Textile Finishing
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Lecture-20
Chemistry of Flame Retardants

Welcome back to the course on textile finishing, before we go further let us see what did we do last time. We have learned that flame retardants are important because most of the textiles are flammable, polymers are flammable and therefore they do pose fire hazards and dangers to the life and property.

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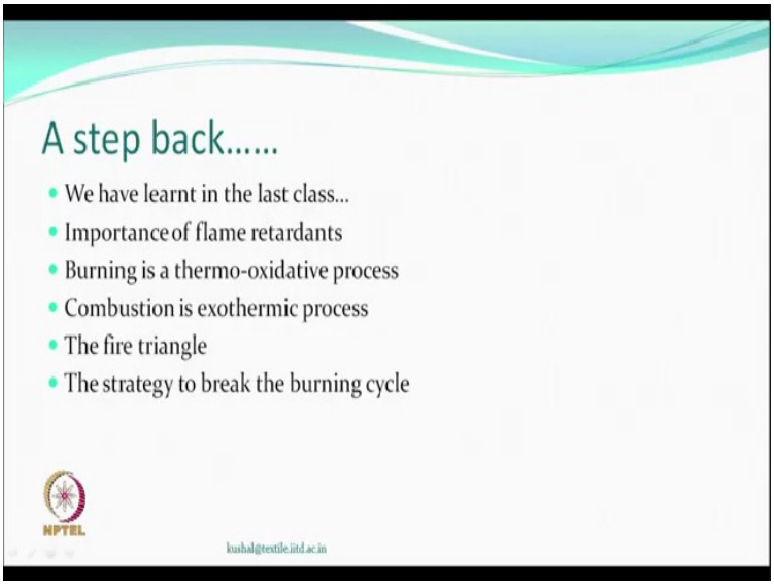

Burning is a thermo oxidative process which releases heat as the burning takes place and therefore this heat can go back and restart or initiate the degradation process. So it can be fed back to the system that is the polymer or the fiber what we are talking about. Combustion is an exothermic process and during this as we said the heat will be released. The fire triangle also we learned about that the polymer burns produces flammable products.

They react with oxygen, if the oxygen available and then heat is released and of course we did talk about some of the strategies that you can adopt. So that this fire triangle can be broken.

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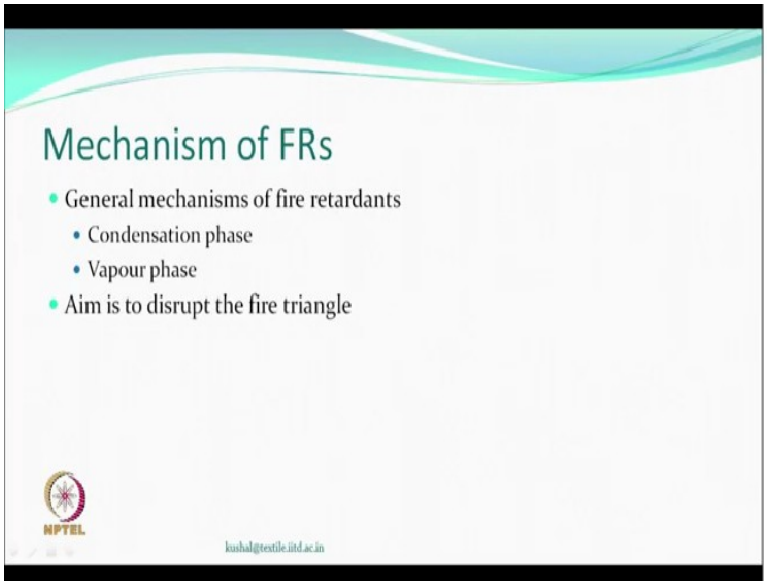

Generally we did say that there are 2 basic mechanisms, one is called a solid phase or condensation mechanism and the other is a vapor phase mechanisms, we did learn something about them. The aim of all these things where whichever kind of a compound that may be used will be to somehow disrupt this fire triangle right. So today we will learn little bit of the chemistry of some of the fire retardants and introduce various types of possible frame retardants.

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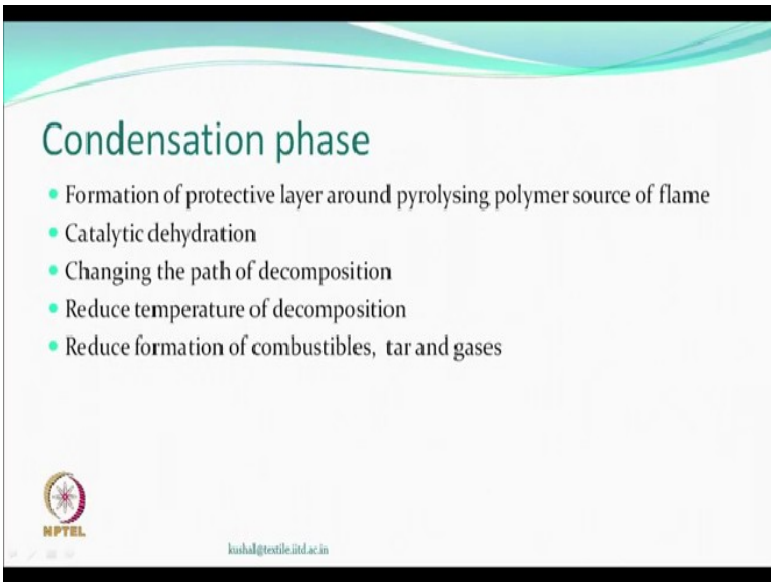

So the condensation phase as we talking about is basically related to formation of maybe a protective layer around the surface or the area of the polymer which is burning so around that if

some protective layer could be created, so the flame will not very directly go it has to go through this protective layer or they can work like a catalytic dehydration, acids can be used and that can alter the path of the composition.

