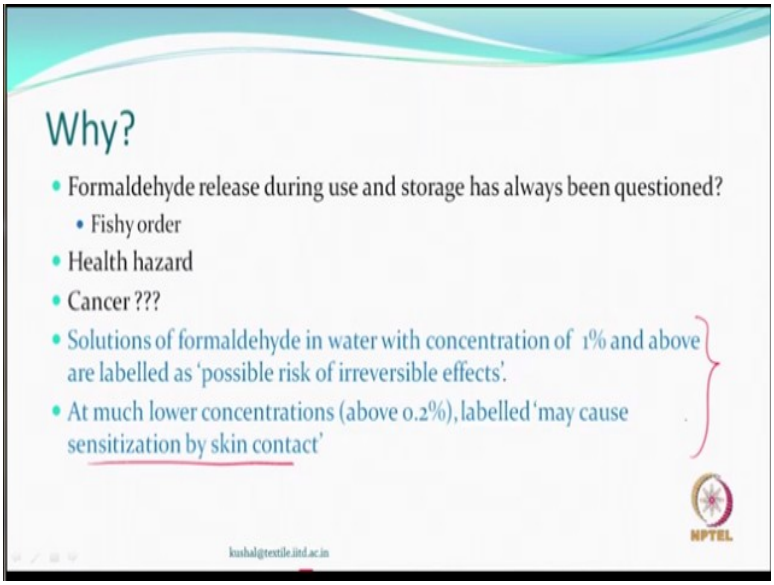

But today people are also talking about that this formaldehyde could be a health hazard, if that becomes true then obviously one will like to avoid it. And therefore we said we will talk about some compounds which are non formaldehyde based compounds. There have been some studies on animals like rats where it has been shown that formaldehyde can cause some cancer, although till today this is not been detected on any human, but still people have started looking the release of formaldehyde as a serious problem.

And not because of order but because of the health reasons and if that we so then we may be tempted to discuss agents which would not release formaldehyde. So, as for as guidelines are concern, people have said that the solutions of formaldehyde in water if the concentration is more than 1 or have a possible risk of damage and damage obviously irreversible damage. So, if

that happens so people should avoid that but 1% is a very large concentration, 1% would not be released from fabrics right.

But at lower concentration much lower concentration let us say concentration some in the range of 0.2% labeled above may cause sensitization when you contact with the skin comes in contact with such type of concentration which is low concentration but then. So, these are some of the issues as such the humans are concern, so people may therefore like to be more cautious using any such compound.

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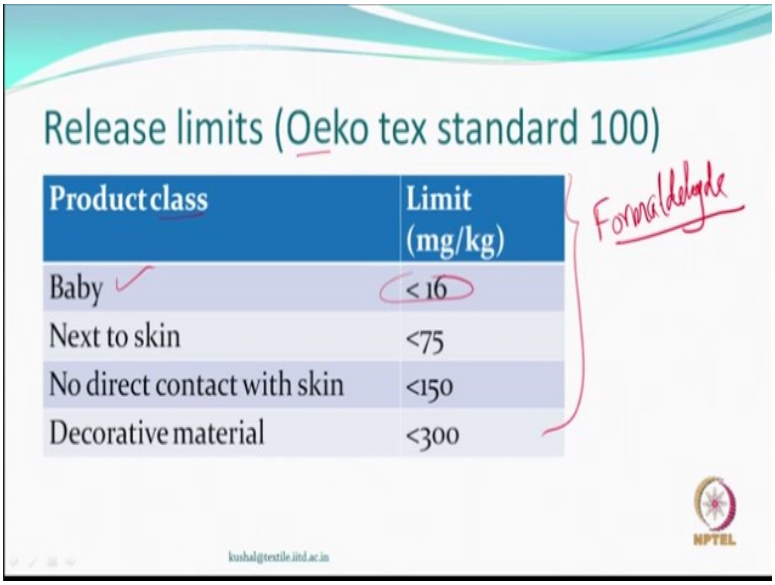

So, various standards have been setup across the world one of them is an Oeko tex standard which prescribes many types of compound which should be less than a certain percentage as for as the formaldehyde is concerned. The limits have been defined, this is one of the examples, so is the universal kind of an acceptance for products which are for babies you would like that to be less than 16 in fact you would like to be 0 but then 0 can be there only if you do not use it.

So, less than 16 milligram/kilogram is what type of standards that people may like to agree, if it is next to skin like underwears and so and so forth garments which touch the skin it should be less than 75 . If there is no direct contact with skin then maybe 150 such type products could be there which have require less than 150 and if they are decorative material like curtains other such stuff then you may have standard which is less than 300 milligram/kilogram.

So, the standard is concern there also not obviously looking at a 0 release of formaldehyde but obviously limited release very very low release may be ok but more than this will be questioned. So, that is why it is good to talk about compounds which can crosslink and a formaldehyde free or they do not use formaldehyde in their preparation.

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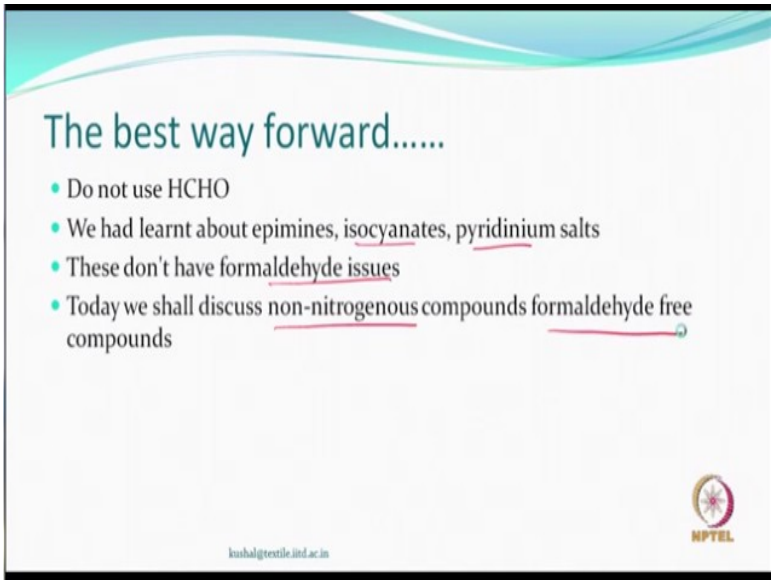

So, what is the best way forward , best way forward is do not use it right. So, we did learn about other chemicals which were epimines, isocyanates, pyridinium they also do not have formaldehyde in them. So, well okay nitrogenous do not have formaldehyde we can use them of course they may have other difficulties for example pyridinium itself which comes to the byproduct may not be the best thing to happen, isocyanates are also very reactive and their storage is an issue obviously will be an issue.

