Textile Finishing
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Module No. #04
Lecture No. #08
Control of Formaldehyde release

Welcome back, to the class on, Textile finishing.

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Till now, what we have learnt? We have learnt, that there are, Non-Formaldehyde based agents, which are nitrogenous in nature. And, these can be used for, cross-linking. These include, Aziridinyl compound, Isocyanates, Piridinium salts. So, all of them are, Non-Formaldehyde, but have Nitrogen, as one of the elements.

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We have also learned, that there are, Non-Formaldehyde, Non-nitrogenous compounds also, which can be used for cross-linking, such as a combination of, Glyoxal and Glycol mixtures, Polycarboxylic acids, Acid chlorides, Vinyl sulphones, and so on, and so forth. Therefore, you have an, Methylol based compounds, Non-Formaldehyde compounds, Non-Formaldehyde Non-nitrogenous compounds, all of them can be used for cross-linking. It must be remembered, that some of the agents, may not be used by a, Pad-Dry-Cure process.

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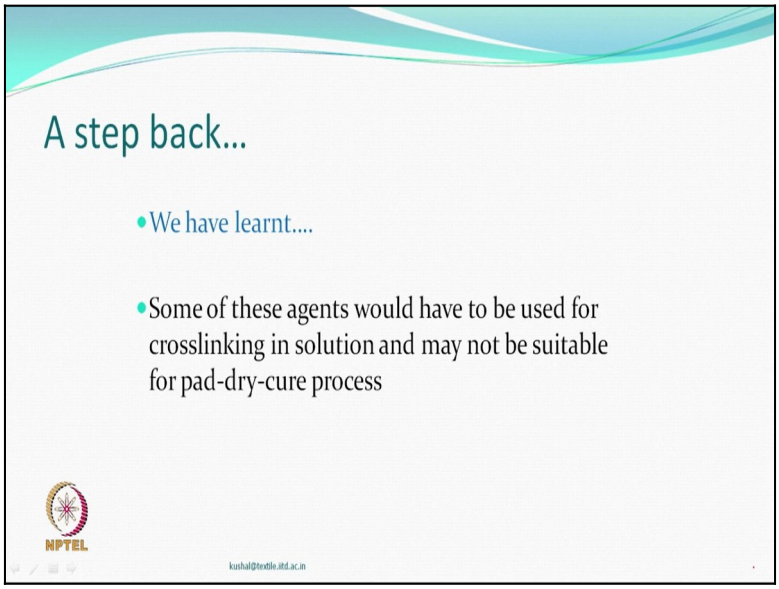

That is the, pad-dry-cure process, may not be suitable. And so, they will have to be, used in solutions. So, in some sense, cross-linking in solutions, are in wet state, that may have to be done. So, that is what, it is, depends on, what is the need, one can use these chemicals. Previous to that, we had learned, what kind of catalysts, etc, can be used.

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Today, we will discuss, one important topic, and that is, release of Formaldehyde. Now, what should we do, what are we going to be talking about it, let us see. So, the question, that remains is, the Formaldehyde is, some type of an environmental issues are there, with the Formaldehyde release.

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And so, what should we do? Should we use, zero Formaldehyde based compounds, that Formaldehyde free compounds, or we can use Formaldehyde based compounds, but with a controlled release. What do you think? I mean, it is always good, if you could use compounds, which have nothing to do with the Formaldehyde. So obviously, there would not be any formula, at release.

But, there are very efficient compounds, which are Formaldehyde based compounds, which effectively do the cross-linking, and are efficient wrinkle recovery agents. So, that kind of finish, should we completely discard, all those compounds, which have been very efficient, or can we do something about it, let us see.

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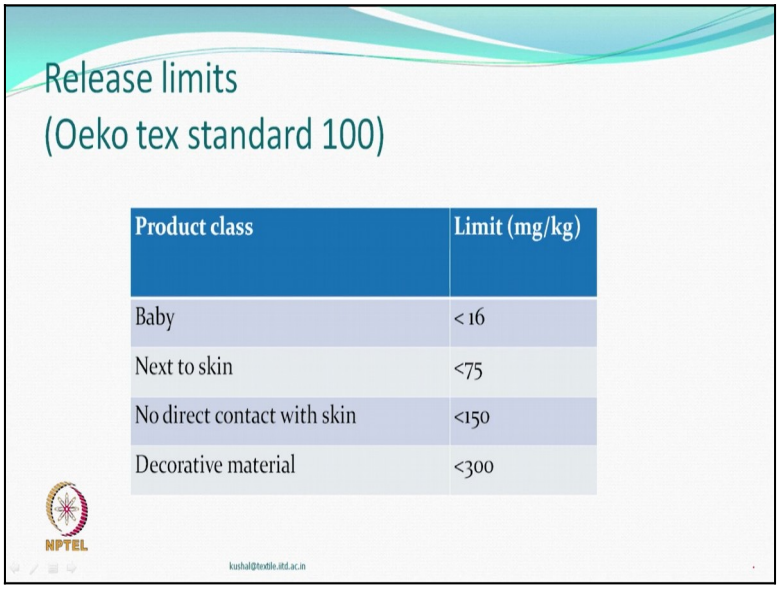

This table, we had discussed, in earlier lecture also. What it says is, the international standard therefore, are not talking about zero Formaldehyde, but they are talking about limits, how much Formaldehyde release, if at all is allowed, for a certain type an application. For example, baby's garments, obviously, are more strict, in these regulations.

And therefore, for example, in this case, it is written, less than 16 milligrams per kg, is the limit. But, if you look at decorative material, the limit is, 300 or less. So, we, as an international body, not talking about zero Formaldehyde, but we are talking about limit. If the release, is within the limits, it is hopeful, that is not going to be very harmful.

And so, we should also, look at the possibility, of using already established cross linking agents, and look for methods, with which, the release the Formaldehyde, could be reduced. That could be, a very wise angle, to think about. Suppose, then we decide, that okay, we would like to see, how we can reduce, control, the Formaldehyde release. All right. So, what would be the, your strategy, what can we do, so that, this happens, less.

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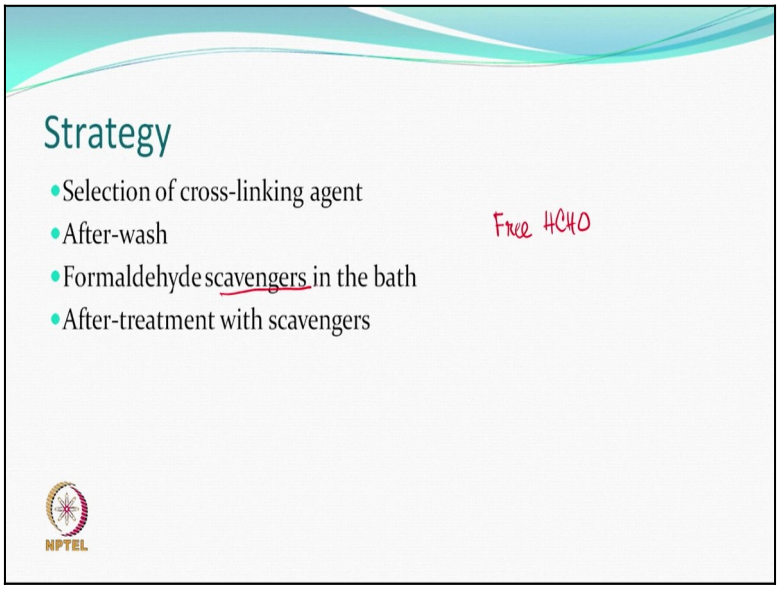

So, let us say, one of the thing, which obviously people will talk about, is selection of cross-linking agent. So, we are not talking about, a cross-linking agent, which has nothing to do with the Formaldehyde, like Formaldehyde free cross-linking agents. That, of course, would have no problem, if you can use them, there is no issue at all. But, we are looking at, the Formaldehyde based cross linking agents, which also, some of them, may be more resistant to hydrolysis.

