Textile Finishing
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Module - 6
Lecture - 15
Water Repellency Continued

So, welcome back to this class on textile finishing. Before we go further, let us just revise what did we do last time. So, we did learn about the theory of water repellency.

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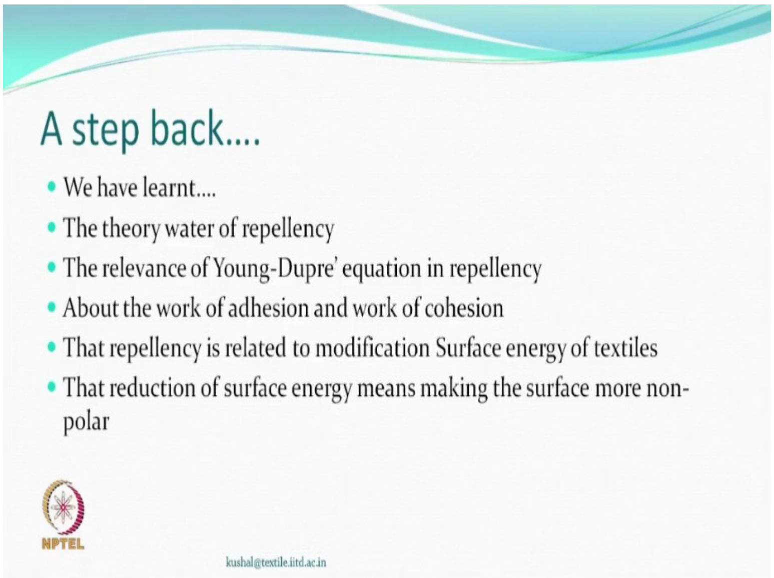

And the relevance of the Young and Dupre's equation in terms of determining whether it is going to be repellent or going to be more attractive to let us say water or any liquid, the solid surface that we are talking about. And we also learned what is called the work of adhesion and what is the work of cohesion. And we did agree that repellency is related to modification of surface energy of textiles; and that the reduction in surface energy generally means making the surfaces more non-polar. Okay. That is what we have learnt.

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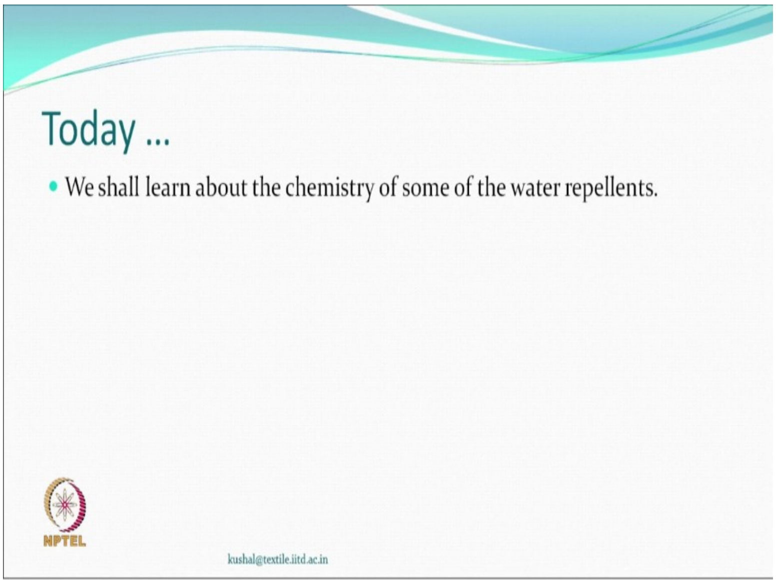

Today, we will spend some time on learning about chemistry of some of the water repellents. And general reason why we are using these. So, let us recall again. Surface energy of textile is an important criterion in determining whether the surface going to be repellent or not. Okay. We are talking about water repellency. So, what do we need? what do we need? Do we need to increase the surface energy or decrease the surface energy? What do we need? You want to increase surface energy or decrease surface energy, if you are looking at water repellency. Alright.

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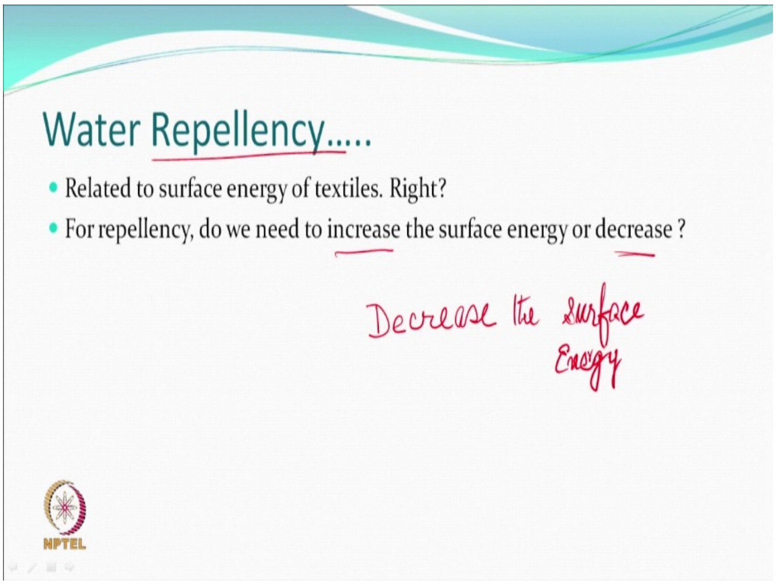

If you are looking at water repellency, should we increase or decrease? Yeah, we should do all hard work to decrease. Alright. That is what we should do.

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So, let us say, some water repellents, we will try to work around as to what they are.

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Look at this. You remember something? Waxes. Hydrocarbons like alkanes; they have been suggested. Why have they been suggested? Because, they are hydrophobic in character; hydrophobic. If they are hydrophobic in character, so they should repel water. That is the minimum thing that they should do; otherwise, why are they call hydrophobic. So, simple logic. If you want to repellency, use hydrophobic agents, create hydrophobic surfaces.

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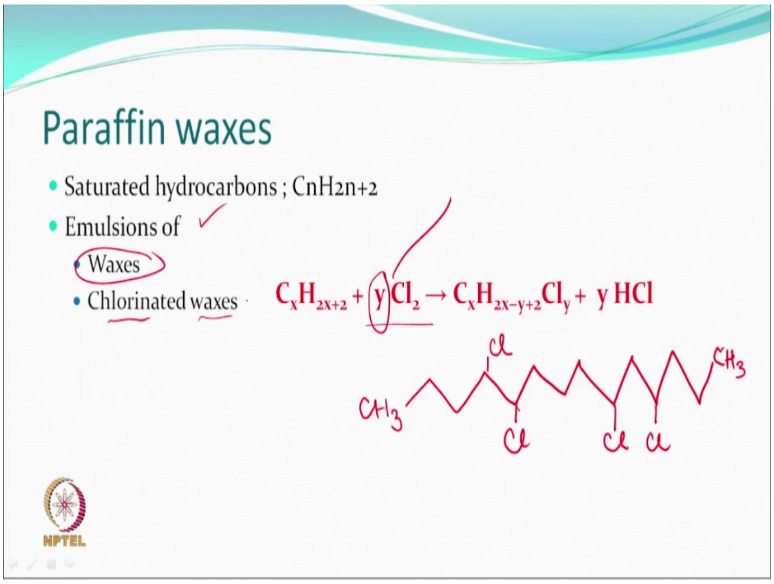

So, you can use as emulsions of waxes. The wax is what we just talked about; paraffins. Also, modified waxes like chlorinated waxes also can be used. And this chlorine, if it is available, can do something else also. We will talk later about it. But they definitely are hydrophobic agents. And if you apply onto a textile, a hydrophobic agent, the water is going to be repelled. So, you are looking at water repellency.

So, the chlorinated waxes obviously have been reacted with chlorine, so that the chlorine gets attached and becomes part of the molecule. Therefore, they are called chlorinated waxes. But they do melt. They can be turned into emulsions, converted to emulsion which can be applied. And this normally, hydrocarbon for example. You have CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2, CH_2; whatever number there we are talking about; and then you get into the end of the hydrocarbon.

And if you want a chlorinated hydrocarbon; so, probably you may have done this. So, you have a chlorine atom here. And maybe very near here or some spaces are left and then it is there, how much chlorine you want to attach depends on how much you have taken. So, these kinds of slightly branched therefore by chlorine itself has been considered as one of the flame-retardant.

Like, if you know the PVC cables which the electrical cables are connected or covered with the PVC, right, coating. So, the chlorine is an important one as per the flame retardants is concerned. So, it can be a wax which can be applied. And you can simultaneously hope to get some flame retardancy as well. But in any case, they definitely are waxes. They can be dissolved. They can be emulsified. And you can apply onto the textile.