And they cannot be applied through aqueous medium various kind of things can happen. So, although these do not have any issues, so the formaldehyde release concern. But it is good to have some options other than these compounds as well. So, we will talk about non-nitrogenous compound which are also let us say formaldehyde free okay.

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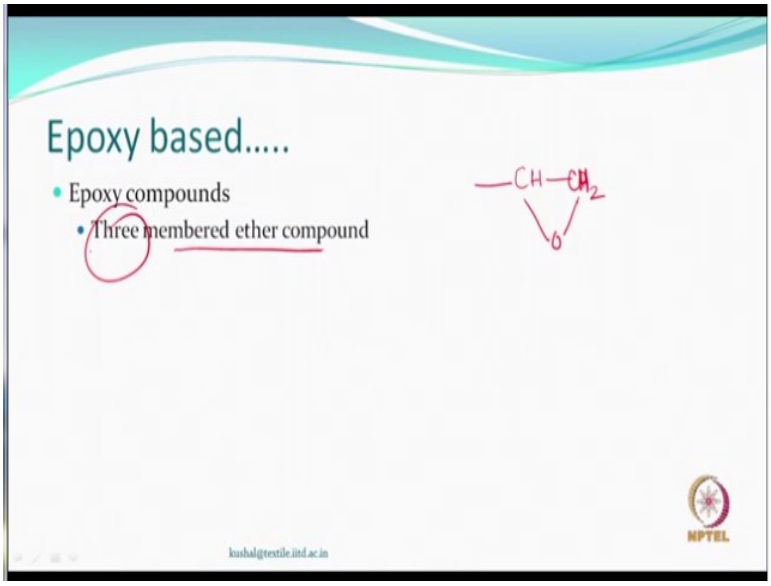

So, one of the compound which is very potentially an important compound for crosslinking are epoxy based compounds, alright. So, -CH-CH_2-O and so they are in some way a 3 membered ether compounds ok. 3 membered ether compounds. Now these are very important compound then use for many purposes but can be used for crosslinking also. Because they are 3 membered means what it means they are also reactive, that mean they can also react at low temperatures and give you covalent bond.

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They would require alkaline medium to be active and they as we said can work at lower temperatures. Sometimes you may also use them in from solutions and pad dry cure may or may not be the option.

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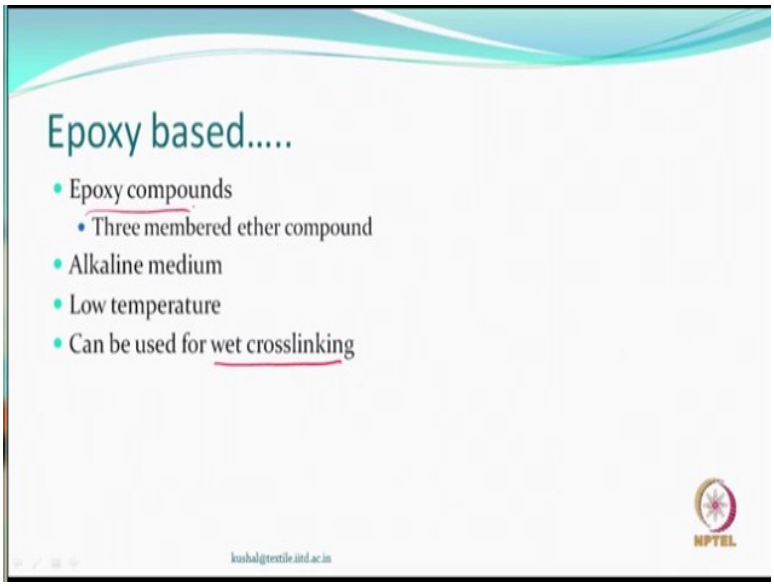

Therefore people have used it for wet crosslinking also again remind wet crosslinking means that the fabric is wet. Another interesting option of this type of thing one is the pad dry cure where the fabric has padded dried and then cure, other is wet crosslinking when the fabric is actually in the solution. Today people have talking about the middle path which is called the moist crosslinking at the moment we are now discussing about that.

But we are looking at the epoxy compound which can be used for crosslinking and obviously you can see that these compounds have no formaldehyde.

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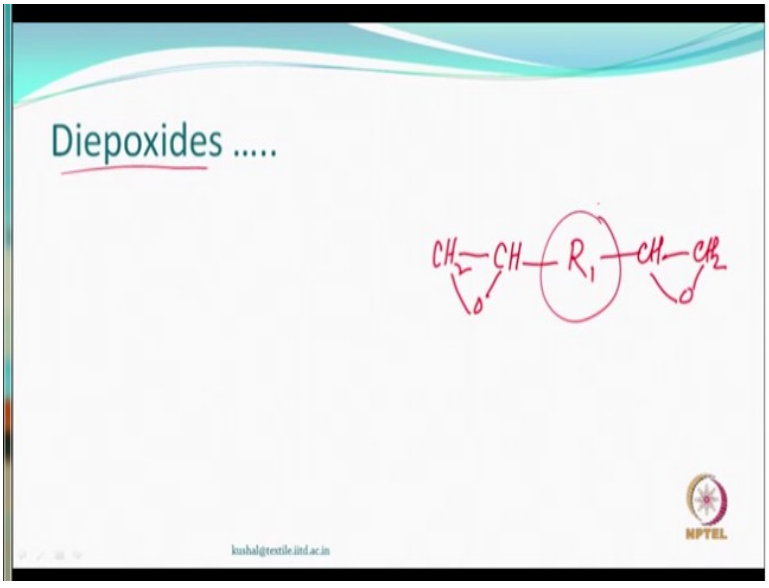

So, very simply in organic chemist get excited whenever they want to create molecules very easy to create molecules based on what we call is compound which are diepoxides this R_1 which is holding these 2 groups on both sides can be anything very aliphatic, aromatic, long chain, short chain depends on what you want to do. And we can appreciate that if the length of the chain will change molecular chain then the properties are expected are going to be different but nevertheless, it gives a good opportunity.