I am sure, we are quite aware, that DMDHEU, is more resistance to hydrolysis resistant to hydrolysis, compared to compared to, for example, uniform aldehyde. Therefore, you have a possibility of selection. A DMPU, may be more resistant to hydrolysis, compared to, let us say, DMEU. And therefore, if we have a choice, we should be able to select, certain cross-linking agent, which otherwise, are going to give, less Formaldehyde.

So, that is one strategy, which you can adopt. The second strategy, which people have suggested is, After-wash. Now, technically speaking, this is not a very attractive proposition, but it is a very effective proposition. In the sense, that when you finally finish, a product like, you have made a wrinkle resistant fabric, which has gone through, padding, drying, curing process, in a Stenter, you may not like to wash it, because already been done, very nicely.

And, that becomes an issue. If there is a Formaldehyde presence, in the treated fabric, either as a free Formaldehyde, or otherwise, then it will get released, during storage, during use, and so, objectionable. Therefore, must be something, must be done. So, if you do the after-wash,

then this so-called free Formaldehyde, this definitely can be washed off, and then you can take care of the liquor, in one way or the other, which is the wash liquor. All right.

The question that remains is, well, whether it is attractive or not, we shall see. Other strategy could be, using, some type of scavengers, Formaldehyde scavengers. Now, these scavengers, obviously will pick up, the Formaldehyde, if it is available, and not let it be, as free, they will become in some sense, bound. So, these scavengers are chemical compound, which can be, added to the bath. This is one option, that one has.

So, you have a cross-linking recipe, with cross-linking agent, and their catalyst, and wetting agents, and so on and so forth, add, some amount of Formaldehyde scavengers, in that bath. And, so we hope, certain amount of problem could be solved. After-treatment, with the scavengers, that means, fabric has been finished. And, you are not satisfied, with the release, once you have tested it, then you may like to give, an after-treatment with scavengers. All right.

So, these are some of the alternatives, available, which can be used as, a good strategy, to control, the release of Formaldehyde. So, as far as selection is concerned, we are sure, that if you have a good agent, which does not release, too much Formaldehyde, is a good idea. Once done, let us look at the, after-wash.

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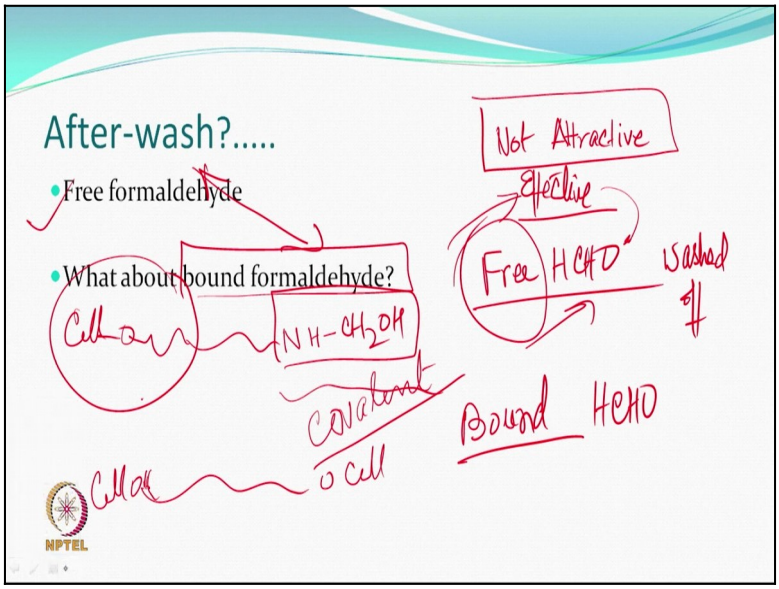

As I mentioned, a few minutes before, after-wash is not a very attractive proposition. Why? It is effective, but not attractive. Why, not attractive? Well. You have finished the fabric, completely. Now, you want to wash it. That means, the liquor again, comes to picture, wash liquor. And then, after that, you have to dry again. So, energy and water, both are going to be consumed more. Who likes that? Nobody.

And therefore, in a sense, whether we talk about economy, we talk about energy consumption, this cannot be considered, as very attractive proposition. So, what do we do? Should we, forget about it. But, no, it is an effective process. And, what is the effectiveness of this? That, anything which is free Formaldehyde, this will be washed off, surely. Of course, therefore it becomes effective. So, anything, which is free, on the fabric, will be washed off.

If that happens, then obviously, we will be having less amount of Formaldehyde, to be released, and we can be, happy about it. Now, the question that remains is, it is always possible, that, the Formaldehyde, which is not cross-linked, but is bound. For example, the cross-linking agent, which has one such group, which was supposed to have cross-linked, has not cross-linked, while the other one, end of this has, let us say, cross-linked, covalently bonded, shall we say.

So, this part is, this end of the cross-linking agent, has been covalently bonded, the other is free, could not, for some reason, react statistically. Can, after-wash, remove this bound

Formaldehyde? I am sure, you would agree with simple wash, this bound Formaldehyde is going to be difficult, to be removed. Are you, getting the point? So, after-wash can be effective, to definitely remove free Formaldehyde, but may not be effective, in removing, this bound Formaldehyde, because this bonding is also covalent. Is that right?

So, there is some limitation. But, we are quite sure, that this bound Formaldehyde release, is a slow process, which will depend on, hydrolytic stability, of this point, this area. This part of the cross-linking agent, if it had actually cross-linked, that if this particular thing had cellulose, on both sides, let us say, reacted, then the hydrolytic stability is much more, so release is much less. We are not saying, zero, but much less, compared to this part, which is a pendant hanging part. All right.

So, release can be here, during storage, during washing, during heating, and so on and so forth, certainly nothing compared to a free Formaldehyde, it will just evaporate, and come into the vapour form. So, good amount of problem is solved, but not all. So, yes, free Formaldehyde can be released, however, the bound Formaldehyde, can have some issue. Right. The bound Formaldehyde, can have some problem. All right. So, we see, what else can be done.