That means the way the pyrolysis was taking place that may get changed and therefore this can happen through the catalytic dehydration, they may help in reducing the temperature of decomposition because only at certain temperature certain type of products are found which may be fire hazards in that sense and so if you reduce the temperature of degradation decomposition you may be able to save or restrict or retard the process of burning and degradation. Also during this process of this alteration they may reduce the formation of tar and gases.

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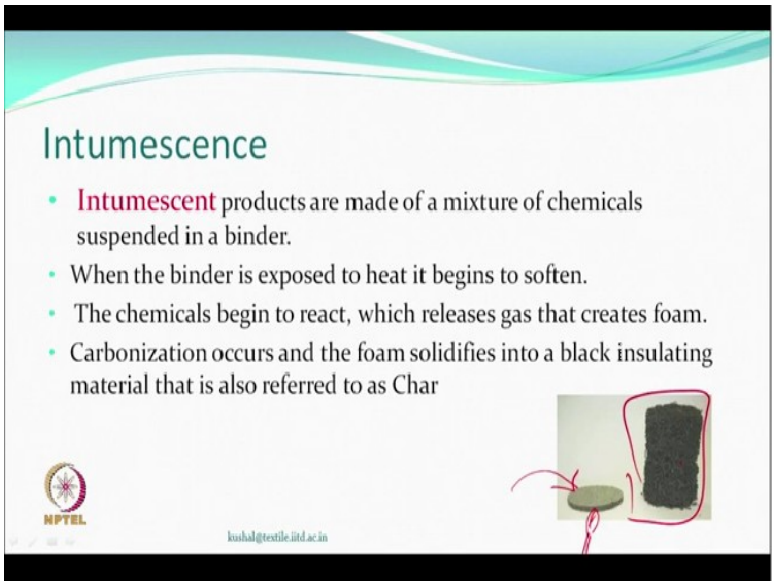

So one of the type of compounds which are called intumescent compounds the products and this phenomena is called the intumescence. They are the one the types which actually try to create a boundary and they create formation of large amount of charge and thereby reducing the diffusion of the oxygen or the flame coming close to that product, you may have at some stage or the other scene some such products.

So this compound is a mixture of a binder and when this binder you know gets the heat because of the burning and so on so forth, it will get softer and will start in some sense let us say melting and the chemicals which are there they will start reacting they may start releasing gases so foam

can be created. Now this form if it is a carbonaceous product also as the carbon keeps burning, then it will insulate the polymer from the heat.

So what happens is the hydrogen get burnt so it is called the carbonization, the form can then solidify and start insulating, the color of course is black and generally it we referred as char. So we did talk about last time in a char to tar ratio and so on and so forth. So you produce more char, you may have seen some products like a tablet of an intermittent mixture which may be solid.

And the moment you put certain amount of fire to this and start burning because that polymer is there it starts burning there are products which are inside they will start burning and suddenly a large volume would be created which basically is a char black very soft material that remains but the volume of the sleaze increase because it is formed, forming was taking place.

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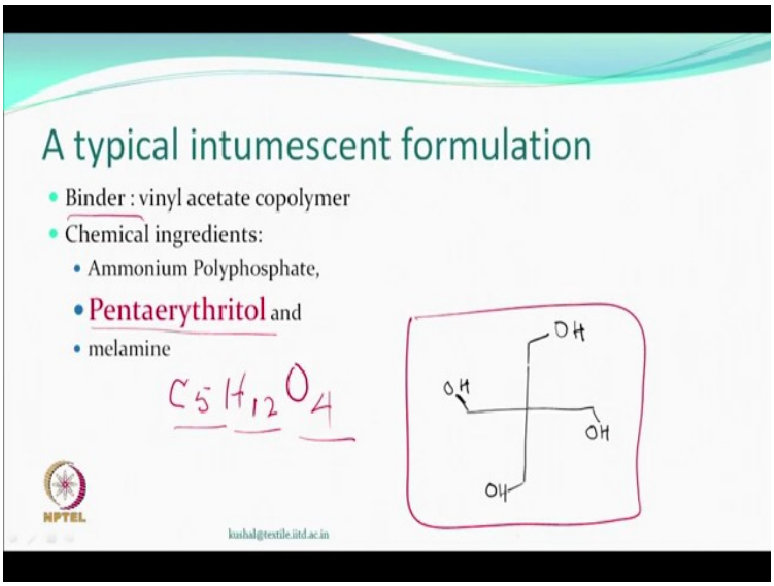

Some of the interesting compounds that are can be part of this type of a intumescent product can be one compound called the Pentaerythritol which is basically $C_5H_{12}O_4$ and approximate structure is like this. So you have 4 hydroxyl groups which are in a way connected to CH_2OH CH_2OH CH_2OH and of course in between you have a carbon there. So there are the compounds like ammonium polyphosphate or melamine which you know already can also be there which will start producing gases as they compose themselves.