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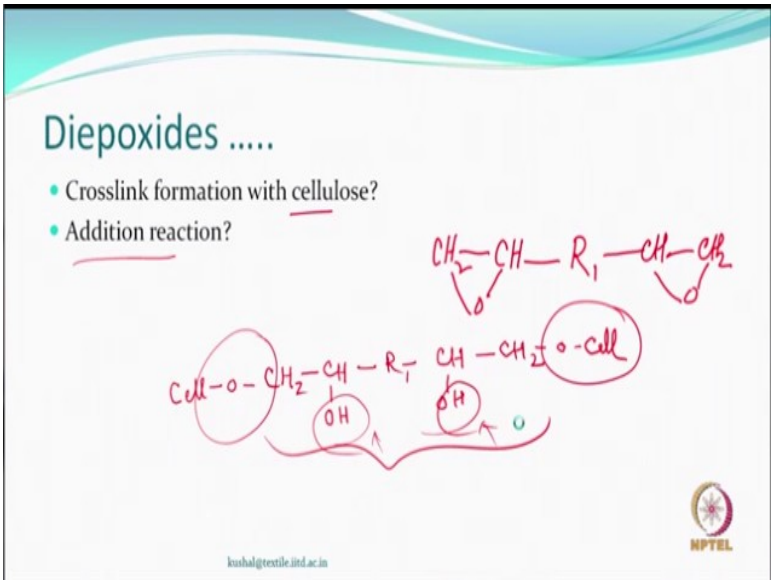

For us to look at the epoxides, so how does is react let us say with cellulose, so we said they will react and with cellulose and form a link. So, if you have 2 molecules of cellulose then one can form this crosslink of this type, now what is this, it is again form 2 ether groups. So, the only thing that is changed is the link in between this as I said this if it is R_1 then this also can be R_1, so you can have but at the interestingly the 2 hydroxyl groups which can be used for making a crosslink are generated because of this ethoxy link.

So, in some way the hydrophilicity of the cellulose is going to be maintained right. And remember is this reaction is an addition reaction ok there is ring opens and cellulose or any other hydroxyl group for that matter alcohols can also react. And you will get additional group pendant group which is the hydroxyl group. So 2 hydroxyl group have been crosslinked 2 have been created.

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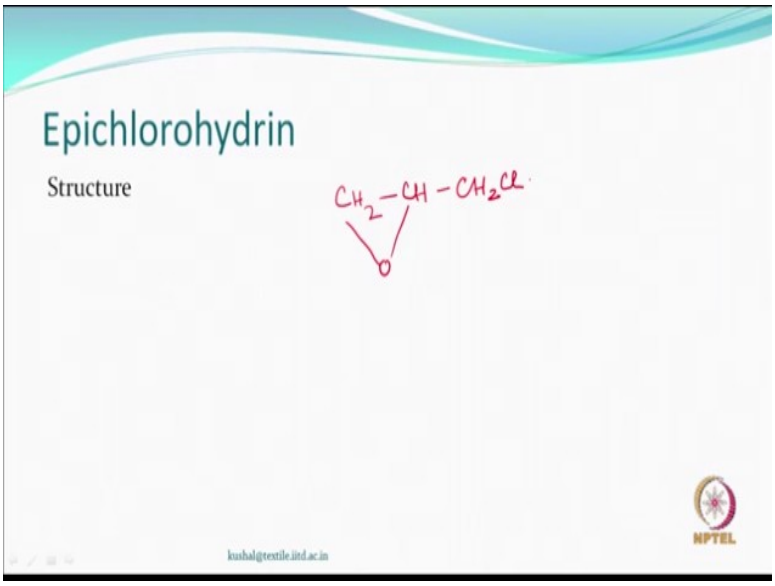

Interesting compound in this category is epichlorohydrin, so it is an epoxy compound which has a chlorine available also but once the reaction takes place this chlorine can go. So, if somebody wants say that I like to use epichlorohydrin as a crosslinking agent then one would always get confused as to how an epichlorohydrin can give a crosslink, it can only give a covalent bond with 1 hydroxyl group being engaged where it appears that this compound can actually form crosslinks.

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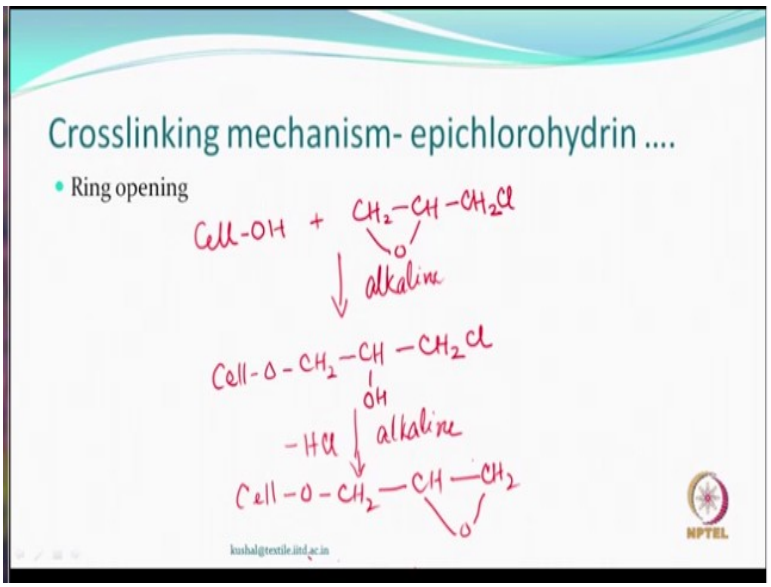

So, this crosslinking obviously like in the other also happen by ring opening mechanism let us say we have cellulose and then we have our epichlorohydrin in alkaline conditions, the ring opens and you will get 1 link of the type that we just saw. So, 1 link is formed and now after

formation of the link we do not have any epoxy group left and then people then say well this is not a crosslink.

So, what happens is this particular compound in alkaline conditions again we lose this HCl which will get neutralized and then you can get this anyway was already reacted and then we get you see that. So, one reaction after having it is the epoxy group has again been reformed now it is been reformed then obviously it can link it can crosslink or it can react.