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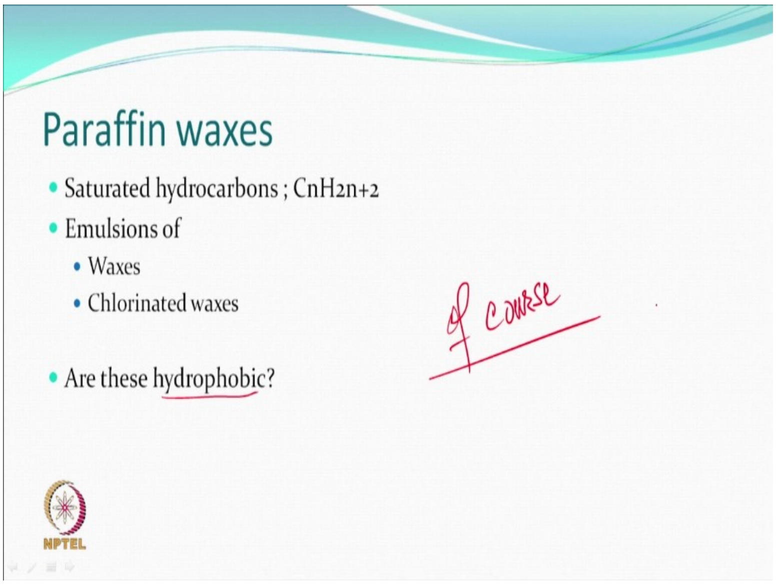

So, this question has been answered. Are they hydrophobic? Of course, they are hydrophobic. And that is what becomes the way in which you want to say.

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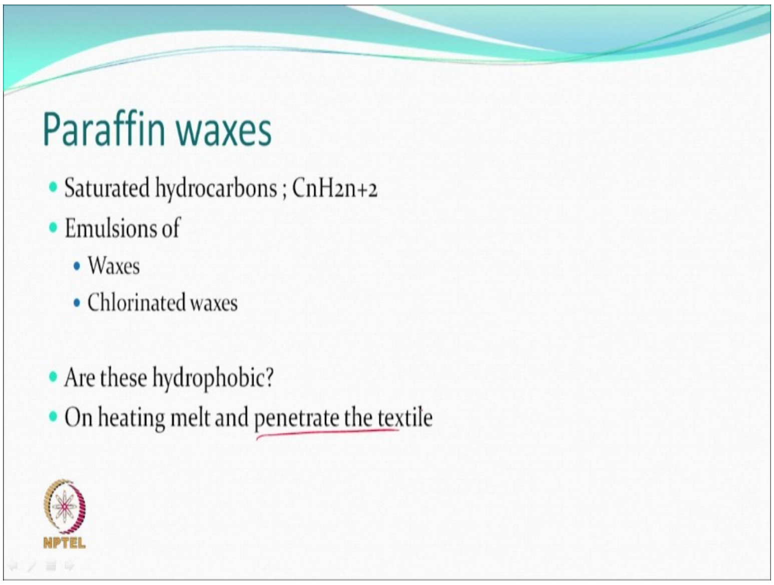

And we expect that, when we go to higher temperatures, they are going to melt. Because, they will have a melting point which will be much lower than any other thing that we can think of, 60 to 80 degrees or less. So, you can apply, and they can penetrate into the textiles also. In some sense, if they are more, then it can actually cover the interstices also. Other than repelling, they may do, increase the resistance of penetration also. Although, in repellency, it is not our aim. Right. So, what do we learn here?

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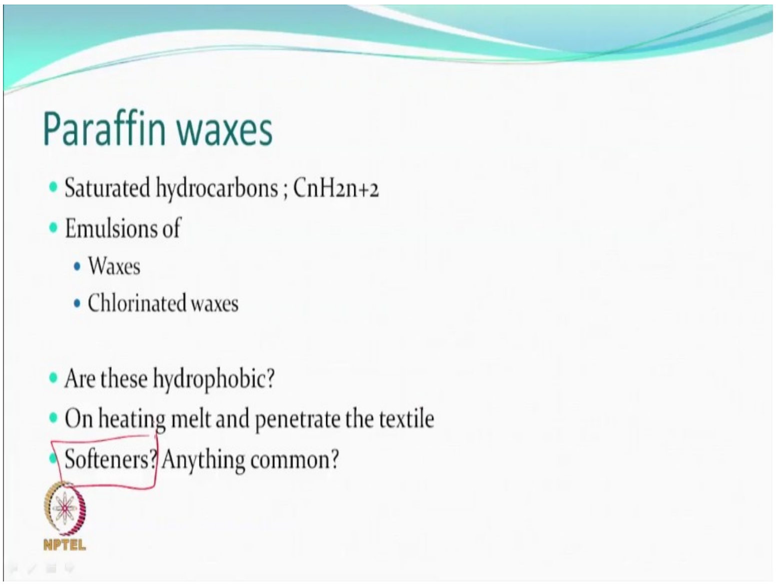

You remember softeners? Anything in common? Softeners also had a hydrophobe. Right. So, you, that means, a hydrophobic systems, if they are applied in different quantities, can obviously give softness, reduced friction, which they have to do. But because they do not like water, therefore they can be also used for or used as water repellents. And the processes can be very simple, pad and dry.

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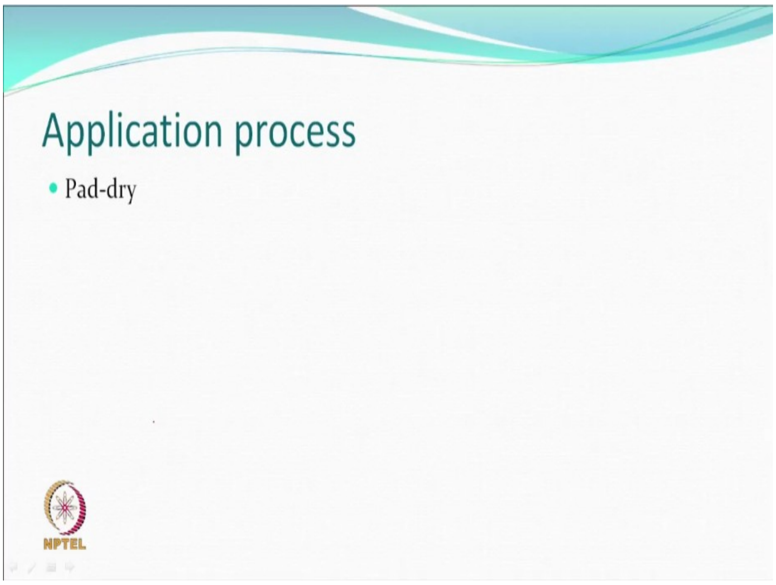

Because we are not expecting any reaction here. And they just go onto the textile surface and stay there. There are some of these things can be used for tents and so on so forth; can work, theoretically they do give the repellency effects.

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Learning from here only, from the waxes. So, you had the stearic acid, is one of the things. You can use any type of a long chain hydrocarbon, alcohol or an acid which can work. But, just taking some of the examples based on a stearic acid. Okay.

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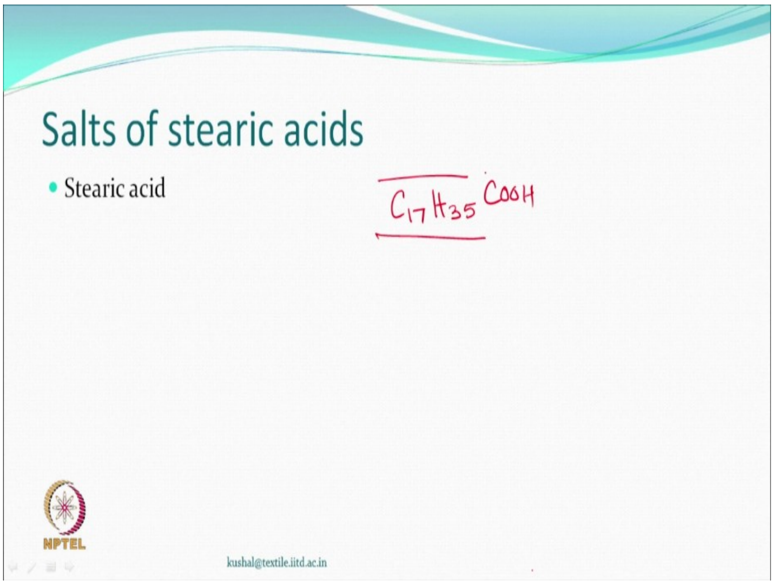

Stearic acid, you remember, is; or let us put it the other way. By itself, although it is an acid, it is not so much soluble in water. But it has got this hydrophobic entity which is going to help in repellency. Alright.