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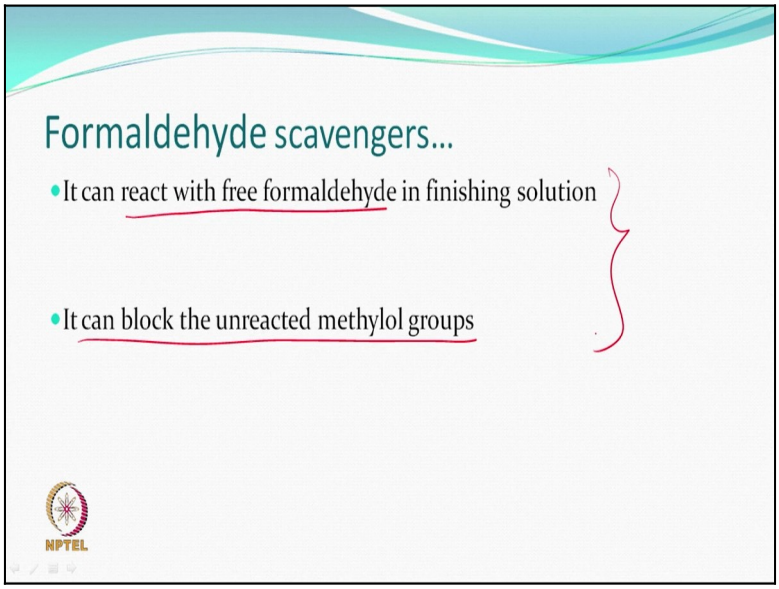

So, we can now think of, some other chemical agents, which we are referring to as, scavengers, Formaldehyde scavengers. These scavengers, can react with free Formaldehyde, if it is in solution. All right. They can also block, unreacted Methylol groups. So, thereby, they will be able to add value, reduce the possibility of hydrolysis, not make it zero, but

reduce. So, this is possible. So, they can be added to finishing agent, or finishing solutions of every bath. That is how, it can work.

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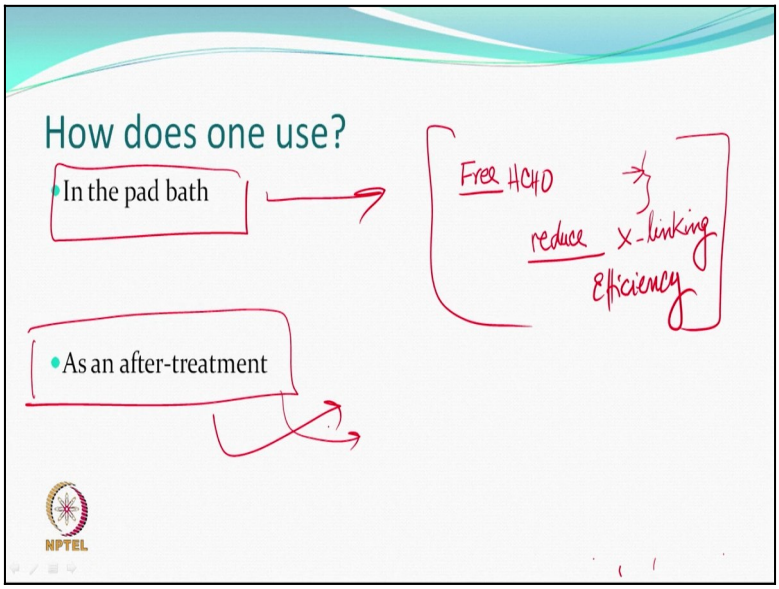

So, as we mentioned before also, you can use these scavengers, in the padding baths, or use them as an, after-treatment. Okay. So, scavengers can be used, either in the pad bath itself, so that together, with the cross-linking agent, the scavengers also go, to the drying and curing process, and control by, combining by the free Formaldehyde, combining with the unreacted part, or end of the cross-linking agent. So, that is one possibility.

But, if we use in the bath, so they can definitely remove, free Formaldehyde, the bind with the free Formaldehyde, but at the same time, if they can bind, with the Methylol groups, then it will be difficult for the Methylol group, to cross link now. So theoretically, what we are saying is, that they can definitely block, but at the same time, it may reduce the cross-linking efficiency. All right. So, what it means? You are compromising. You are compromising, on the effectiveness of the cross-linking itself.

Because, something which could cross link with, the cellulose, the hydroxyl group of cellulose, now has been bound, by some other agent, which is going to happen because, both of them are present together. So, this one becomes a limitation. Usefulness is there, but there is a limitation. As far as, the Formaldehyde release is concerned, you may be able to control it. But, you may have to agree, that there is going to be less cross-linking, and therefore, wrinkle recovery agents can drop, although Formaldehyde release, would be reduced.

The other is an, after-treatment. And, after-treatment means, what? After-treatment means, that you have already finished the fabric, and now you want to control, the presence of Formaldehyde there, by an after-treatment, with the scavenger. In this case, we are quite sure, cross-linking has already taken place.

Whatever has not cross-linked, is any way, available, and that could be bound. Anything, which is free, there is a Formaldehyde is there, it should be removed, or blocked. So, theoretically, although, this adds to the cost of production, or not, this will be the most effective way, of reducing the Formaldehyde, good for the user.

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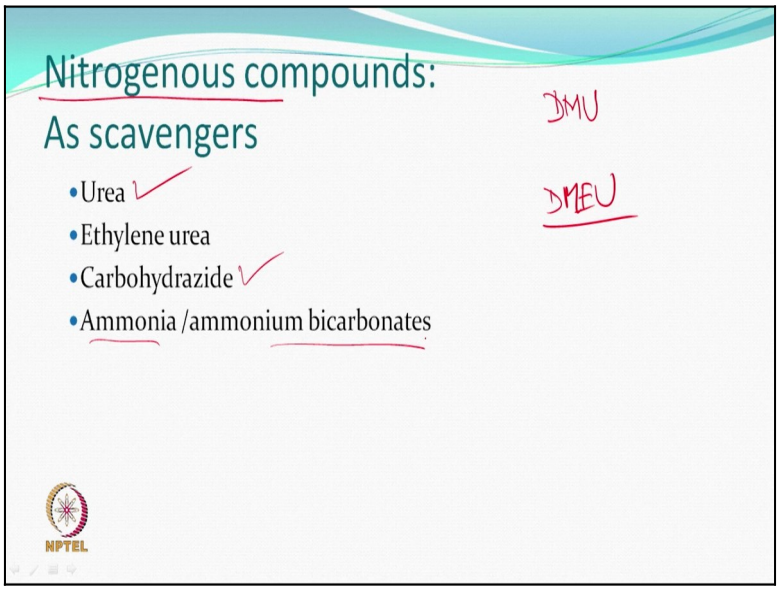

So, some suggestions, which are there, in terms of, scavengers. These scavengers, must be able to react. We have said, some group, called the Nitrogenous. Look at this, you have an interesting compound called, urea itself. Do you remember, we have a cross-linking agent, which is Dimethylol Urea, how was it produced. Obviously, it had a Formaldehyde, and urea. So, if there is a free Formaldehyde, or anything else, that is available, theoretically, urea can react with Formaldehyde. Similarly, other urea's, like DMU, how was it produced?

It was also produced by, Ethylene Urea. And so, if you use this, the Formaldehyde can again react with this. And, of course, other than that, there are other compound, which have been suggested, which is one of the interesting compound is, Carbohydrazide, which is relatively more reactive, and therefore it can bind, effectively, quickly anything, which is free Formaldehyde, and so on so forth. And, of course, Ammonia, or Carbonates, Bicarbonates of Ammonia, can also be used as, scavengers. Okay. Let us look at these, one by one.