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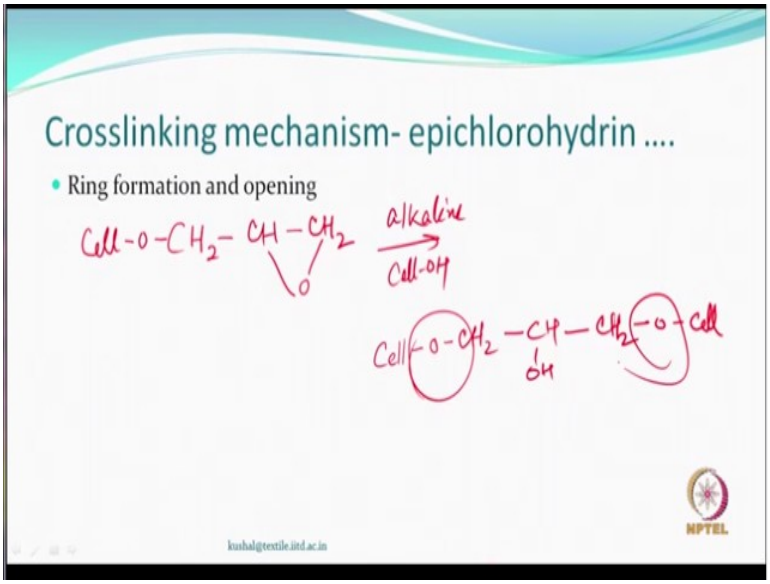

For example now we are talking about, so we had cellulose and an epoxy group attached to this cellulose this is what and then again in the alkaline medium you can get in the presence of cellulose another molecule one can get right. So, you get crosslink even with epichlorohydrin, that is epichlorohydrin by itself has got 1 single epoxy group. But an interchange takes place after 1 crosslinking.

So, you have ring breaking, then ring formation and then opening and then crosslinking, all that can happen, so an epichlorohydrin can also make a crosslink right.

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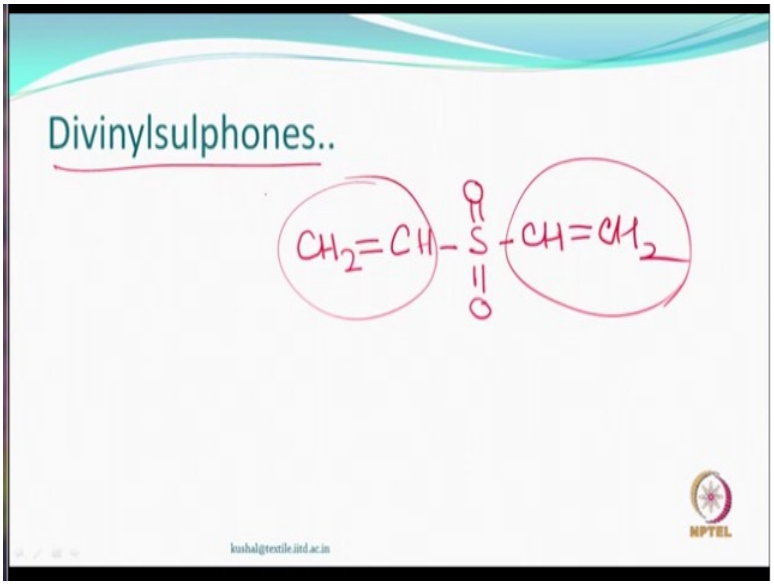

Then there are the compounds which are called disulphones you may have been taught about reactive dyes which are called vinylsulphone based reactive dyes. Sometime they are also known as remazol alright, so that type of a group reacts with cotton and also with silk and wool in alkaline medium, the covalent bond can be formed. Now instead that we can have a simple compound like this for example divinylsulphones. So, instead of having 1 group you got 2 groups alright, so theoretically it can crosslink.

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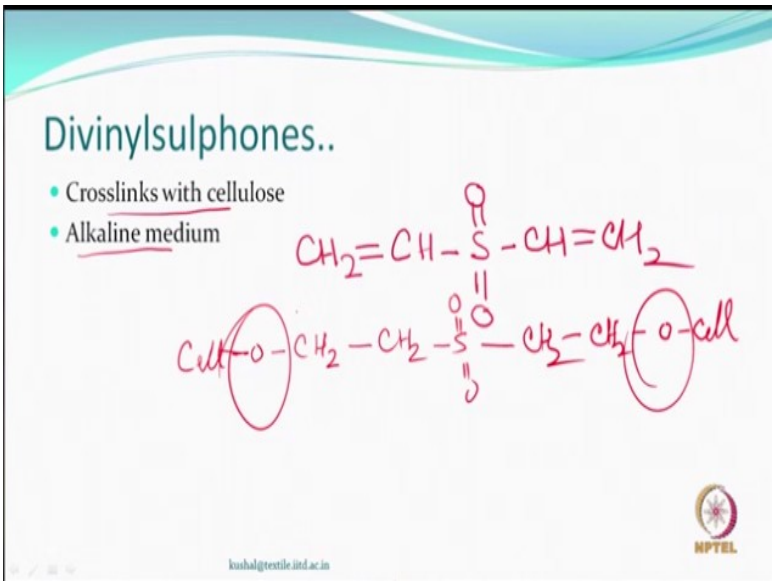

So, it will react in alkaline medium like the reactive dyes and it can crosslink with cellulose and what will formed. Interestingly if you see this also is an ether link being formed, so you can have crosslink of course there is 1 sulfur has come in between but that is ok where it can react with

right with cellulose. And if these groups had reacted earlier with reactive dies, so you can always have situation they will react I mean the groups which were used in reactive dies for reaction with cellulose and wool and silks.

So, they can also react with cellulose, wool and silk that is silk and wool are basically proteins right. So, you have some other option you had the epoxy option and you have divinylsulphone option.

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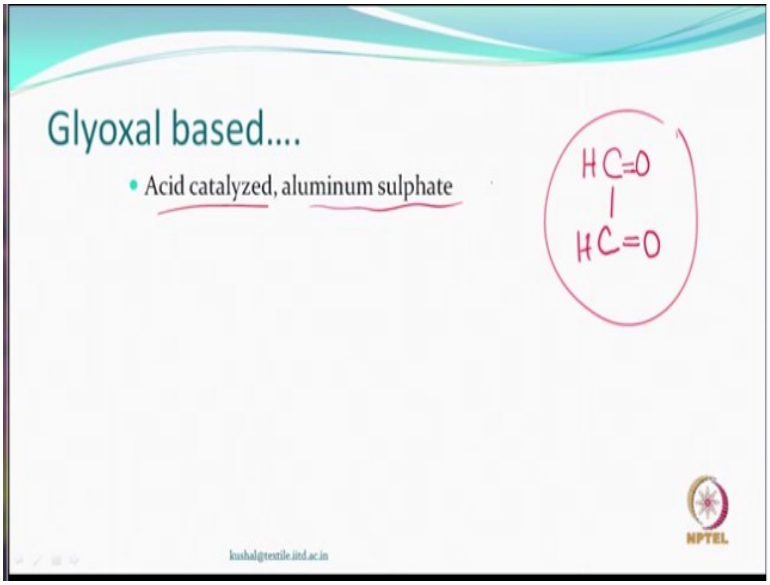

Then there are other compounds which are not formaldehyde but glyoxal, this compound is use these days as suggested to be used these days in acidic medium approximately compound some of the catalyst like aluminum sulphates could be used. And you can go through a pad dry process, you can go through a moist cure process and one can get a crosslink.