And at the same time you have a binder which is becoming softer and so in this so-called melting mixture you have gases being formed and bubbles getting generated and of course they get out during this process of course the hydrogen will also burn and then you will finally have more of carbon carbon carbon and so that becomes a carbonaceous charry material. The binder as we said is the vinyl acetate copolymer can be other compounds also, but this is one of the common thing.

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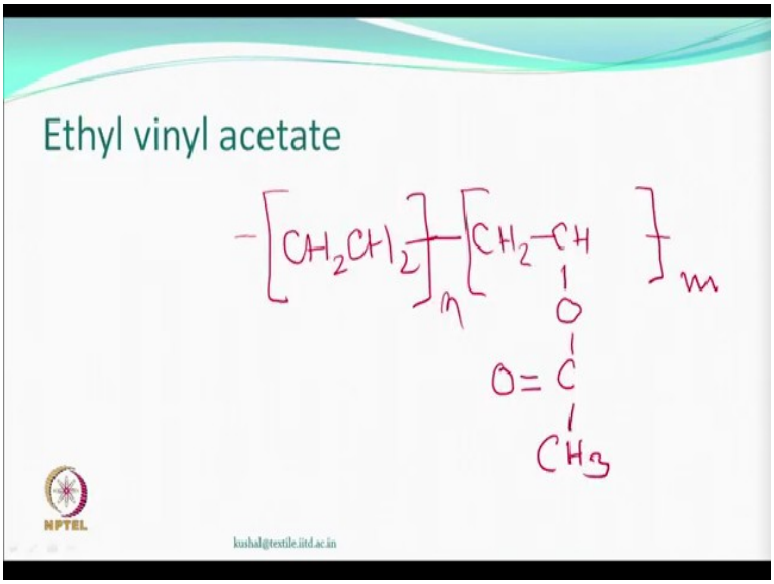

The example can look into ethyl vinyl acetate which is as I said copolymer, so this is one which is going to be holding these compounds which can form gases and then foam and as the carbon compound gets heated up the hydrogen will slowly get out by hydrogen extraction methods and reacting with which a way and finally get out and suddenly you have a large amount of foaming charry compound all around.

So it stops, so if you can apply these kinds of compound to any product polymer wood cellulose then it would by its own create such environment.

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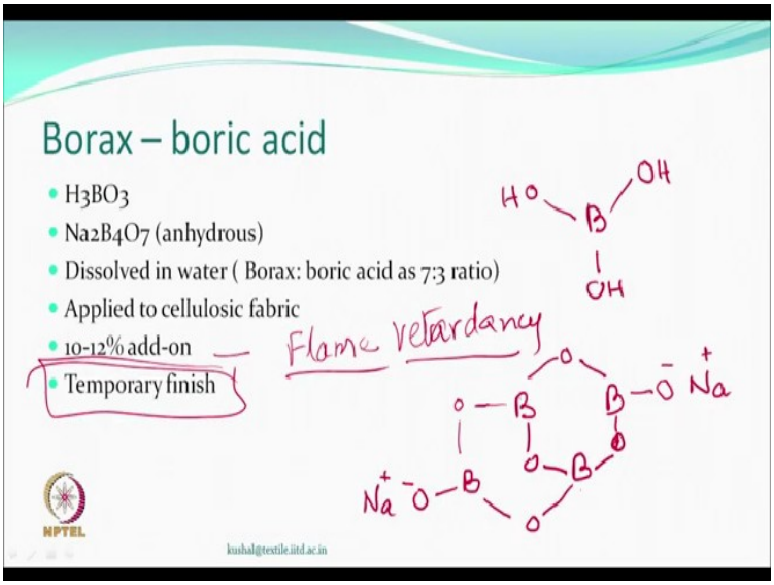

There is another interesting product mix which people had been using for flame retardancy borax and boric acid mixtures alright. So boric acid is H_3BO_3 which you are familiar with, this also is acts like an acid and a flame retardant. The borax on the other hand is a sodium salt of borate which is a complex bound it is a very complex kind of compound, but more than that all around this it can have approximately 8 molecules of water as a water of crystallization they are generally associated.

So whenever you keep anhydrous material in the atmosphere you will make we will see that it is it will absorb a lot of water. So once it absorbs water so during the flaming, burning, this water will be released first, so you can say one compound which is some molecular weighted and also got almost 8 molecules of water associated that also you can see well obviously one of the mechanisms which was there that if it degrades by itself.

And produces some compound which require for their let us say water getting into steam required the heats the heat can be reduced so that is one but which is important. So very simple methods like pat dry cure methods could be used curing acne is not required pat dry because no chemical reaction was expected. So pat dry can be applied to cotton viscose in such type of material jute and then if you have approximately 10%, 12% add on it would give flame retardancy.