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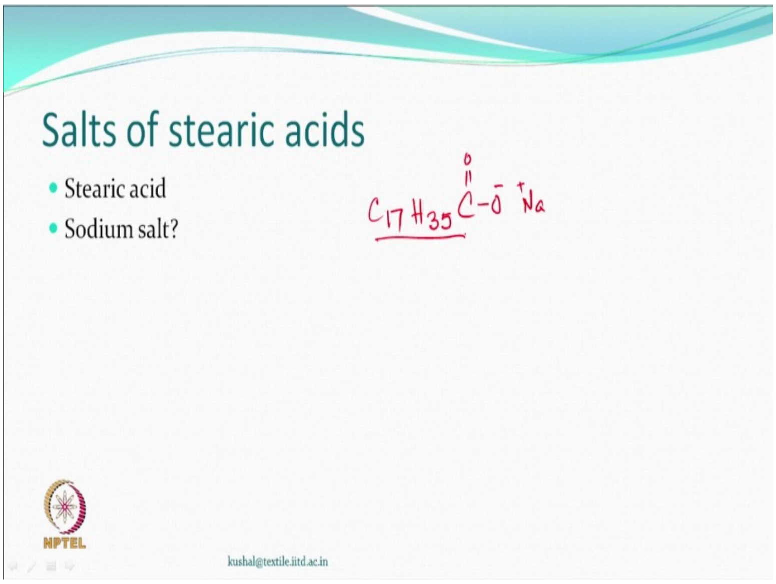

If you have the sodium salt of this which may be, you recall. Alright. The sodium salt is; if you remember, is it water soluble? Sodium salt, is it water soluble? And you remember this compound somewhere? So, this could also be used as a softener; Interesting. But, because of this hydrophobic nature again, you can probably think of it as a surfactant as a water repellent also.

But, because of the solubility, the permanency may not be there. But let us see, if you remember the ordinary soaps with which people use to wash fabrics and we say the hard water is a issue, because the scum would form. Right.

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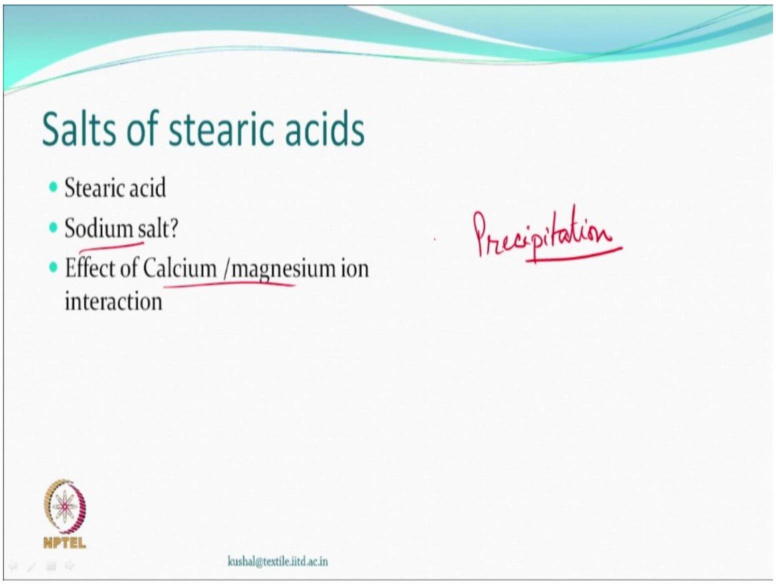

So, if the sodium salt gets replaced by calcium or magnesium salt. You get precipitation. Right. That means, they are not water soluble anymore, because of the bivalent nature of these ions. Okay. So, this interaction, if happens, then the sodium salt gets replaced by the calcium magnesium and they become relatively water soluble. So, what it means is, the durability could be increased. That is one.

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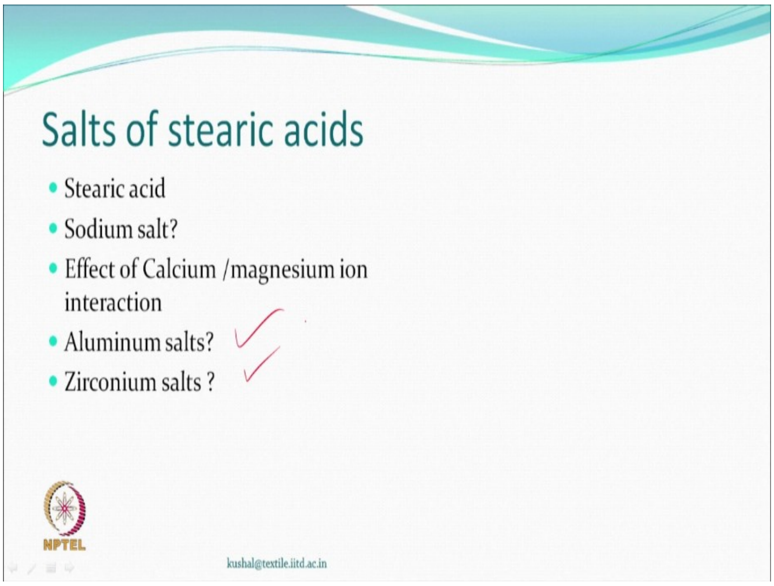

And people have tried things like aluminum salts of stearic acids and zirconium salts of static acid, which can act as efficient water repellents.

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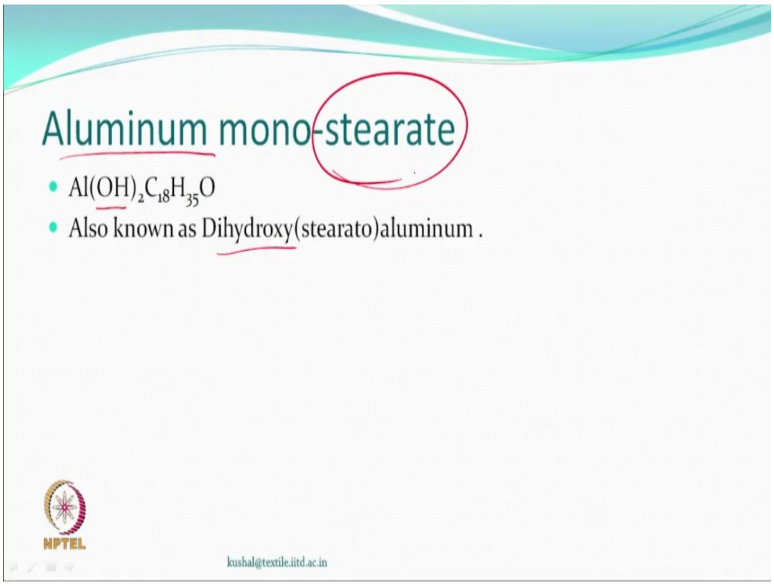

For example, aluminum mono-stearate. It is also known as, got 2 hydroxyl groups; therefore, it is also known as dihydroxy stearato aluminum. Alright. The, so what is important obviously is the stearate part of it. Others are somehow to ensure that there is some adhesion that it is not water soluble. But still, it can adhere.

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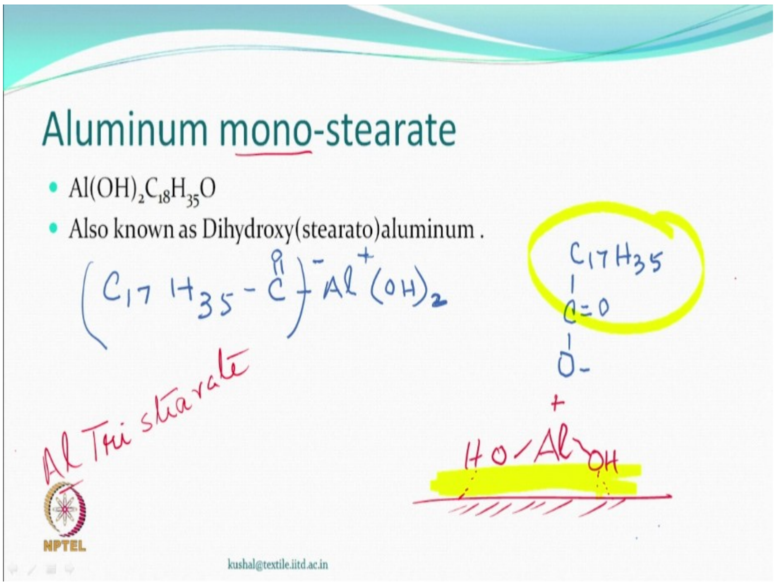

So, this compound is again, has a stearic group. Aluminum has got 2 hydroxides and is ionic, but not water soluble like a sodium salt. And what can happen also is that you have these hydroxides which can also get associated. Aluminum is there. This stearic group is already here. And so, all this becomes some kind of an association can happen with the textile surface, while this part would give us the hydrophobicity; and therefore, repel repellency.

And this part will not only give a non-solubility, but also will have possibility of some type of attraction; possibility of some type of an attraction. Right. Now so, it is not just the mono-stearate that can be used, you can always have a tristearate or distearate. So, aluminum tristearate; which would mean, it becomes very large molecule which would have more number of stearate; also so with one. Definitely solubility will be very, very low in water. And so, in some sense you can say, permanency will be more.