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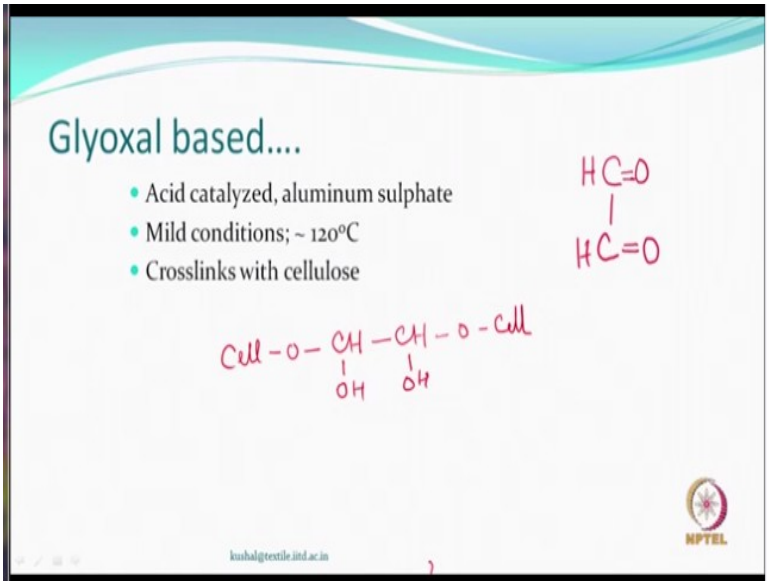

So, one can think of mild conditions and reactions can happen ok, so if this will crosslink with cellulose, so you are likely to get reactions of this type does it remind you something it is discussed with the epoxy compounds also making 2 hydroxyl groups right 2 hydroxyl groups. So, you again have no problem of hydrophilicity as such only thing is in between these there is no group alright. So, this area is just C-C bond carbon-carbon bond, but interesting.

People found it is a very good replacement for as a crosslinking agent which can use conventional pad dry cure methods medium obviously if temperatures can be less you can obviously have less losses due to heat. From the performance point of view now we are looking at performance I mean that do we keep washing many times and over and what happens. People found that one other alternative using this could also be as best and give better performance actually.

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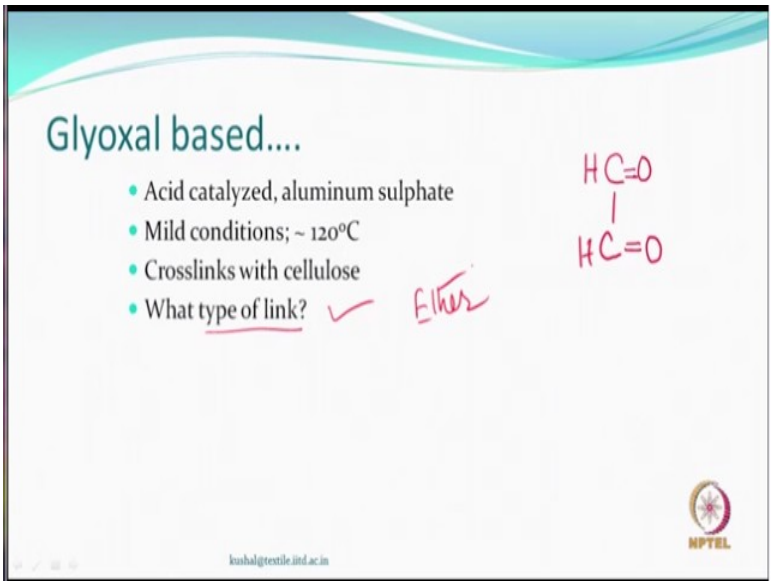

So, in this case we had seen that the link obviously is what type ether.

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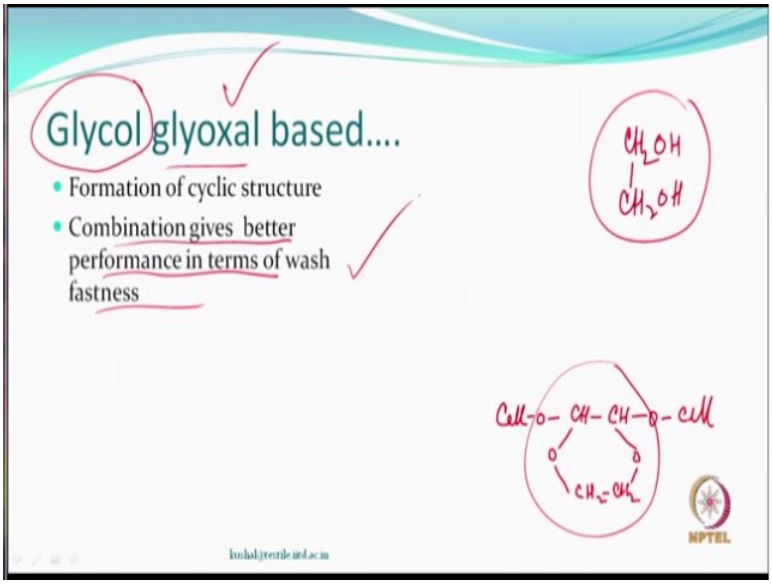

So, for reasons that we want to improve the performance, so people said if we have glycol along with glyoxal then it is possible that we may be able to create a cyclic structure and performance could be better. That we are looking at hydrolytic stability, that we do not want the bond to break easily, so that the performance is better. So, if you use glycol this is what we call is a glycol, see similar compound but that was glyoxal and glycol similar looking bond, this is basically hydroxyl based system, where do we use glycol otherwise.

You remember somewhere use glycol in textile, yeah in the manufacture of polyester itself you need glycol is not it ok. So, this compound by itself may not be obviously the choice what happens is when you use along with glyoxal you can make a ring structure. So, the 2 hydroxyl groups remember the 2 hydroxyl groups which were there those 2 hydroxyl groups can then react and by a dehydration process and so you get a cyclic ring.

By this the performance improves and so this is one of the very good alternatives to N-methylol compounds which people have been suggesting which is also formaldehyde free.