It is been very very successful anytime anywhere if you want you can just mix them just heat it a bit solution will be there and you can apply dry and this is ok, so when it is a dried fabric when subjected to flaming it is going to retard the flame, you may see the glow in this case but the major part of the degradation process will be stopped, what is the temporary finish, because no chemical covalent bonding etc. reactions are expected in this.

So every time you wash apply this also and one can be safe people can apply through a pad dry or you can have a spray and dry but important thing you must know down here is that be generally the amount of a flame retardant required to achieve a satisfactory retardancy is high, you know 10 to 12% we have written sometime can be more required also based on how severe is the flaming condition.

Unlike for example softening treatment, unlike for example resistant treatment or even soil repellent with from fluorocarbons, all of them require much less amount of material much less amount of add-on but for flaming it is very very severe and the burning conditions are severe and so generally a higher add-on is required in flame retardants of the flame retardants.

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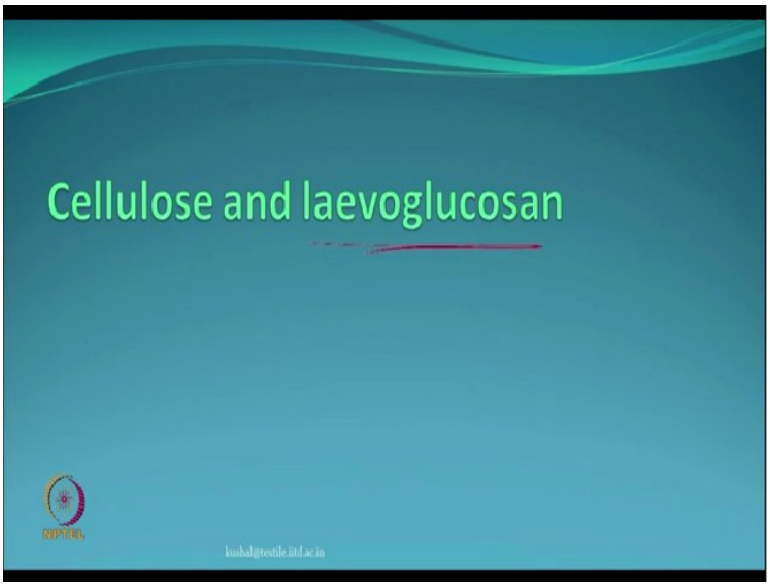

So now we talk about other mechanism which in a way is changing altering the path of decomposition. This particular example that we are giving is based on the cellulose polymer based fiber fabrics is the formation of laevoglucosan.

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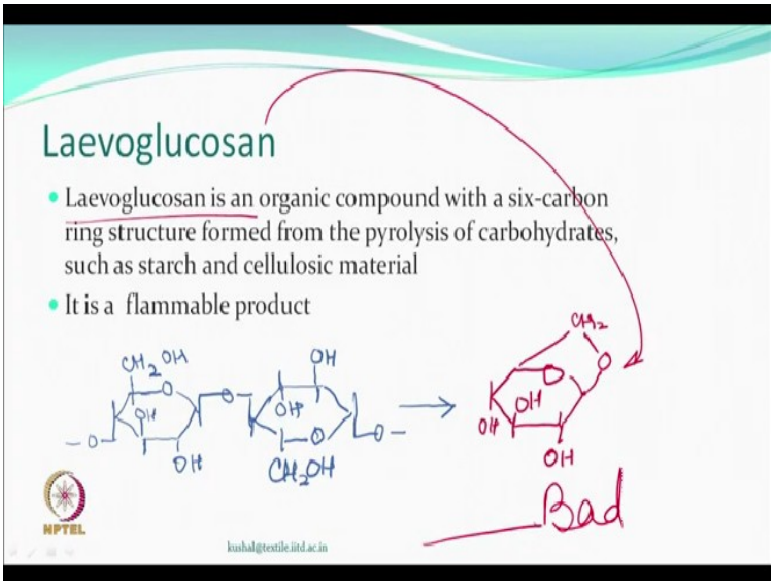

The laevoglucosan is a product which is a tarry product which can form the gases and so it has a ring structure which gets formed during the pyrolysis of carbohydrates such as cellulose and starch ok. So this compound is a in a way a dangerous compound which is because it is a flammable product it easily supports burning supports creation of a flame. So this for example is our general cellulose molecule a carbohydrate in a way.

So when it burns it can make a product like this alright, it also is a product which is called the laevoglucosan. So this is laevoglucosan, it is a bad product. So if we do something in this cellulose burning process and if this is avoided then we are altering the path of decomposition path of pyrolysis ok.

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In this category a good number of phosphorus based compounds are there which can do this alter the path of decomposition.