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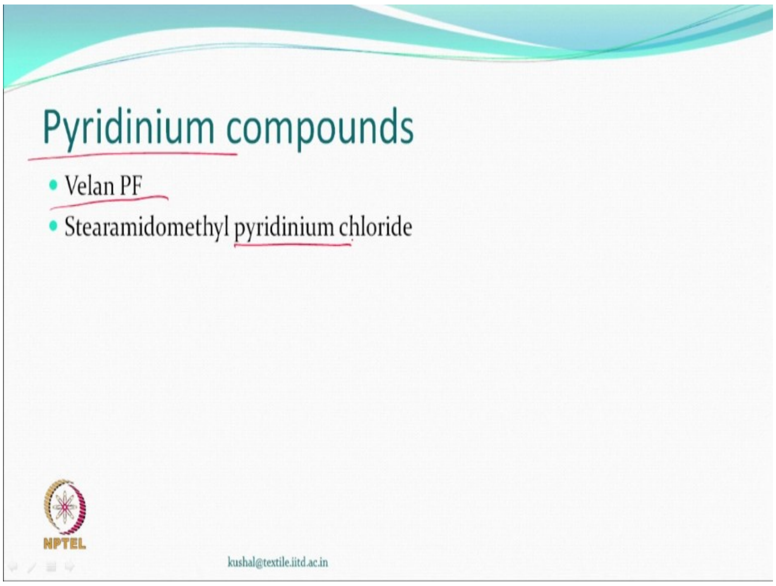

Then, if you remember, in our earlier discussions, we had used somewhere a pyridinium compounds also. You know, they can be in some sense, can react. So, they will be reactive. They can make in a way, covenant bond also. If you remember, they can make covenant bonds. We had talked about in cross linking agents as well. Velan PF was one of the commercial reactive water repellents based on the pyridinium salt. Okay. It is called the stearamidomethyl pyridinium chloride.

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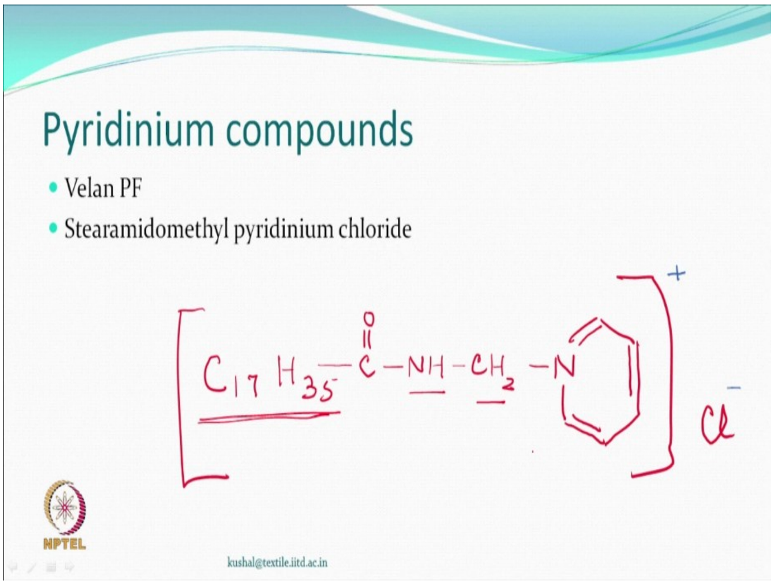

And this is the stearic part. This is the amido part. This is the methyl. And you have the pyridinium chloride. So, you remember, pyridine will go out; HCl will go out; and you will have; let us say, with cellulose or any other such group, you can, hydroxyl group of cellulose; it can make the covalent bond also. So, you can have in some sense a reactive group. So, this would go out. Finally, what will remain is only this group and not the pyridine. Pyridine will go away as a byproduct. Right. This what we remember.

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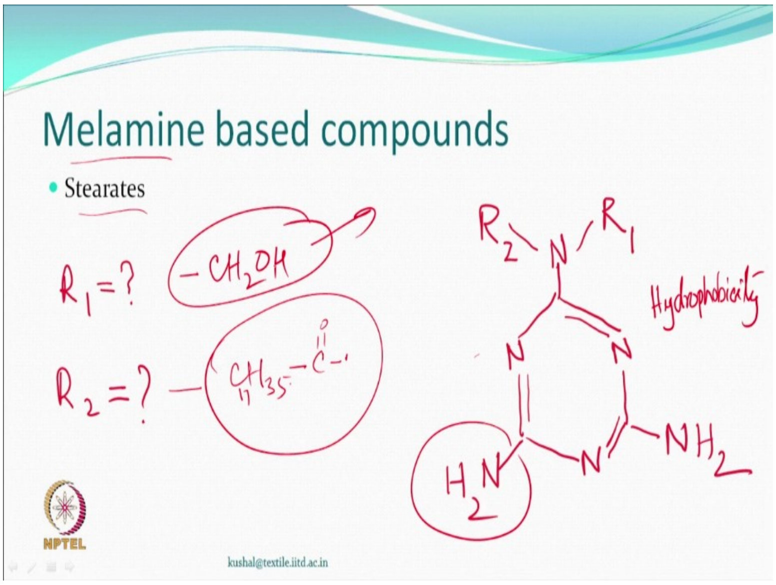

Melamine also are quite familiar. If you have stearates based on melamine based compounds, they can also be available. And you can also make them reactive. And how do we make them reactive? Well, in this case, for example, you have R_1, R_2. If the R_1 is let us say CH_2OH. Then, it can react. We know that. We need not have more CH_2OH, because one of, we are not interested in cross linking.

We are only interested in some formation of a covalent bond, which can happen. Right. And the R_2 can be whatever you want. You can have stearates. So, you can actually think of, you know, a stearate. That means $C_{17}H_{35}COO$-. This group can be attached here. If you want more of R_2s, so you can replace one of the H here and you can make another compound which can be attached, for example here.

And you can replace this group in a way with R_2. That is the, it will be connected with, like this only, but with another steric or stearate group. So, that way, you can increase the hydrophobicity. Reaction with the substrate can occur through this. If there are more of these groups, then they can make a network structure if the substrate is not reactive. And then, they can make a film.

Therefore, permanency or shall we say the wash fastness of this could be improved. Hydrophobicity will improve based on the length of the R_2 as far as this, the carbon chain length is concerned. And also, how many of this, you are going to be adding to this melamine compound. So, you remember? So, whatever kind of a thing that we have used before, all those kind of, you know groups and compounds can be used for water repellency as well. And now, they will be generally reactive, let us hope.

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Then, if you remember, we did earlier talk about silicon based compound, but now we are talking about the silicon based water repellents. So, what do you recall?

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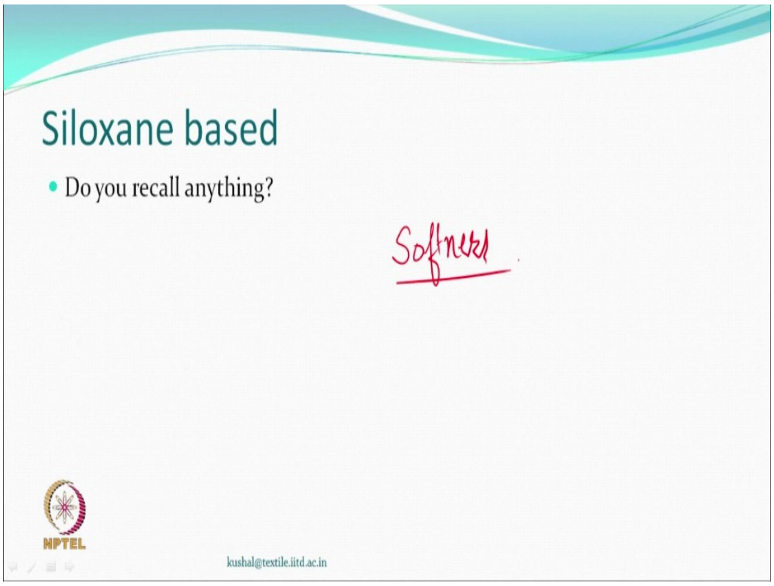

The siloxane based compounds were used for what? As softeners. Right.

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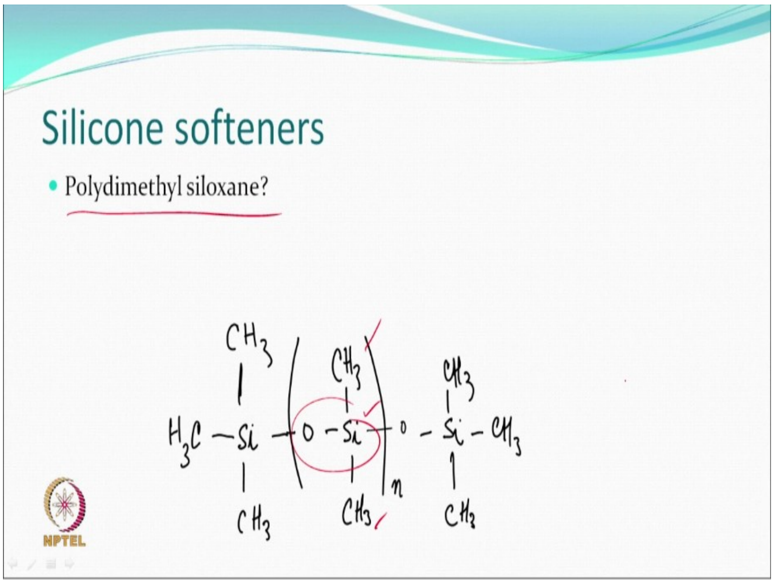

This is one of the examples, you remember? So, you had the silicon group. And this is the siloxane dimethyl polysiloxane. So, because of this, lot of methyl groups, it would give surface friction reduction. Alright. That is what we had seen. And how did we apply them?