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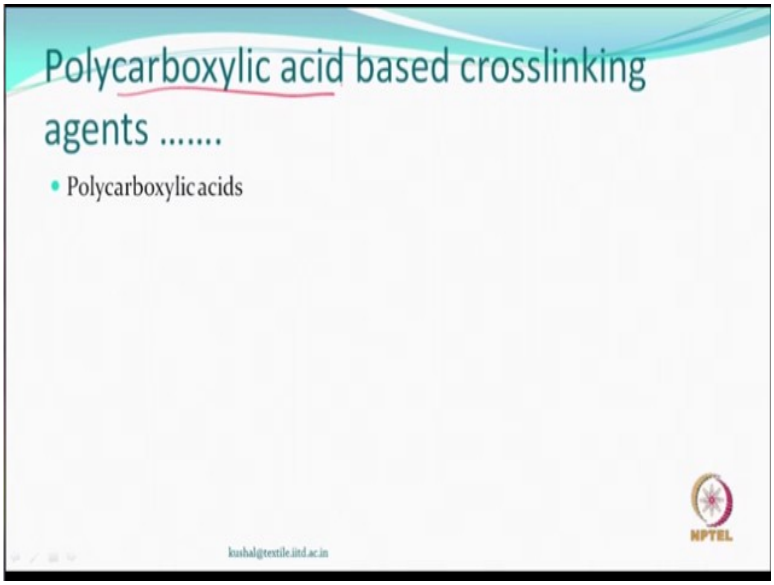

The other compounds in this category are going to be in the class of polycarboxylic acids polycarboxylic acids obviously have more than 1 carboxylic acids. Carboxylic acids in mild alkaline conditions can react with alcohols to create a covalent bond what is that bond, bond will called to be ester bond ok. So, if there are theoretically if there are 2 carboxyl groups and you can create 2 ester links, so you can obviously make a crosslink.

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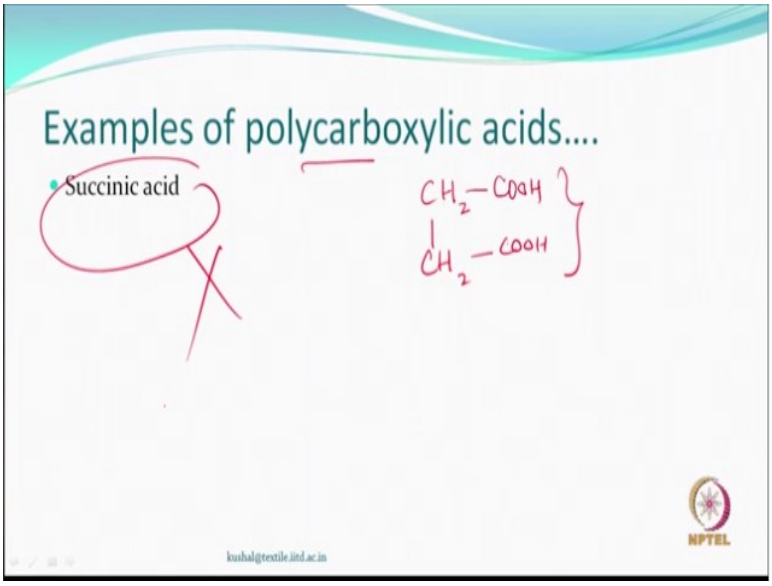

So, that is why the polycarboxylic acids have become interesting for the finisher. Various types of polycarboxylic acids are available like succinic acid is one which you probably recall simple carboxylic acid.

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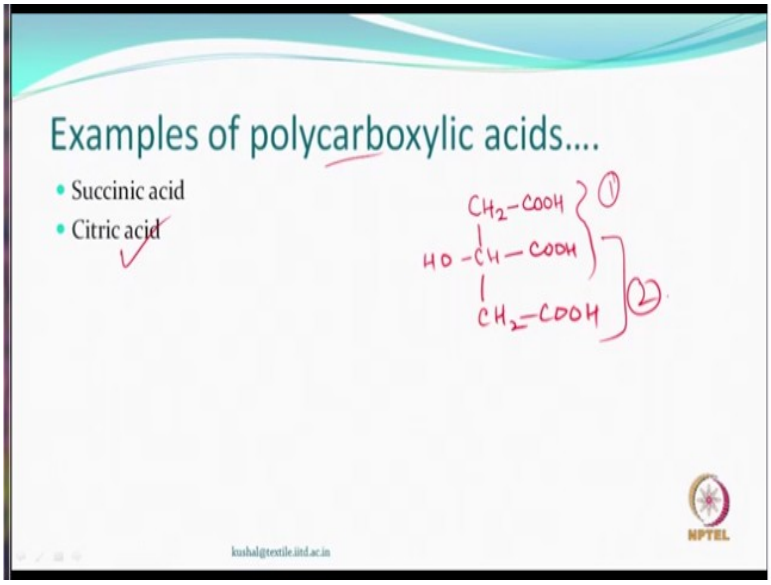

Other carboxylic acid citric acid which as is 3 carboxylic acids in it is structure but if you recall it is also a hydroxy acid, so this is also an example of polycarboxylic acids.

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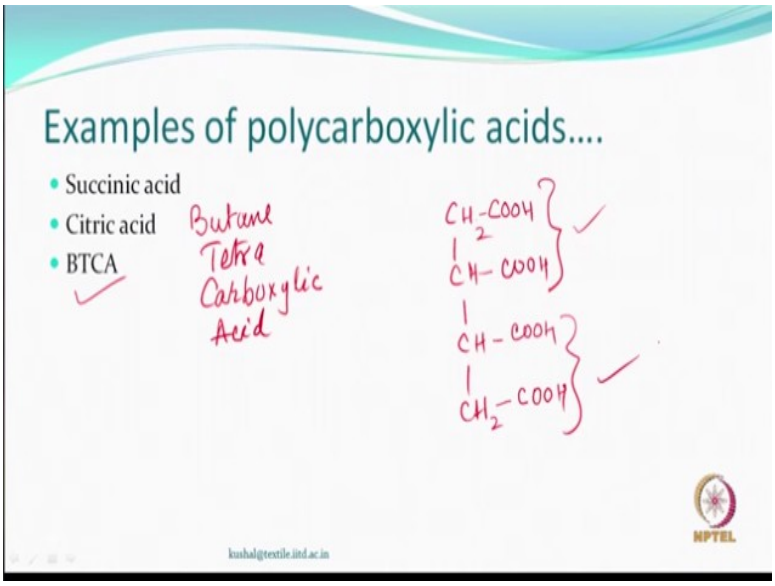

Another interesting example is BTCA which is butane tetra carboxylic acid butane tetra carboxylic acid commercially these days people just say BTCA an interesting compound and this compound would be something like this, so there is a butane alright. So, butane tetra carboxylic acid, so there are some of the examples one can always have more examples, now the question is can all of them be considered as good crosslinking agents.