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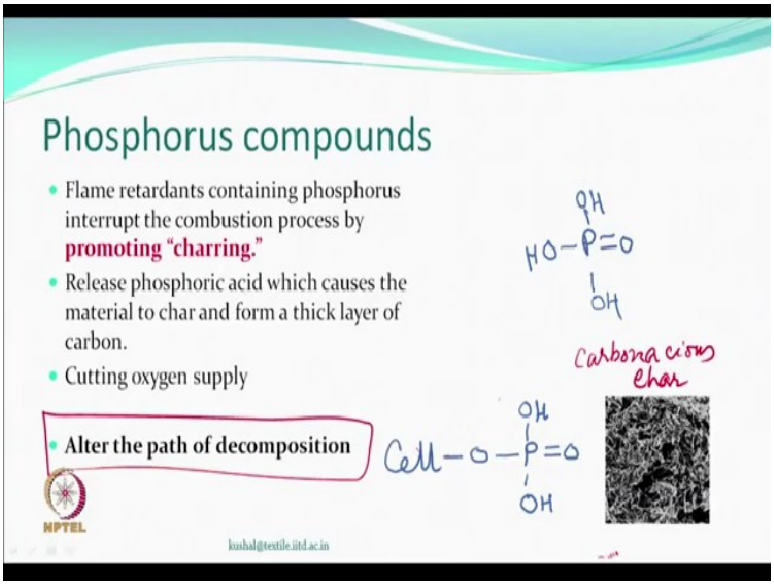

So one of the compounds which we will talk about will which is the phosphorus based compound is phosphoric acid or ammonium phosphate, it promotes charring interrupts the combustion process by promoting charring. That is one of the things if it had reacted for example this is like cellulose phosphate ok, this is a cellulose phosphate. So once you have done the reaction let us say by a pad dry cured process using phosphoric acid or an ammonium phosphate or ammonium polyphosphate and things like this.

Then on a finished structure you would have something like this, so it is covalently bonded, so it remains as a with the fabric, reason obviously is we want this to be more wash fast ok, it more durable. So during this burning process this compound will release phosphoric acid which would help this charring process which would help in catalytic dehydration after the char is form they can say the oxygen supply can be cut off.

And so the burning process can reduce because during this process phosphoric acid gets released and this is what we were talking about alter the path of decomposition and if you look at the burnt structure you may get a char, char may be as we said is very amorphous, soft formed up material which could be let us say consider as the carbonaceous material. So mostly it expected that would be carbon only.

And a carbon which could not become carbon monoxide or carbon dioxide which also can become if you go to very high temperatures then the thing that will be left behind will not be carbonation material also it may just become an ash, in case there were inorganic compounds in it. If there were no inorganic compounds for whatever reason then it may just vanish. So everything can become a gas.

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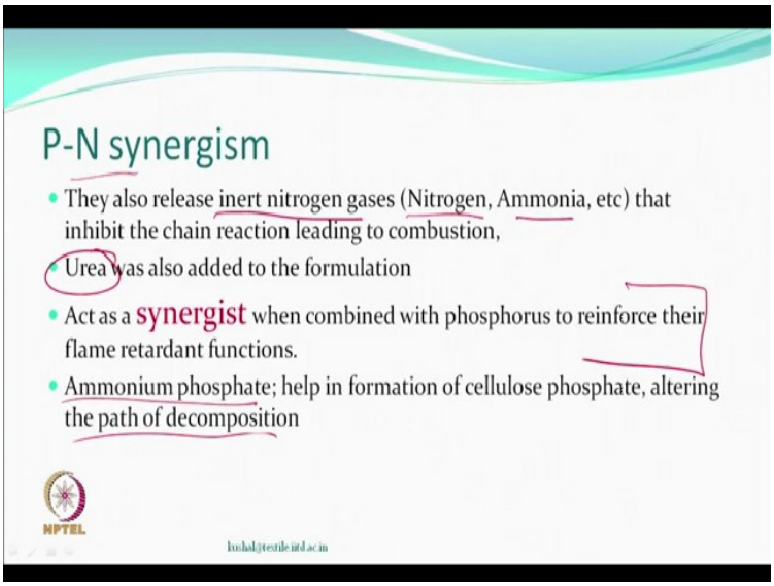

There is another phenomena which people observed and that is called if the most the phosphorus compounds like this phosphoric acid, poly phosphoric acid or polyphosphates were found to be good flame retarding agents. But they also notice that if nitrogen compounds are also present

along with it then there is a P and synergism that is phosphorus nitrogen synergism and that obviously helps to retard the flaming process further.

That is what the synergism is all about, so if ammonium compounds are also present like instead of phosphate you have ammonium phosphate you have ammonium salts. For example or otherwise compounds like urea and other nitrogenous compound present along with it, then there is a possibility that release of inert gases like nitrogen ammonia etc. can take place, they help in inhibiting this chain reaction that is taking place.

Remember we said that if some such gases which by themselves do not burn, they can dilute the gaseous environment also. So they can do things like this, so if nitrogenous compounds are also present along with the phosphorus pound the effect is better. Therefore sometimes people do use compounds like urea while they are doing pat dry cured process. So this is what is the take away and we can always remember that this would help.

So as we mentioned before also ammonium phosphate would finally get to the phosphate ammonia will get released and become cellulose phosphate, phosphate will be phosphoric acid during this decomposition process, if that happens then automatically the effect will be seen the flame retardancy effect will be observed.