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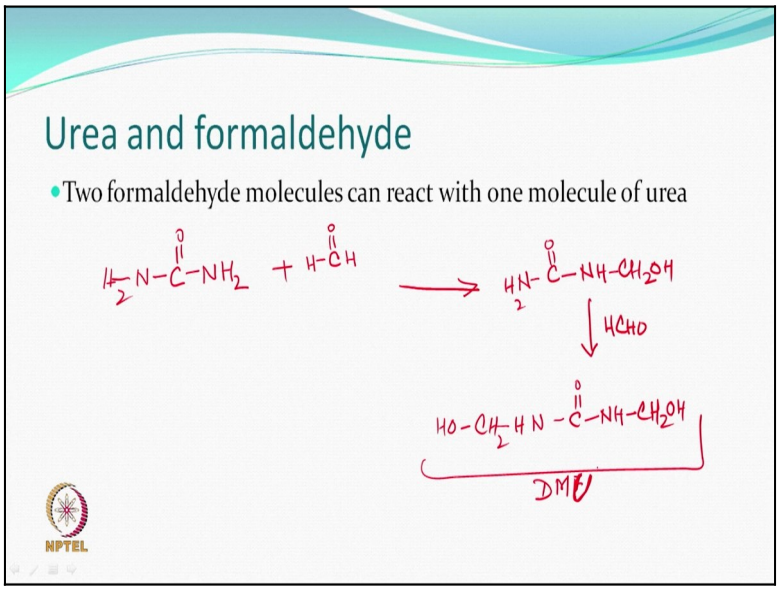

Urea and Formaldehyde. So, let us see, how was that possible. So, you have, urea. This is, urea. And, if we add a Formaldehyde, this will obviously give us, a compound like this. You recognize, this compound. Yes, this is the N-Methylol group. Right. So, it can further combine, with Formaldehyde, and give you, in effect, another N-Methylol group, by reacting with the other molecule, and you get. So, if you look at this, do you recognize this?

This compound is almost like, the cross-linking agent, we were using, earlier. But here, the role is reversed. There, we may have worked hard, to make a cross-linking agent, which can be reacted with cellulose. Now, there is the free Formaldehyde, available anywhere. And, it can react with the free Formaldehyde, to make a compound, which then can be removed, washed off, or kept, as it is.

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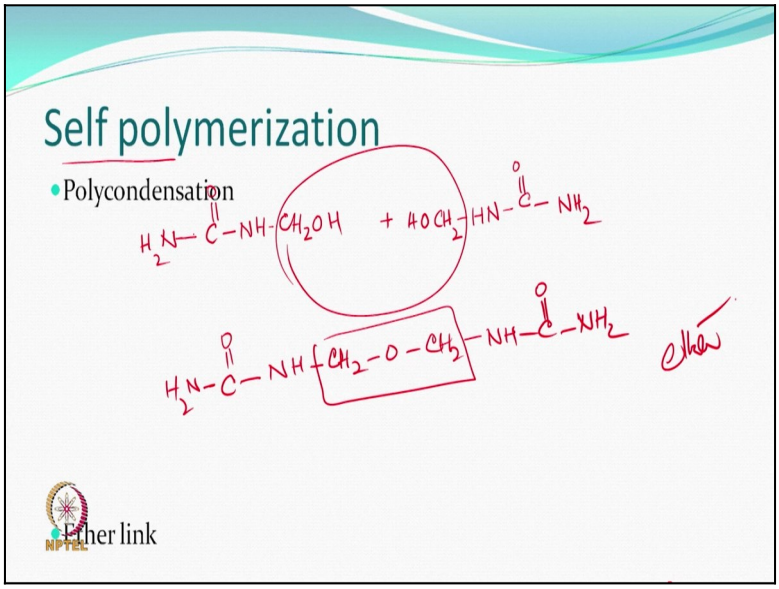

If you remember, these 2 types of groups, can actually react with themselves, and Self-Polymerization is something, we talked about. For example, if you have a compound, which is which has this N-Methylol group, because of the urea, that we have added. Let us say, this was only NH_2, in this end. But, you have, another agent of the similar type. So, one can think of reaction, in this area. And, what you likely to get is, a link like this. All right. So, what is this? This is, Self-condensation, all right, or a Poly-condensation.

So, you have many small molecules, and we will keep combining. So, this is self-condensation reaction. And, what kind of a group, they will be forming, is we are quite aware, of this kind of a group, which is, Ether. All right. So, this Ether linkage, can be produced. Therefore, you could produce, a bound Formaldehyde Foam based compound, which is the N-Methylol. You can produce, polycondensed material, which would also be bound by, many Formaldehyde units. Another possibility, also is there.

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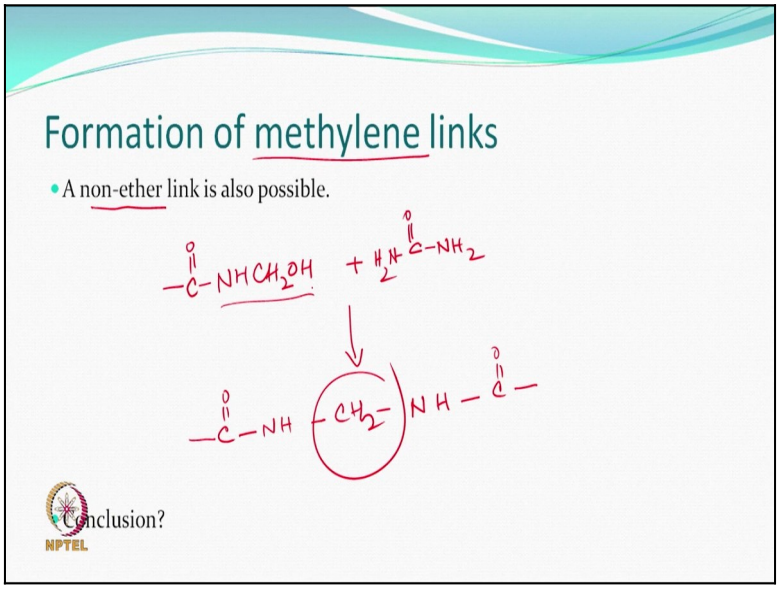

If, the Urea is available, and a Non-ether link, which is, let us say, the Methylene link, can also be produced. How you do that? For example, if you had the same compound, which was partially formed. We have seen that, same compound. And, instead of this, you have a simple urea, which was also available. And then, what can you form? You can form, another compound, which will look like this.

So, this link, is the Methylene link, which is a Non-ether link. So, you can produce, an Ether link with polycondensation, you can produce a Methylene link, with a reaction, with the free urea, which is available, along with this bound N-Methylol group. So, this reaction, will also be there. And of course, the formation of Dimethylol Urea type of compound also, is possible.

So, in some sense, the urea, if you add, in the bath, or as an after-treatment, you will be able to bind, free Formaldehyde, and also react with the bound Formaldehyde, to produce a different kind of a group, which will be relatively more stable, to hydrolysis. That makes sense, yeah. So, what is the conclusion? What is the conclusion?