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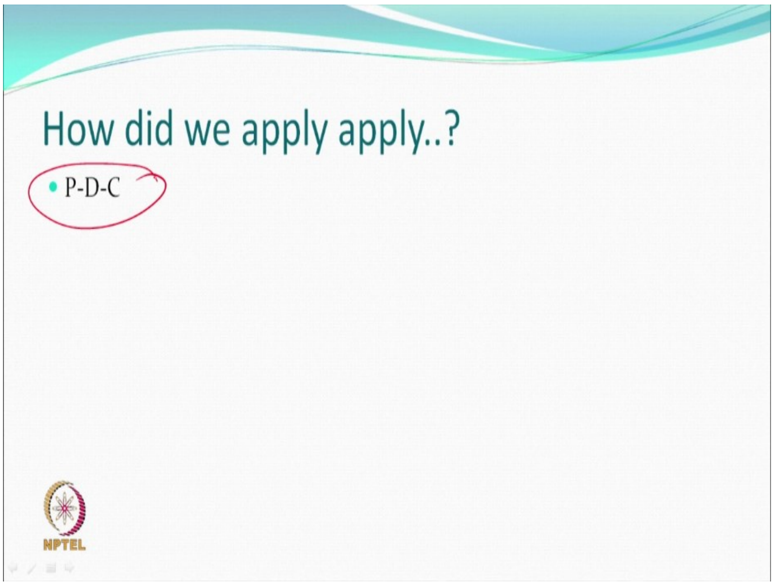

How do we apply to the textile? We applied through a pad-dry-cure process. Because we believe that, based on whether there is a part of the group is reactive; or otherwise, they can make a film like thing on the surface of the fiber yarn or thing. And you get softness. Now, the question that remains is;

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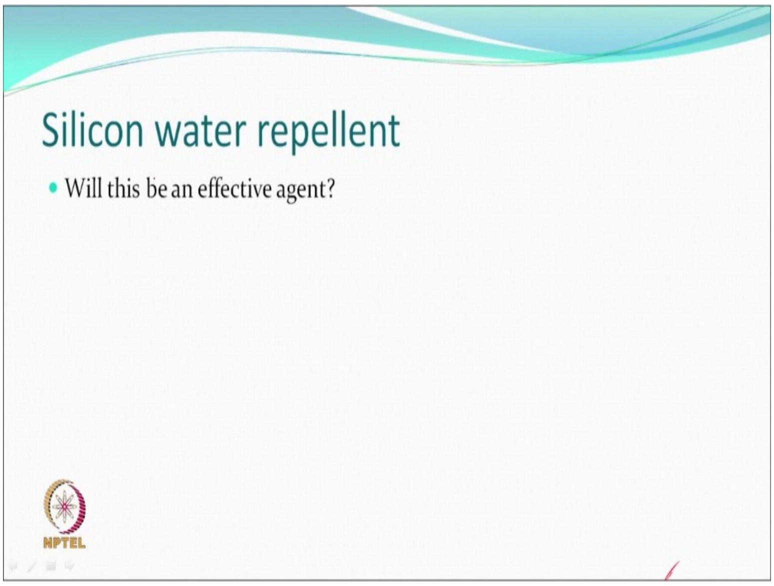

Is the way we have used this material; is this material good enough as water repellent. Is this material good enough as water repellent? So, people found, well, it was not good enough as a water repellent.

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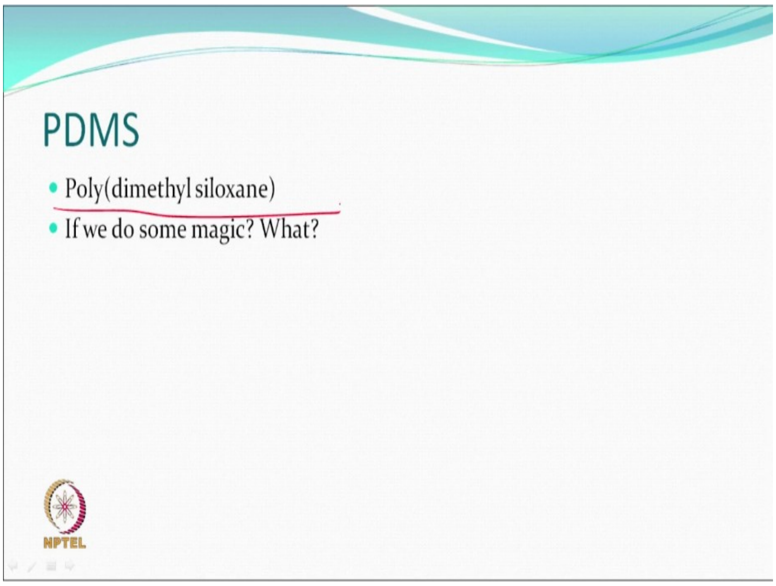

So, as it is, if you just apply the way we are applying for the function of softening, this compound may not be very suitable. Because, inherently, there are methyl groups, a large number of them maybe. But unlike, for example a hydrocarbon. This is not that kind of a hydrocarbon. And in between, there is a siloxane link between these things. So, can we do some magic? What magic are we talking about? The magic in some sense depends on catalysis, organometallic catalysis.

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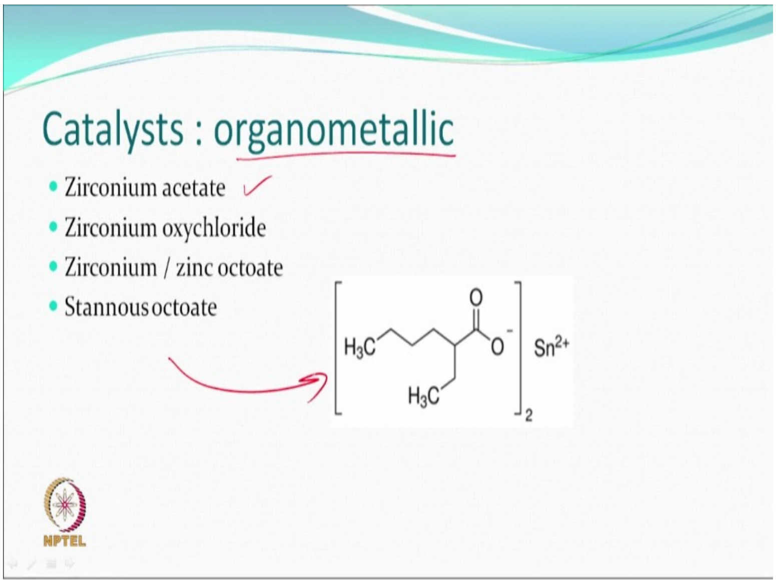

So, the catalysts which have been suggested; some of them are listed here. The zirconium acetate or zirconium oxychloride or zinc octoate, zirconium octoate or stannous octoate. Stannous octoate example is this. If you use them during the pad-dry-cure process, what we see is interesting thing happening. And what is that interesting thing?

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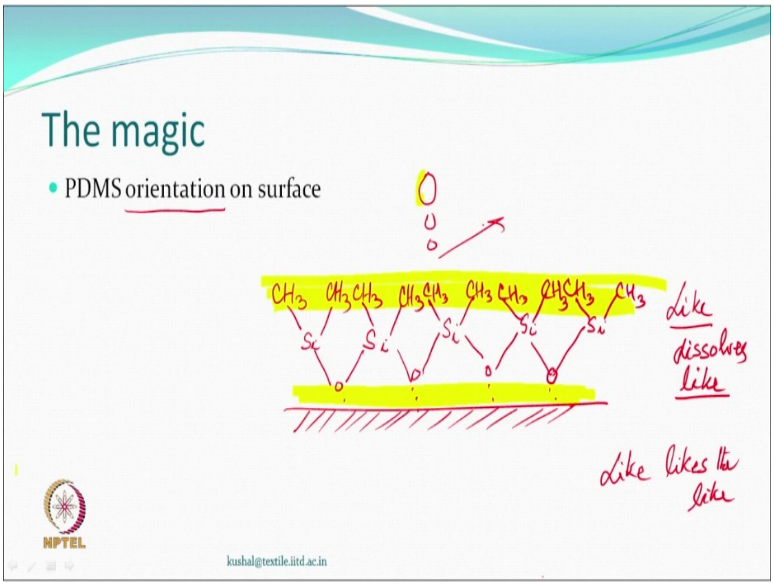

So, you have a textile surface. Because the catalyst, what happens is the orientation of this compound or the polymeric compound on the textile surface is controlled. Did we say that silicon oxygen link is a polar link? And what do we have? If because of these organometallic catalysts, if the orientation can be changed in such a way that this silicon oxygen moiety is facing the textile which is generally more polar.