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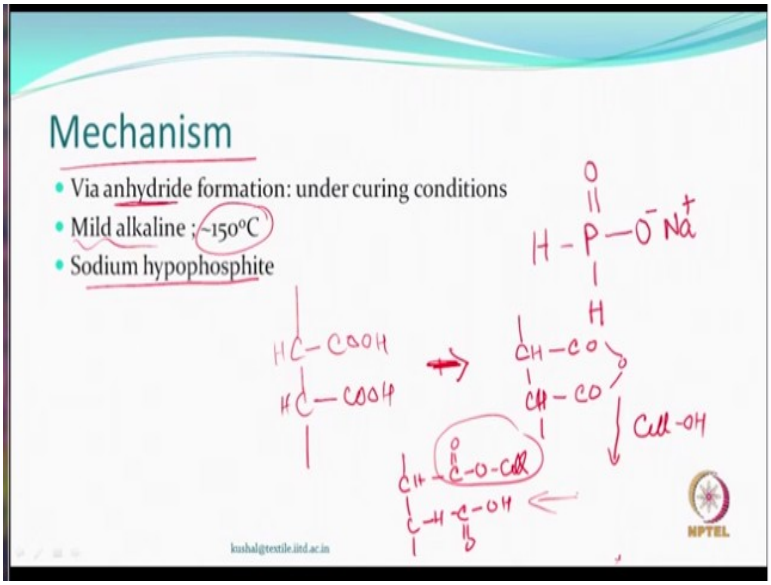

The mechanism of reaction and now remember we have to have conditions where the fabric does not get detoriated and you are able to do the reaction and therefore the conditions that people are obviously using is approximately this 150 degree is mild alkaline conditions. One of the catalyst which is quite popular is mild alkaline is hypophosphite sodium salt of hypophosphite. Now the

mechanism of formation of a crosslink let us say with cellulose goes via an anhydride formation mechanism.

If you can form an anhydride then under these conditions reaction can take place, under more severe condition reaction can take place even without this. but let us say we are looking at conditions which are suitable for our textile finishes. So, let us say, so what happens is so you have polycarboxylic acid under the conditions it first will form it first will form an anhydride.

So, you first form anhydride, anhydride formation is like a dehydration reaction right and then in the presence of the conditions that we have mentioned if you have cellulose also present then we can expect reaction of this type. And this after this reaction will be back to carboxylic group, so the anhydride breaks reacts with cellulose and makes this link and the other group of the carboxyl group is now free.

Now this carboxyl group, the second carboxyl group that we are referring here can also react with cellulose only if there is a possibility of formation of an anhydride link again ok. If that does not happen then under these conditions crosslinking will not be possible, so let us go back. Let look at this BTCA can it form anhydride and crosslink yes of course these 2 groups can form anhydride, these 2 groups can form anhydride and they can form crosslinks and after crosslinking you can have free carboxyl group.

So, there are various combinations there are possible in BTCA the most popular maybe this one where the 2 end carboxyl groups do anhydride the formation and then reaction takes place and then you get the crosslink. We go back again and let us see citric acid, what will the citric acid do, the citric acid also will be able to make first anhydride group make a covalent bond then one of them will be released then the 2 of them will make another anhydride.

So, first anhydride then the second anhydride formation and you will again get a crosslink ok. If you go back further then this is succinic acid can we make yes of course first anhydride will be formed a link will be made and after crosslink after covalent bond has been made you will get 1

free carboxyl group but then in this free carboxyl group as no other near carboxyl group with which it can make an anhydride if it cannot make anhydride it will not be able to crosslink.

So, among the polycarboxylic acids also succinic acid for that matter will not be able to make crosslink it can only make 1 link which is a covalent link alright.

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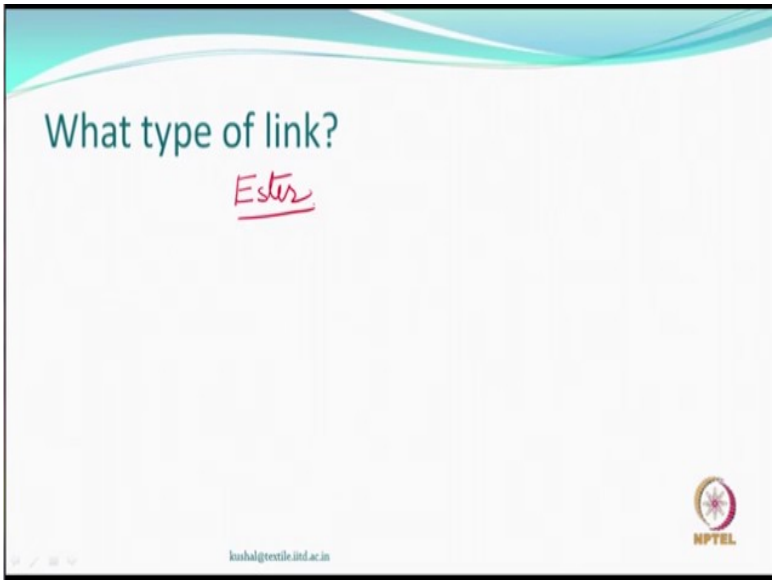

So, this is where we are and so we are now asking another question what type of a link? Ester right and form an ester link. In many cases before that you saw what links is more less most of the links were ether links alright. So, the difference between the stability of these 2 rings is the ether links are more stable in alkaline conditions let us say you have washing condition which are alkaline and if the washing conditions are acidic then the ether links may have some difficulty in its stability.

Reverse is the case here ester links are less stable or more susceptible to alkaline hydrolysis. So, these are the differences between the ester and the ether links, so that is one. Let us see if there is anything other possible.