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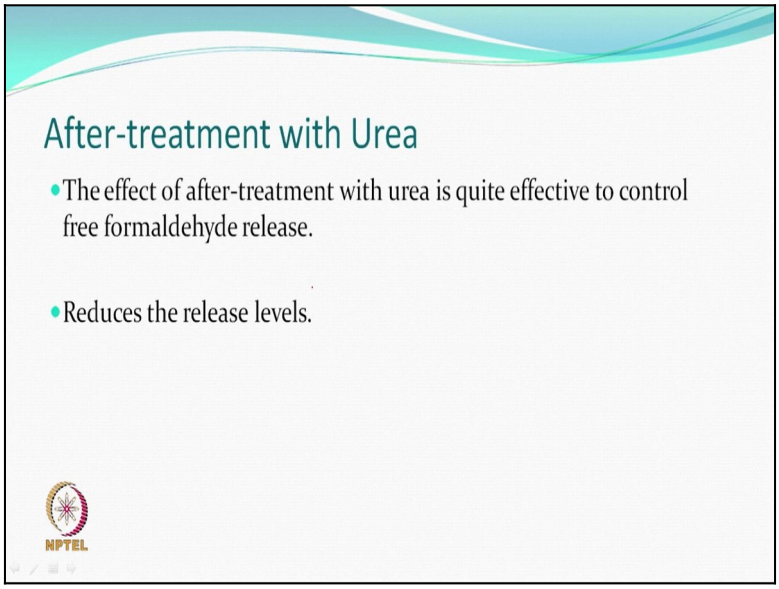

The conclusion is, that the after-treatment with urea, is an effective process, to control Formaldehyde release. And, what it means is, the release levels can come down, to such levels, which may be acceptable, for a particular use. So, depends on, how much have you been able to reduce, the release, application could be decided. It could be, either baby's clothing, or a decorative product, depends on, how much have you been able to reduce.

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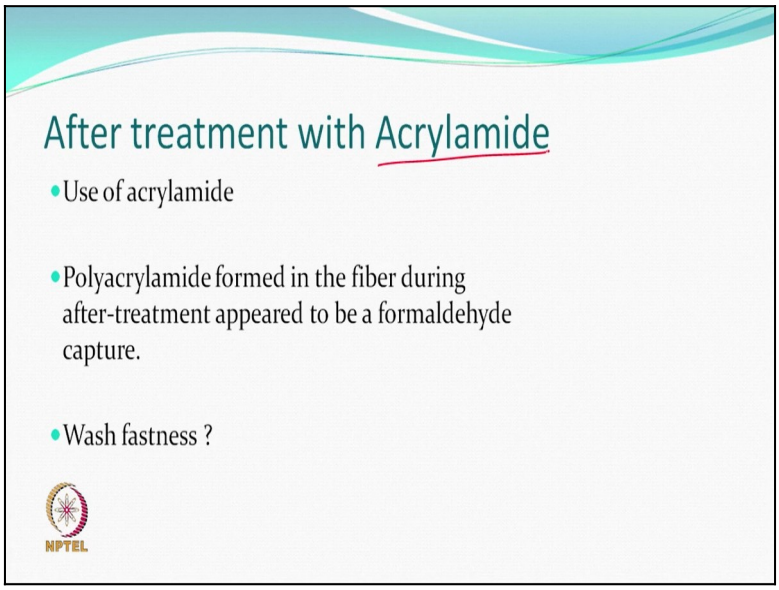

Similar to this, people have suggested, use of Acrylamide also, in the bath, or otherwise, where, these can react, with the Formaldehyde. And, by use of this, if we believe, that during this whole process, not only Formaldehyde, will be bound, but Acrylamide, can also become, Polyacrylamide. And, if Polyacrylamide is considered, then it is something, which cannot be very easily washed off also.

And, Formaldehyde would remain attached to this, for a longer period. And theoretically, we can also say, the Wash fastness, could be better. But, yes, there may be a risk, in this case, if polyacrylamide is there, on the surface also, if it has not been washed again, at some stage, the fabric may get a stiffer handle. Okay. You must remember, one important thing is, when you have finished the fabric, you have packaged it, and you are selling it, if the release takes place, during this period, this is from a customer point of view, is unacceptable.

But, does not mean, that a customer will never wash his fabric, or a garment. Right. If the first wash is controlled, before the first wash is controlled, afterwards the release is not going to be, very high. It is not going to be, very high. And, if they are bound also, then it will be much less. So, you should be able to control, the release by the scavengers, of this type. Urea, definitely was useful, cheaper also.

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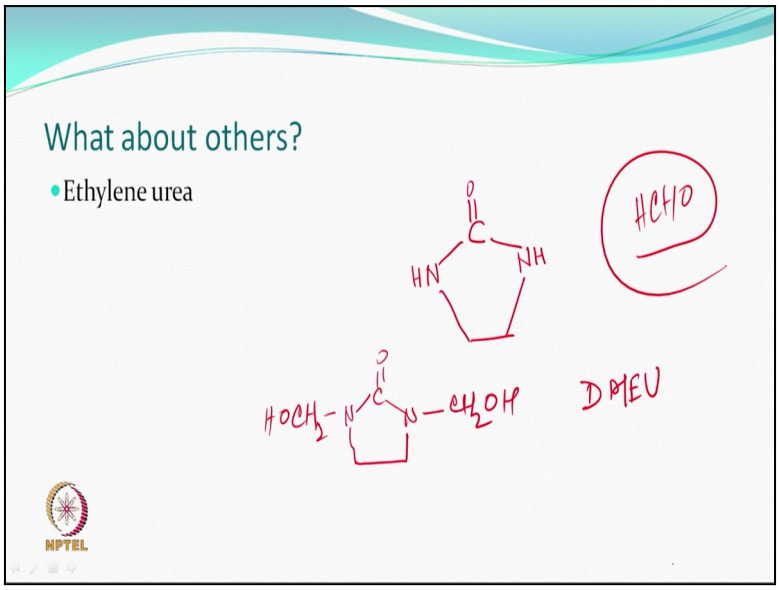

So, when we are talking about urea, you have Ethylene urea also. You remember, this Ethylene urea, we just talked about. It is also urea compound, but a cyclic urea. Right. So, this cyclic urea, is capable of reacting with Formaldehyde, and would produce what, will produce a compound, which we are quite familiar. What is this compound? Well, we call it DME. We already, understood earlier, because of the cyclic nature, the condensation, will not be favoured very much, polycondensation, will not be favoured very much.

But, binding with any Formaldehyde group, binding with itself, it can react to, with another urea, compounded itself, and make Methylene group is possible. But, at least, it has been able

to control, some of the Formaldehyde, which may be present. So, this type of urea's, have also been suggested, as scavengers.