And this group is also polar. So, some polar-polar interaction. Remember, the like dissolves; like is the statement which you may have heard. So, if we replace it by like, likes, the like. So, you have, if you have a more polarity on the surface of a textile and this group also is polar. If this happens, then what is the possibility is, that you have a CH_3 group here; and a CH_3 group here; and a CH_3 and CH_3.

You see, all the CH_3 groups are now aligned outwards. And so, you can see as if they are created another layer despite the fact that they, by sense the CH_3 group is not a big carbon chain. But what you see here is, interestingly, this whole thing behaves like a hydrophobic surface. Okay. And here, you have a polar-polar interaction, so that there is an association with the textile surface. Okay.

So, fastness issues can be handled a bit better. More than that, because you have been able to orient the structure in a manner, therefore, the surface which is exposed to the second phase, which a vapor phase, okay, is interacting with this type of an arrangement. And so, what you find is, if the water droplets come, if the water droplets fall, they will be repelled. This is the magic; magic of the organometallic catalyst.

Say, if this is what is done, then you will get water repellency. If you do not do so orientation, then you will get softening, but not water repellency; is interesting; similar compounds. Of course, you may have a, the compounds in the market which may have the polydimethylsiloxane. And also, along with it, they may have polymethyl hydrogen siloxane. That the hydrogen group will become also reactive.

It can react with the oxygens of either the silicon based oxygens which are there or the substrate oxygen; and it will become a more reactive film which could be, which would have reacted with itself, the molecules; or would have reacted with the substrate. So, that way, wash fastness can also increase. So, part reactive type of a siloxane. The part non-reactive. So, the non-reactive which we have just described here does not chemically bond, but which means is covalently bond.

But has polar-polar interaction. So, fastness is quite good, but can be improved if you add; along with it, if there are reactive silicon compounds like the polyhydrogenmethylsiloxane. So, that is the magic. If this magic is there, then you are obviously going to get repellency.

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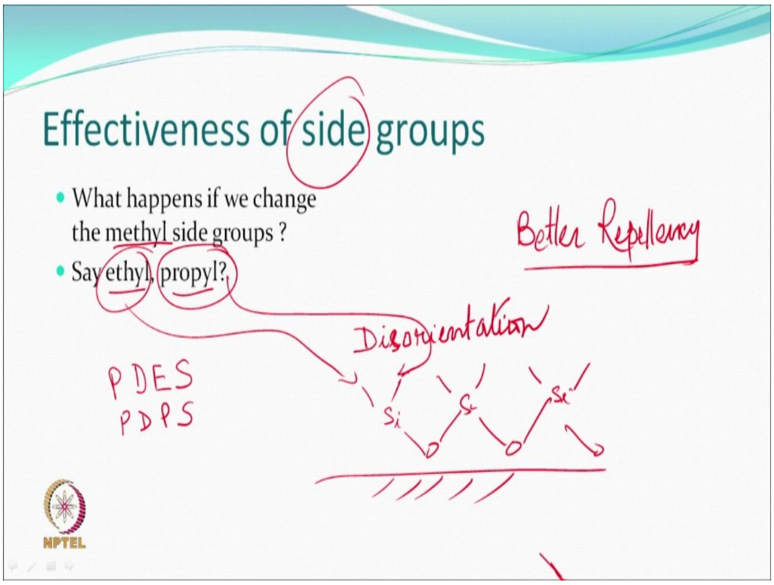

Now somebody asks: well, this is very good. Now, if you just can arrange the methyl groups around the surfaces, in the way we had just described; then we can do a better job. If instead of methyl groups, if we use ethyl or propyl. Because they are more carbon. And if more carbon, that means, more hydrophobicity. And if so many such groups are arranged, then what happens?

For example, instead of having the polydimethyl, you have let us say polydiethylsiloxane or polydipropylsiloxane. What would happen? What do you think would happen? Will it give you better repellency? Will it give better repellency? Actually, they found, no. Why no? Because of disorientation, because the size of these side groups becomes larger. And therefore, the type of thing that we were hoping that; we are hoping that this was covered completely.

But if this methyl gets changed with ethyl or propyl, then the orientation gets disturbed, because of stearic hindrances. The stearic hindrances do not allow these group to orient in a manner which could cover the surface completely, in case, the way we were doing; for example, with the methyl groups. And so, increasing the size of the pendant group, side group is not a good idea.

Although, normal logic would have told that, that is a good idea. But, the whole game here is of the orientation. So, silicon dimethyl, polydimethyl silicon, if was being used, siloxane which was being used as a softener, without let us say the special catalyst; the orientation are not there. They were not really behaving like a repellent. They were, they would repel; compared to, for example, the untreated fabric, but a reasonable level of repellency would not be achieved unless this orientation is there.

So, by using these groups, side groups, which are higher in molecular weight is not going to help. It only helps; or the disorientation; and disturbs the orientation. So, it does not really work.

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So, how do we apply these things? Obviously, we apply through pad-dry-cure. Catalyst is there. The time temperature could be approximately similar to what we do for cross linking. Therefore, these can be used along with the cross linking agent as well. And the previous ones also could be used. Whenever there is a possibility that you could use these agents together, its fine. Otherwise, you have to give a separate pad-dry-cure process which will ensure that there is a, smooth film is formed. And orientation also takes place nicely. How much to apply?

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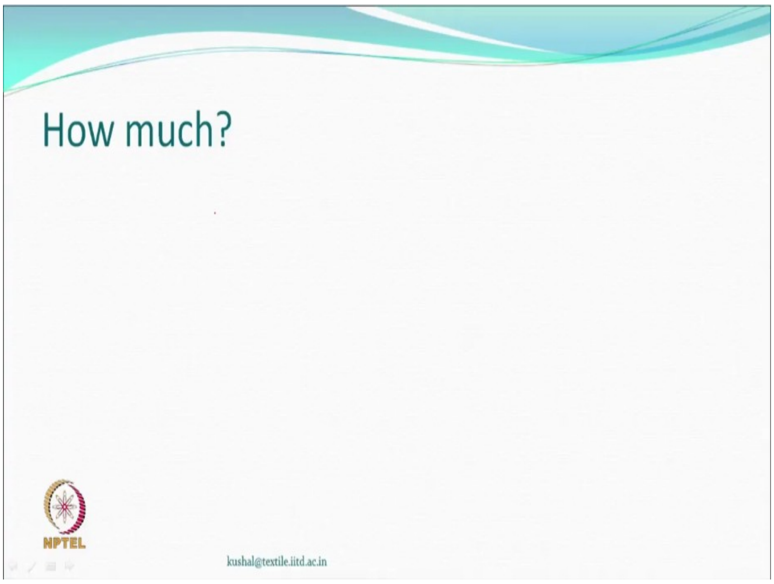

Very small quantities. Less than 1% can actually do the job of a repellency as well. So, we do not have apply too much. So, all these things are going to be available as emulsions which will be diluted to the required quantities and mixed with water; and then, the catalyst and work around for the drying and curing process. So, that will ensure that you have repellent surfaces. Now, if more.

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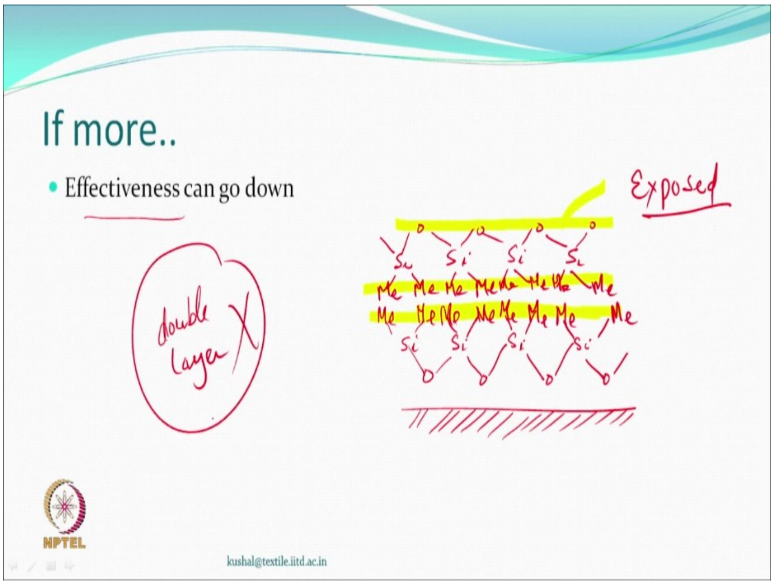

If more means, more concentration. We said about less than 1%, around 1% or less than 1%. If you say, I want to add 2%, it will become more hydrophobic. It may actually not happen. It is always possible that, at a level which was, let us say an optimum level of concentration where you had this oriented structure generally available for you. Say here, we had methyl; methyl, I am just writing that. So, you had all over methyl which was functional as a water repellent.