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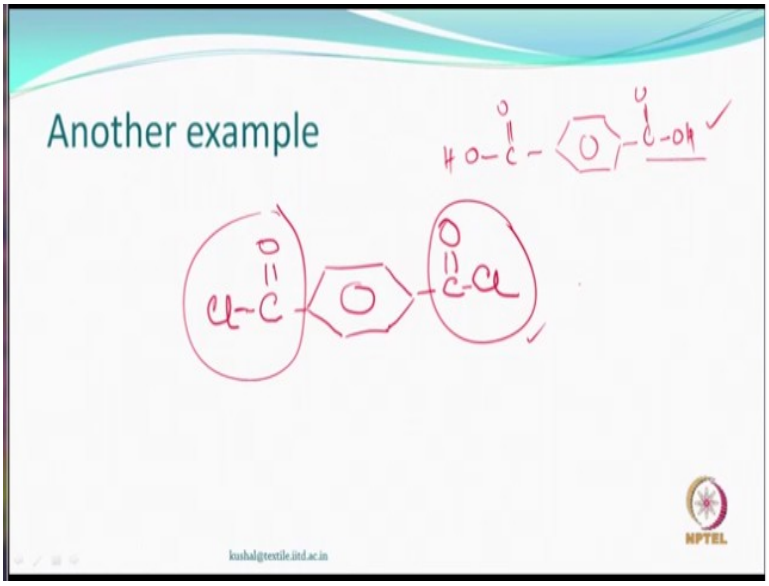

One of the interesting possibilities is using an acid chloride, now do you remember this if this was let us say instead of Cl if this compound was this what do you think this compound phthalic acid, you remember earlier we are talking about ethylene glycol now we talking about phthalic acid you can make polyester. But the reactivity of this is much less compared to and chloride very highly reactive compound. These type of compounds can be used to make do the reactions are room temperature.

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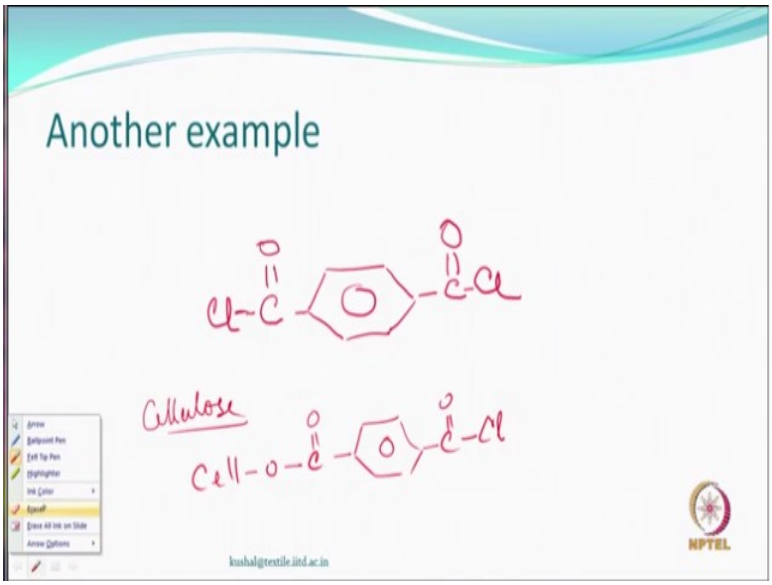

But at the end of the day what will they form what will they form they will also form let us say with cellulose groups of this type. And if you have second cellulose molecule then we would get another link which will be with another cellulose hydroxyl group.

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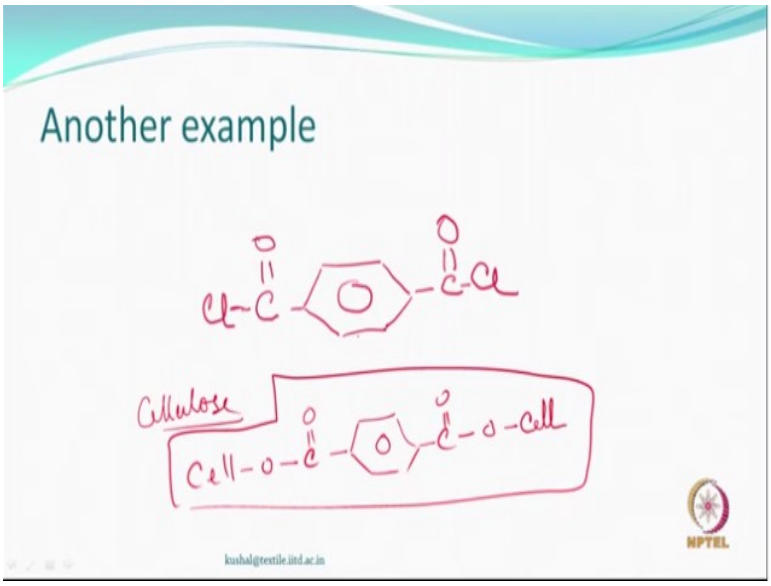

So, if you look at this compound and any poly carboxylic acid compound the differences here the reaction can take place without formation of anhydride. But remember this is chloride of an acid and not the acid itself, so they are reactive at the room temperature or little low temperatures this reactions are possible.

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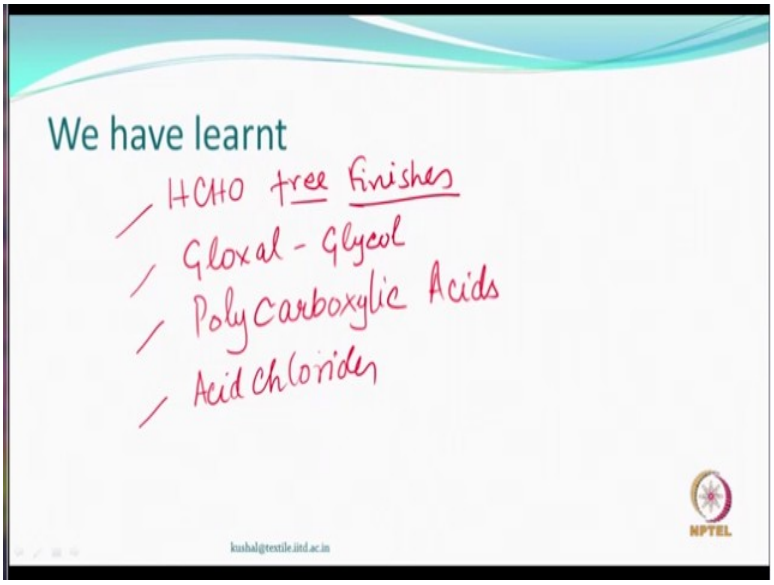

So, what have we learnt here we have learnt that today there is preference for formaldehyde free finishes. And some of the examples that we can talk about is glyoxal, glycol combination other that we can talk about is polycarboxylic acids and of course acid chlorides ok. So, if you use these compound either at a temperature which are mild temperatures of 120 degree centigrade or

temperature around 150 160 degree centigrade or at room temperatures some of these agents can give you crosslinks without involvement of any formaldehyde or some good compounds .So, we stop here and next time when we will discuss some other topic on finishing, thank you.