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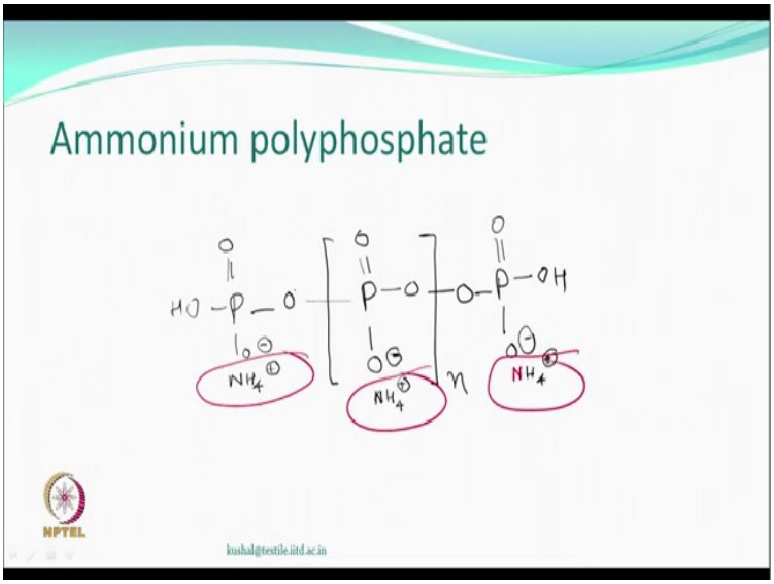

So one of the example also like ammonium polyphosphate, so you have lot of phosphate entities, idea here is that how much phosphorus by itself can be attached. The more the better, therefore says and also in this particular compound you can see there is going to be the NH_4 entities. they may remain associated and because of that it is a ammonium salt of a cellulose phosphate let us say which ultimately will release ammonia, then release phosphoric acid and get to the job.

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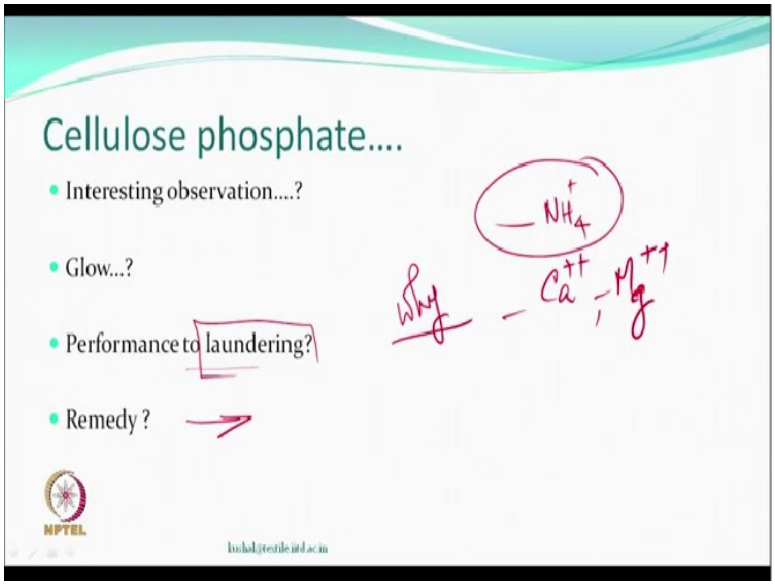

So one interesting thing which people observed about the cellulose phosphate. Now cellulose phosphate or ammonium salt of a cellulose sauce where they covalently bonded the only the ammonium part is ionic, but the phosphate which is the compound is covalently bonded. So one would expect the durability to be as high as one imagines till they say the covalent bond breaks which we expect break only during burning and not before.

But there was an interesting observation and that observation was that when you wash this fabric the flame-retardant finished fabric. The flame retardancy would start reducing effectiveness would start decreasing while they found that the cellulose phosphate was still intact, this covalent brand during this washing had not broken and still the flame retardancy effect was reduced. The important thing is that if phosphorus is there the glow was not there.

So in the borax case we may find that mostly it is flame-retardant but the glow may be there. So one important thing also was that if phosphorus compounds are also present in the cotton waste systems, the glow which we said the temperature of the glowing was higher than the flaming,

slow but it can finish the phosphorus compounds basically help making the carbon into carbon monoxide or carbon dioxide.

And therefore very easily the glow is reduced or inhibited, that is one important thing phosphorous compound, but I just mentioned before the performance on laundering was reduced, performance on laundering was reduced and why did it happen, before we talk about the remedy we must say why this happened, one thing which he found was that the ammonium salts or the ammonium iron was replaced by the calcium and magnesium ions which we know are present in washed liquor because the hardness.

And this iron gets replaced by the magnesium and calcium ions and if that happens they found the performance is reduced while the compound is still intact, so remember we talked about the sphere of influence and the time when these compounds are going to be available. If there is a delay let us say in availability of phosphoric acid during burning that delay will make sure that the most of the pyrolysis started and the action takes place later.

It must take plate quickly, it must take place as quickly as possible, while the ammonium salts were very effective ammonia would immediately get released phosphorus will then get relief phosphoric acid will get released that means and then the inhibition started quickly. But when the calcium magnesium is also formed, it was found that the availability of this phosphoric acid was delayed, because they would not get into gaseous forms.