If we have more compound of this type, is always possible that actually you end up; because surface is gone. That you have the reverse of it, that the methyl groups which are in the other chain actually get oriented in this way, which is, you can consider, because they were hydrophobic, so, they would have a tendency to go to the hydrophobic surfaces. And the polar groups get oriented in the other direction.

So, what do we get? A double layer. But what is the surface which is exposed? The surface this exposed is this. This is the exposed surface. If this is the exposed surface which is more polar. So, our aim was to create more non-polar, right, to make it hydrophobic. So, now this is not going to be hydrophobic. And therefore, the effectiveness can go down. Therefore, optimum concentration of the softener; I am sorry, optimum concentration of the repellent which is the silicon is the one which is going to give you water repellency. Okay.

If you add more, it is not going to help. If you change methyl to ethyl to propyl, it is not going to help, because orientation and a single layer is an important thing rather than creating a possibility of formation of a double layer. We do not want it. Okay.

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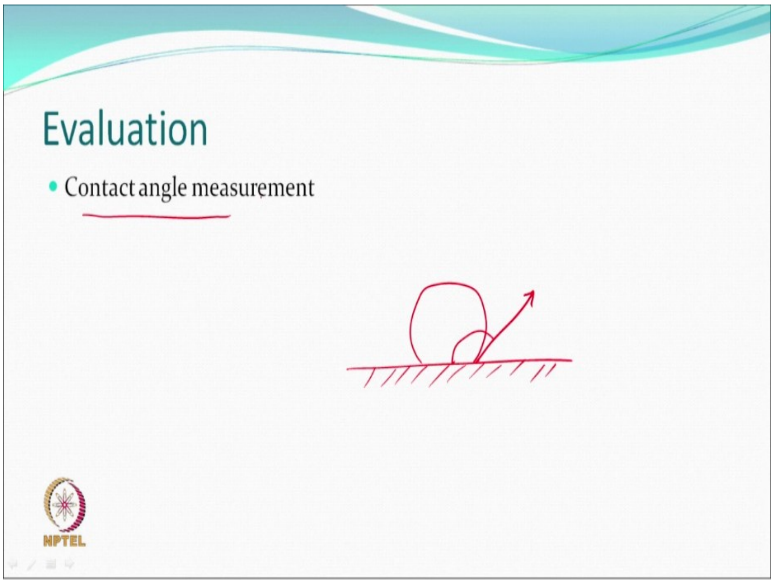

So, let us spend some time before we finish. How do we evaluate? So, we said that, if it is a textile surface and if there is a drop, and if you can see the drop; so, you measure the contact angle. If you can measure the contact angle, then you know, you will know whether it is more repellent or less repellent; whether it is a positive wetting or a negative wetting. So, you can do this.

So, there are equipment which can measure contact angle of a drop which is in equilibrium with a textile surface or any other surface for that matter. So, that is one way through which you can understand as to whether your treatment has been effective or how much effective.

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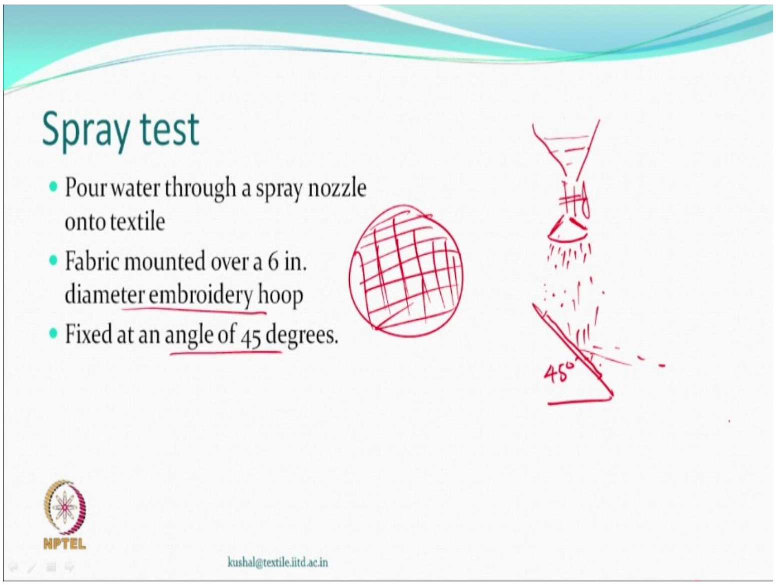

Other tests which have been also suggested and being used for the; is called a spray test. And basically, what you do is actually spray. Because, you are hoping that these guys were wearing, let us say a garment, is going to walk into a drizzle. Something, maybe lighter or a stronger drizzle. And what happens to them? So, what they can do is that you create let us say a shower. And you have water here.

And you may have some stopper. And then, this is a shower. A limited amount of water as described by the standards falling on a fabric which is fixed at an incline; could be any degrees, but let us say 45 degrees. And after all this is happened and the water is gone down, you observe. So, normally, a standard may say, well, there is an embroidery hoop on which you fix your fabric sample tightly. And then place it on an incline. And then have the standard test where the water is fallen and gone away.

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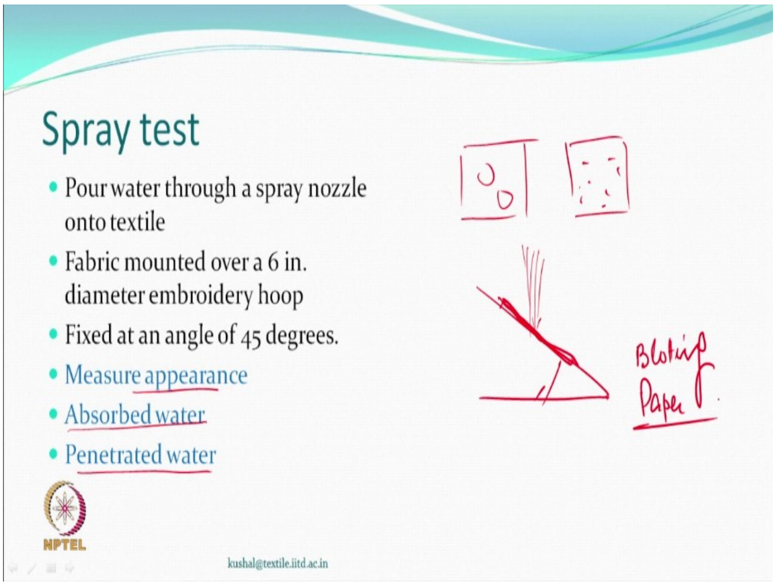

And then do some observations, make some observations. One is called the appearance. So, there will be, let us say standard photographs of highly repellent, less repellent wettable surface which you can check and; say, give on a scale, 1 to 5, a rating. Alright. So, you may have standard photographs which say, well, the drop is really looking or it is already wet; or less wet or more wet.

So, you can compare. Other is, how much water has been absorbed. Well, of course, weight of the dry fabric and the weight of the wet fabric can be measured. Because, people are interested. If it is completely, let us say repellent, then the whole water will go out. Okay. But, it may not be. So, something may be absorbed. So, you may see that there is water being absorbed by the textile which is there.

Or because, we may not have, we are not even interested in having, increasing the resistance to penetration. So, it is quite possible; under this standard test method, some water may go through. So, sometimes people can; a test method for example, may have a blotting paper below the textile. So, when the shower falls, obviously you see all these thing. But if the water penetrates through this, which is, which will wet the blotting paper.

And then, you can, may measure the blotting paper weight; and then calculate how much water has passed through under the test. So, that way, a spray test can give you an indication about the repellency of the fabric; and also penetration of water; and absorption as well.

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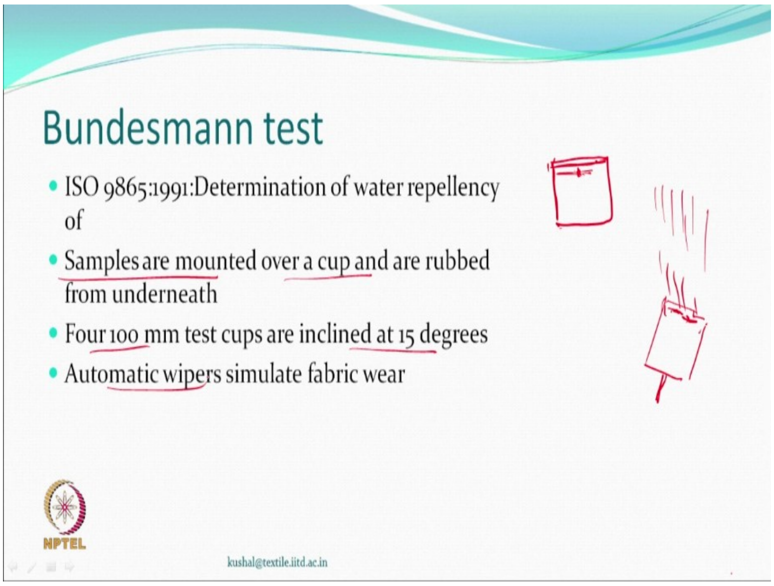

Another test method also; people have used. And there are standards available for this type of a test. It is called the Bundesmann test. And what exactly it does is, tries to simulate a condition, like you are walking in the rain. The textile is not fixed. It also moves relative to your motion. It may be rubbing against the skin. And because of that also, there may be some change in the absorption and penetration of water.