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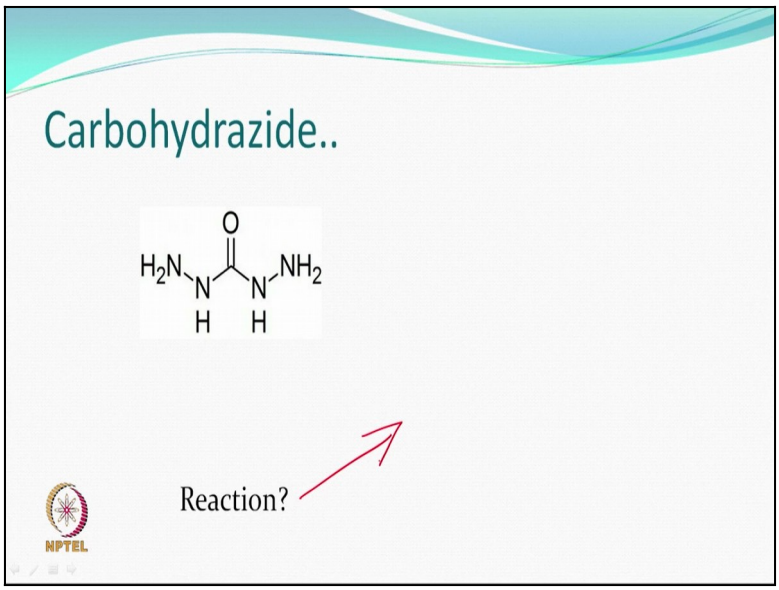

The interesting compound, which has also been experimented with, is Carbohydrazide. And now, it looks almost like urea, but has got more Nitrogen, and therefore, is a much more reactive compound, and can react with the Formaldehyde. I will like, for you to find out, how did the reaction takes place? I am sure, you can do that exercise. If you know, how to do it, with the how to how the urea reacts, if you know that, then obviously, you will know, how to write an equation, which is, with Carbohydrazide. But, it is an effective compound.

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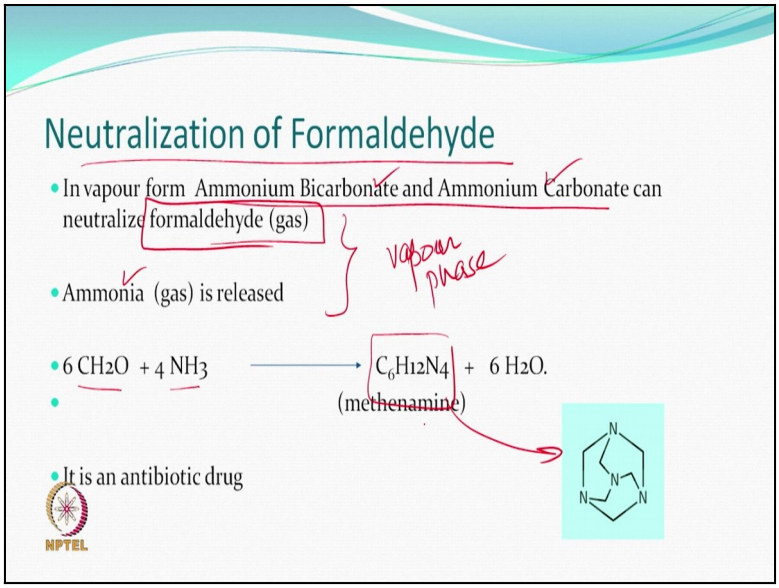

Another application, which has been tried, instead of calling it a scavenger, it is also sometimes known as, Neutralization of Formaldehyde. And, how does happen? Well. If you

use, Ammonia. So, you have, Ammonium Bicarbonate, Ammonium carbonate. And, if this is available, for example, Formaldehyde in a vapour form, can react with what? These Carbonates, and Bicarbonates, can release, Ammonia.

If they release ammonia, what it means is, that both are gases, in the vapour form, vapour phase, an interesting reaction occurs, with Formaldehyde. And, which people call it as, Neutralization of Formaldehyde. And, what is this? So, Formaldehyde 6 molecules, react with 4 molecules of Ammonia, which is being released during this, let us say, curing, post-curing process, and you get this interesting compound, which has a structure like this.

And, this is interesting, in the sense, that this is a drug. This is a drug, an antibiotic drug, which is used to control, urinary tract infections. It controls, the growth of bacteria. And so, it is another interesting by-product. If somebody wants to use this, you can use, control the Formaldehyde, as well as, make another interesting product. So, this also has been suggested, as one of the ways, to control.

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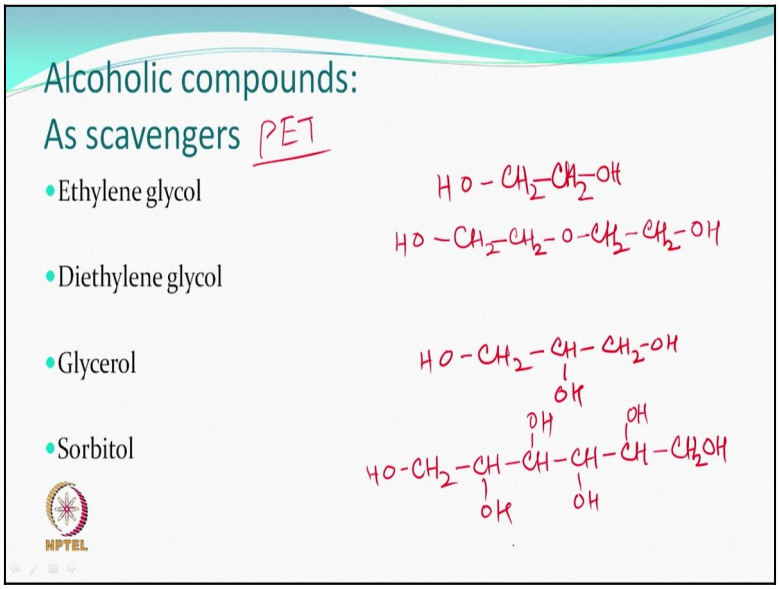

Then, there are other compound, which are Non-nitrogenous. Right, Non-nitrogenous compounds. Some of them, are called the, Alcoholic compounds, which are also used as, scavengers. Ethylene glycol, I am sure, you are quite familiar with this, compound. Where does it used? Where is it used? It is used, in the manufacture of, Polyethylene terephthalate. Right. It is one of the monomers, which is used for, preparation, manufacture, synthesis of Polyester. Right.

But here, we are looking at this, from a different perspective. What is Ethylene glycol, do you remember? Okay. This interesting compound, let us see. Then, another compound, which is the derivative of this compound, called the Diethylene glycol. So, 2 Ethylene molecule, 2 Glycol molecules, would make this compound. Interesting compound, is a hydroxyl compound, again alcoholic compound. Another compound, which has been suggested for this purpose, could be Glycerol.

Glycerol, you know, is like this. It is an interesting compound, again. What are we aiming at? We are aiming that, hydroxyl groups available, can react with also, Formaldehyde, had certain conditions. And, the conditions could be, curing conditions, the hot conditions, that we actually use. If we are going for a simultaneously, padding and drying, curing, then you can add in a pad bath, or as an after-treatment, whatever you want, you can do that.

Another compound, which has been suggested is, Sorbitol, which is, a 6 carbon compound. So, you have hydroxyl group, of course on both sides, but also on other carbons, as well. So, you have 6 hydroxyl groups, available for binding, a Formaldehyde compound. Interesting. More the merrier.