And because of that little delay the compound were less effective, that is why there is a term which we talked about in the classification semi-permanent you know, these type of reactions which were there were found to be deteriorating in performance and therefore they may not have lasted up to 15 laundries and therefore they said well these are semi-permanent type of finished products.

Although remember the covalent bond is still intact ok, so what is the remedy, the remedy is for these compounds was that you treat with dilute let us say acids like hydrochloric acid for example and then neutralized by ammonium hydroxide. Then the ammonium salts will form

again and then find that the flame retardancy is revived right. If something happens but obviously it is difficult for the user to do it in the lab it can be obviously tested and you can check this out.

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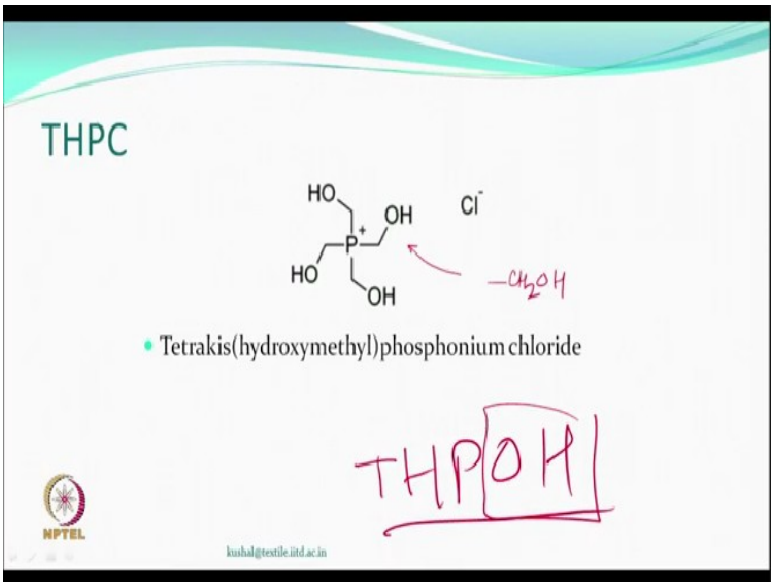

So an alternate story was built around different phosphorus compounds, one of the very successful phosphorus compounds is known as THPC, that is the tetrakis hydroxymethyl phosphonium chloride, this particular compound in a pad dry cure system along with urea or other latinus compounds was very very effective and this did not have the problem of ion-exchange. So you have chloride iron and this group which we are referring to is this which you are quite sure the hydroxymethyl or you probably earlier know it as a methylol group.

This compound is very effective and commercially a successful compound at some stage people wanted chlorine not to be there. So if you replace chlorine with hydroxide then this type of a compound was called THPOH approximately similar efficiencies were seen in this compound. So that is one important for the phosphorus compounds I could say.

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Some nitrogen we said the nitrogen compound by itself may not be very successful but nitrogen phosphorus can be visible. So there are some nitrogen phosphorous type of compound which you may have seen before which was APO.

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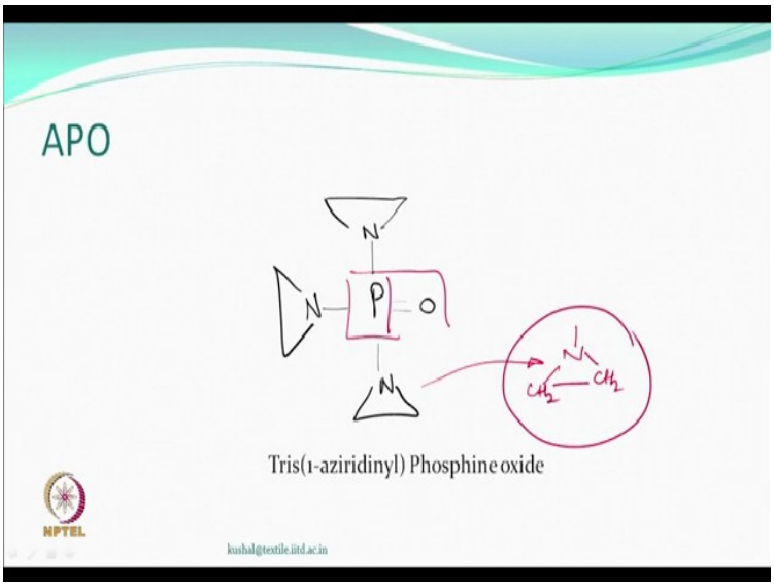

We may have used this compound for cross-linking purposes, but it cannot cross link, this is the group is it a vinyl group which is this of course it can cross link, so it can attach a phosphorus to any polymeric compound which can react like say cellulose itself reactions amines can also take place. So it will attach phosphorus and nitrogen together and finally we will see the effect of nitrogen as well as the phosphorus.

So they are very effective flame retardant compounds which can give you other properties like cross-linking etc. So somebody asked this question well after the fabricants we have to flame then what will happen the previous recovery and it has no meaning, we never as we said design any material to be used after it has been subjected to flame. It is gone, our aim is to protect life and property.