Now see, one is the static test that we did. In the spray test where the fabric is fixed, nothing is moving, it inclines, something falls; and then you measure. But this test tries to simulate a condition where as if the, there is a relative motion between, let us say skin and the textile surface while the water is also falling. And then, you can do absorption, all those kind of things and collect.

So, instead of that, you have a cup over which a sample is mounted. Let us say there is a cup over which the sample is mounted. And this cup is rubbed from underneath. So, there may, there are some blades like a wiper blade, which are moving and touching. They are rotating inside the cup. The cup maybe more than 1. Maybe let us say 4 cups arranged in, on a system where they make about 15 degrees.

So, not very much inclined that way. So, the cup is like this. And there are wipers inside. And then, you allow rain to fall. So, this whole cup system can rotate. The wiper inside can rotate as if it is the simulating; the way the skin and relative motion, the skin and the textile occurs. That type of thing can happen. And so, what do you measure?

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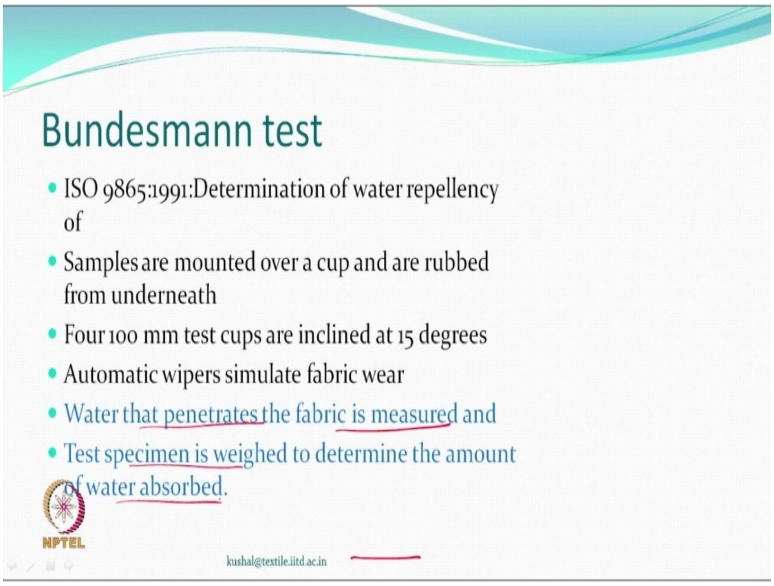

You can measure water that penetrates. You can weigh it in the cup. And the specimen can weigh it for the water absorbed. And this is also, let us say accepted as one of the standards which can be; this test can be therefore used. So, what have we learnt?

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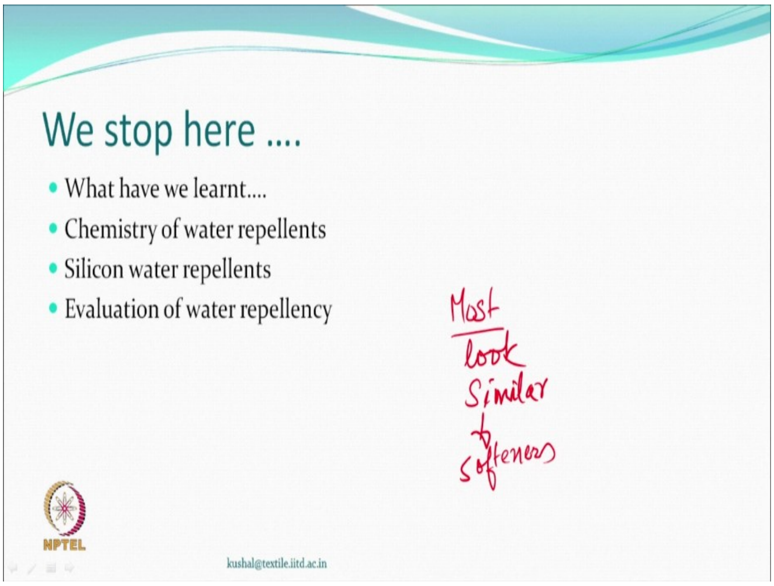

We have learnt the chemistry of some of the water repellents today. And we also understood the silicon water repellents are effective if the orientation is proper of the methyl groups. If this orientation get disturbed, then we will not get a right type of repellency. And evaluation of water repellency is also something which we commented upon. One more thing, which we have also remembered is, most of them look similar to softeners.

That is why we started with a softener; and then we come to the repellency. They are related, linked. Both are surface properties. One is trying, has a aim to reduce the friction. Other has a aim to make the surface hydrophobic, so that water gets repelled. So, some similarity and some expectational differences. So, there are standard methods for testing repellency.

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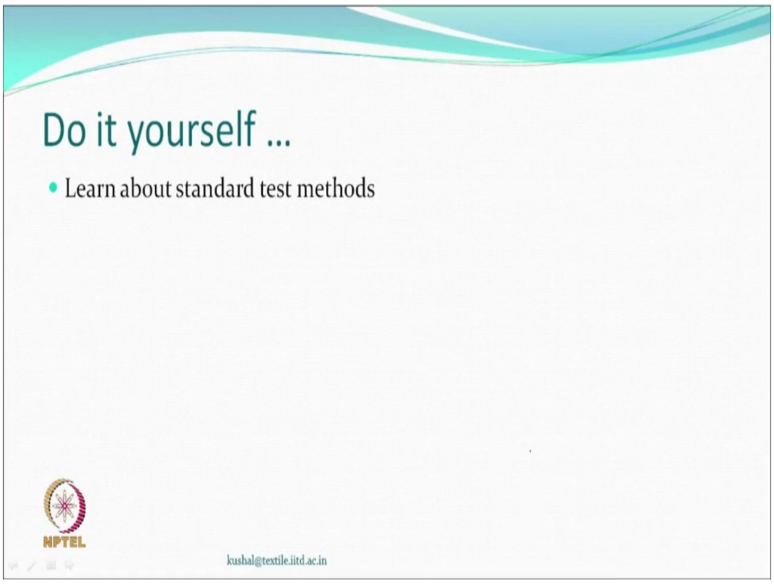

I will encourage you that you go and look at the standards. Whether they are ASTM standards or ISO standards or our own BIS standards. They are available. You can read them, keep them in your notes and learn as much as; so that there is some resemblance of the reality what happens. So, and next time when we meet, we shall be talking about a little bit on the waterproof breathable fabrics.

Now, waterproof we have done. We have tried to do the repellency. And during this repellency issue, we understood that breathability. Breathability means what? That the heat that you generate, generally should go out. That is one part. But the moisture is more important. As we keep working, moisture keeps getting generated. And that should also go out. And that becomes a breathability. So, we will be talking about that.

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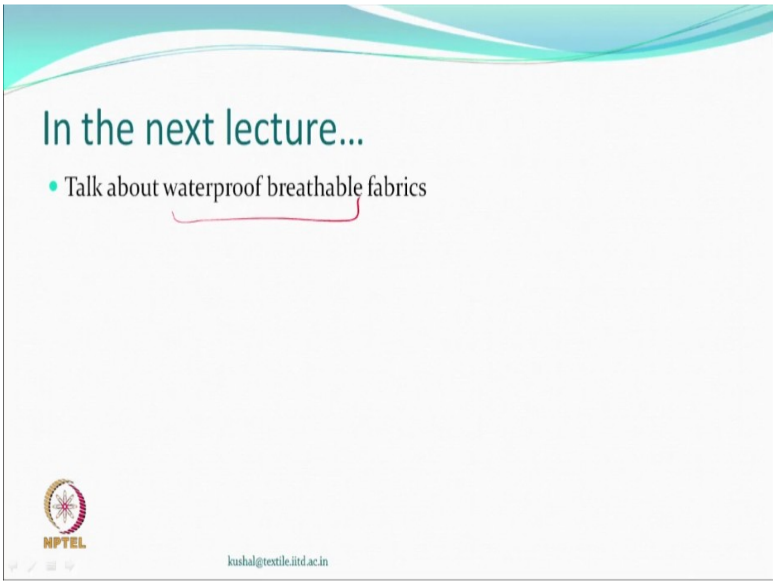

Is it possible to have a situation where you have waterproofing as well as breathability. Because, remember the first case; the waterproof fabric did not allow the air to pass through. Now, we are looking at both the things happening together. So, hopefully, we will spend some time on this topic. Thank you. See you next time.