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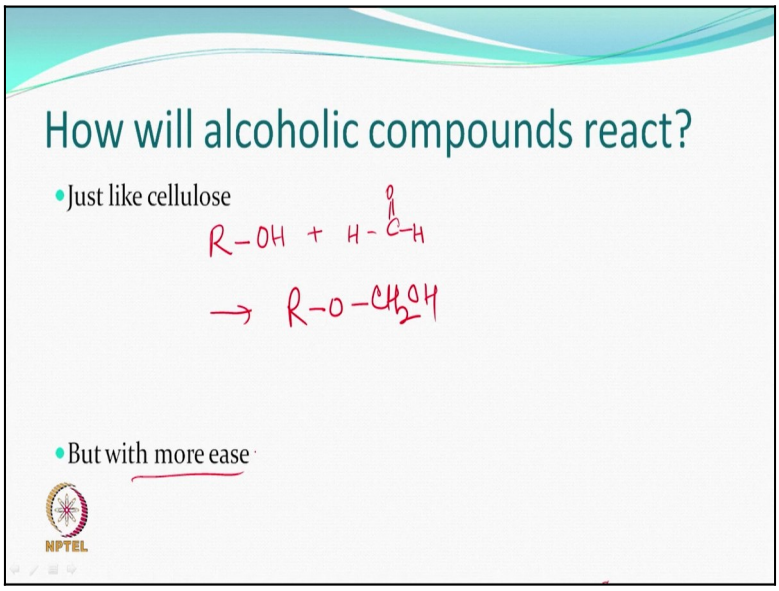

How will these compound reacts? Well. Cellulose also had, a Hydroxyl group. So, Hydroxyl group, obviously can react. So, there is no doubt about that, isn't it? So, we would be able to work around. And, this reaction, let us say, with some alcohol like this, we represent this, ROH + Formaldehyde, can give, through an addition reaction, a compound, which will be,

like this. Interesting. So, you are producing, another compound, which is binding, and alcoholic. So, the only thing is, it can be done, at a much more, simpler, easier conditions.

Because, these groups are available as molecules, which can be, anywhere, wherever, Formaldehyde is required, and statistically, possibly, some reactions like this, can be done. It is definitely an interesting proposition. And, we would be able to therefore, control the release of these groups, as well. Similarly, reactions can take place with, the other Hydroxyl groups available, which could be, another CH_2OH group, which can also react.

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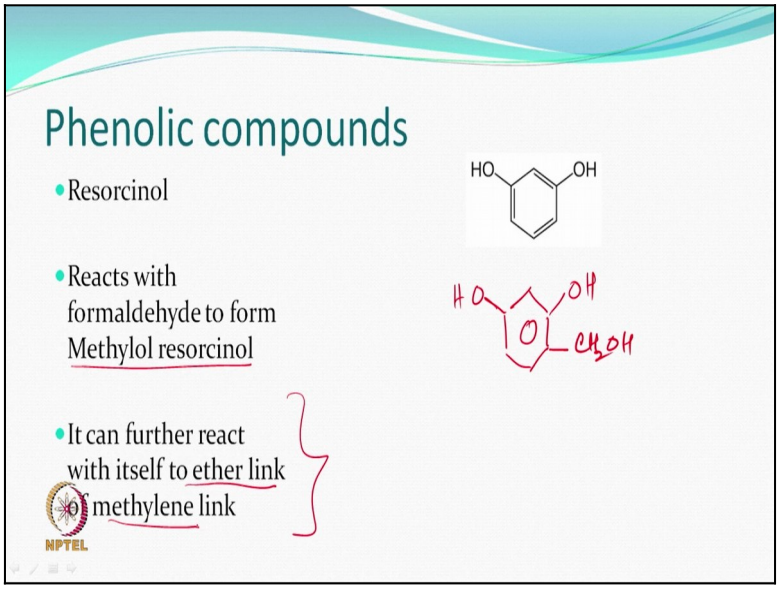

Similar to these compounds, Phenolic compounds, have been suggested. One of the interesting compounds, that you have, is known as, Resorcinol. Right. Resorcinol. And, this compound is also in some sense, is similar to what we have seen, and theoretically can make, Methylol Resorcinol, which would be, let us say, the same compound, after some reaction, can add, let us say, it has been suggested. Therefore, Nitrogenous, Non-nitrogenous compounds, have been suggested, which can be used, to control the release of Formaldehyde.

They can be used, in the pad bath, or as an after-treatment, one will have to be being selective, one should be selective, on what kind of process that you want to use. Theoretically, this compound, which has been formed, can also react to make, either an Ether link, or a Methylene link. So, I would like you, to do this yourself, in your notebooks. I do not have to, write it down. Almost, similar to, what we did previously, with Urea.

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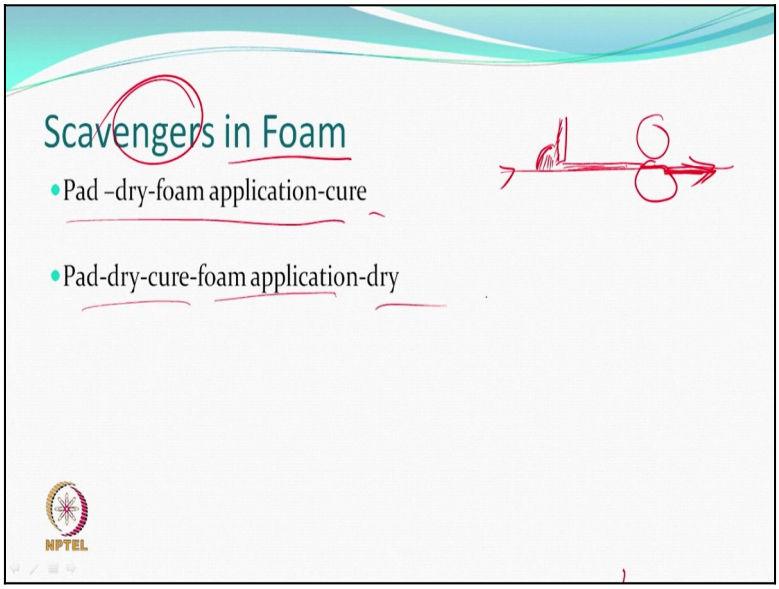

So, when we talk about application, of course, you can apply, through a pad dry process, padding process, you want, even if you are giving the after-treatment, you can pad through scavenger solutions, and then dry and cure, if it is required. That is the, Padding process. So, we are quite familiar with it. But, people have said to avoid, excessive use of water, and excessive use of drying, therefore reducing the energy required, through this process, people have used, Foam.

You must have heard of, Foam finishing. If not, we will talk about it, sometimes. That is, what is a Foam? Foam is, some liquid and air, which has been injected into it, and you have bubbles. And, Bubbles mean, a large amount of volume, of this bubble is air, the skin of the bubble, is basically made of liquid, which contains, the scavenger also, and of course, some water.

So, in some sense, what are we doing is, instead of diluting, making a dilute solution with adding more and more water, you are diluting this solution, by adding more and more air. Advantage, you can appreciate. That, once the Foam is applied, which can be applied by, any method, that you can think of. You can coat it. There are coating methods. And, you break the foam, by any method like, passing through a nip.

For example, there is a nip roll. The fabric is passing through, this nip roll. Here, let us say, you had created some applicator, which can apply Foam. So, the Foam, which contains the scavenger, is being applied, and it get broken, here. And then, you have, less wet fabric moving out. Obviously, if suppose, 80% is air, or 90% is air, then the water is very less. So,

your energy required to drive, will be less. Use and consumption of water, will be less. And mostly, it will be, scavengers.

So therefore, from energy point of view, people has suggested, that you can use Foam. Well. Whether you use, a Pad-Dry-Foam and cure, which is okay, or you can use, Pad-Dry-Cure-Foam and dry. So, whichever process, one wants to use, in his own wisdom, can be used. But definitely, this is not looks like a very interesting proposition, from the application point of view. Compare it with, let us say, padding, where lot of water, will have to be, also used. You understand, you remember, that wet expression. Yeah.

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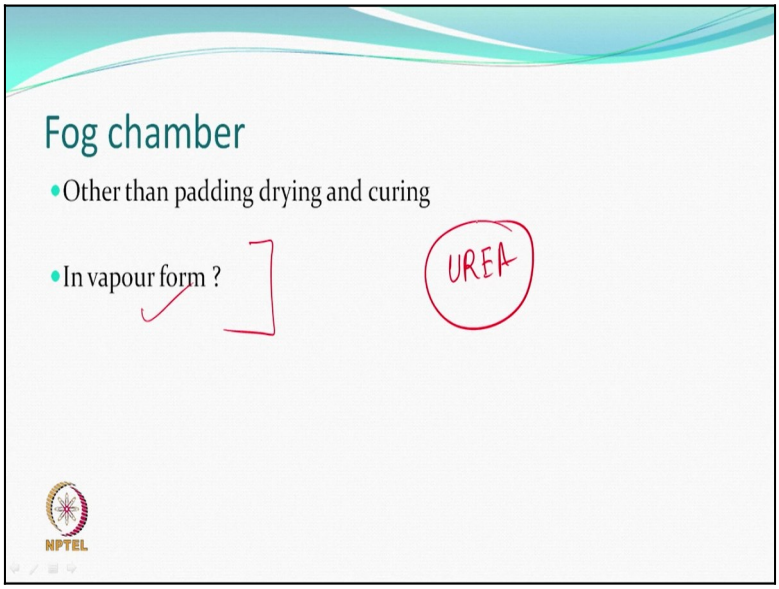

Interesting, Fog chamber. That is, you create Fog, Mist. And, if possible, let us say, while you are curing, if there is a free Formaldehyde, is going to go where. It is going to go, in the air, as a vapour. If, in this situation, you introduce, Fog, or a Mist, by atomization process, okay, then, both are in, in some sense, in the vapour, in the environment, of the chamber, or a Stenter, or whatever you are using, and they react in the vapour form.

And then, in the vapour form itself, they can be extracted also, and then of course, treated very nicely, like you have a scrubber, through which, this exhaust can pass, and then, you can remove these compounds. All right. This becomes, a very interesting way, to treat. So, Fog chamber is, another application system, where the scavenger is also, in some sense, in a vapour form.

And, the Formaldehyde also will be, in a vapour form. And, reaction takes place, in the vapour form. In the foam fog chamber, Urea itself, has been used. Again, interesting way to apply. And, these things can happen, almost, as you are going through a padding, drying, and curing process, okay, reaction can take place. So, let us see, what have we done, today.

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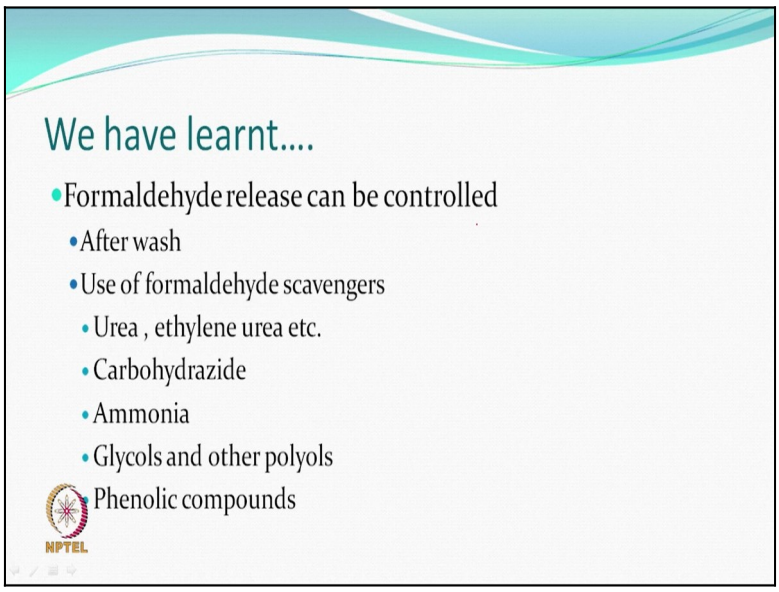

We have understood that, if you can use Formaldehyde, free cross linking agents, obviously, there is nothing like, it is the best solution, we do not have to worry about it. But, a good number of agents, which are formaldehyde based agents, or effective cross linking agents, and from them, we would like to work on the, controlled release. And therefore, there can be various methods.

One of the method, of course, is the after-wash, which we decided that, at least for free formaldehyde, it is a good idea. Or, scavengers, which can be used, in the pad bath, or can be used in, after-treatment. Whether, Urea, Ethylene urea, etc, they can be reacted. Carbohydrazide, Ammonia, Glycol, other Polyols, as well as, various Phenolic compounds, can be used as, scavengers.

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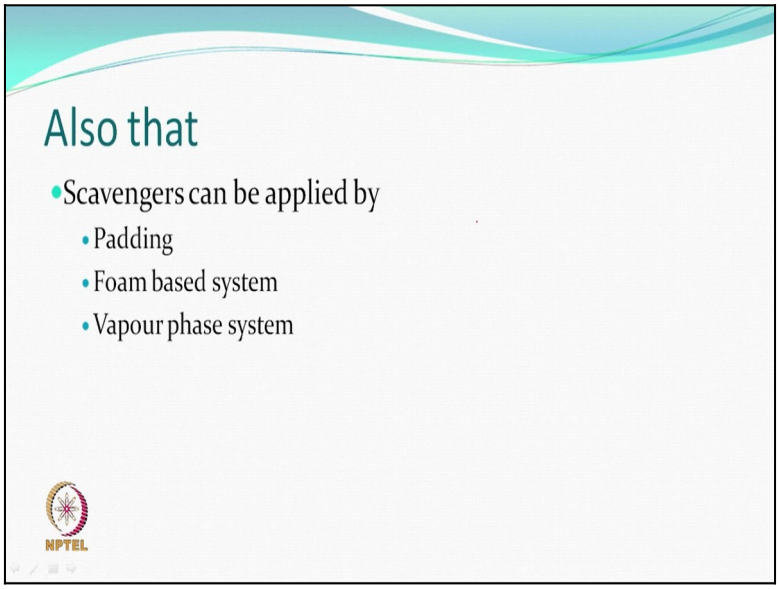

And also, we learned, that you can of course, apply these by Padding process, you can apply them, through a Foam based system, or in a vapour based system, these scavengers can be applied, effectively. Finally, obviously, to reduce, the release of formaldehyde, in the environment. So, we stop here. And, in the next lecture, we will take up, another finishing process. Till now, we have been talking about, cross linking agents, anti-crease, or crease resistant, finishing process. And now, we will take up, a next finishing process, which is, Stiffening process. So, Stiff finishing, which we will have a look at it. See you, next time, Thank you.