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So most of these compound the fastest combatants generally acted in the condensation phase. So the other mechanism and therefore the compound which will work in those that phase the other phase which is called the vapor phase. Let us look at them now.

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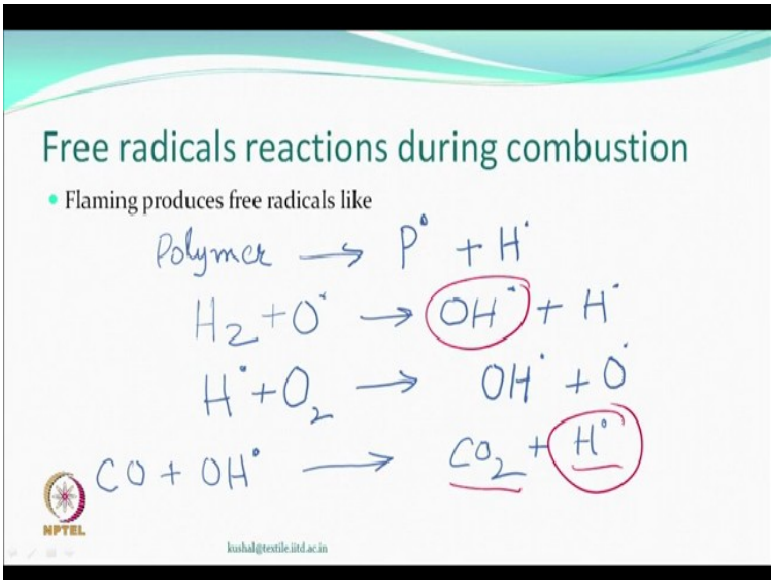

So during combustion, so free radicals get generated, so the polymer is there which will have hydrogen abstraction and so you get free radicals in it and obviously they are very highly reactive species anything which is available close to them. Let us say oxygen comes in contacts things will they will start reacting or they can react with anything else. So this is what will keep on happening.

So if there is hydrogen has been released because hydrogen may be present because of let us say this protecting by itself, so hydrogen gas can be produced, then you can have the oxygen which can also which is being supplied as we say it is a thermo oxidative process. So oxygen is being supplied and so oxygen can also get into oxygen radical and if there is hydrogen available it can create radicals which are hydroxyl radicals.

They can again react with themselves or they react with let us say this to make water. So all such things will keep on happening during this combustion process, the hydrogen radical can react with oxygen to again produce this and another oxygen radical you see all this will keep on happening, if carbon monoxide is available then it can become carbon dioxide and again hydrogen radical is ready.

So these small small entities of the hydroxyl based or hydrogen radicals will keep on getting generated and reacting with oxygen available or go and you know react with whatever carbon compounds may be there to keep the reaction going till neither the polymer is available nor any carbon for that matter is available, it is all finished. So there is no product, the flame anyway will go out alright.

But till the polymer is there this will continue, this process will continue if gaseous products are being formed they will go into the environment then this flame environment will be having all these kinds of various free radical reactions.

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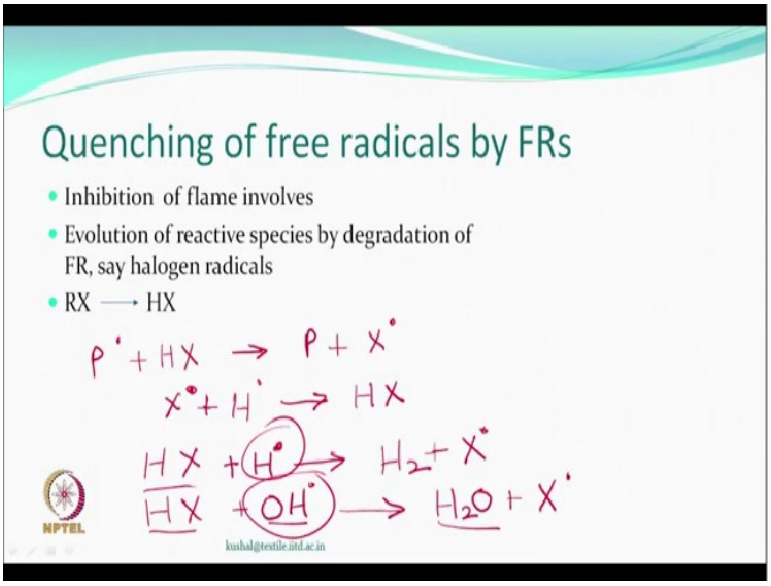

So one of the mechanisms during in the vapor phase which operates is called the quenching of free radicals**.** Quenching means that this free radical which was available for further promoting various kinds of other free radical reactions can be quenched. So there is a free radical which comes some other chemical comes and then reacts with this which may not be flammable. So this particular very reactive species becomes almost unreactive that is called the quenching.

So inhibition of the flame means that there is an evolution of reactive species by degradation of the flame retardant, for example halogen based compounds can do this kind of a job. For example if this is a flame retardant which is halogen based flame retardant can produce gases like halogen gas, if suppose this was a chloride compound than to be HCl, if it was a bromine based compound.

Then it will be an HBR and so these type of gases will be produced and these gases will by themselves are not flammable ok, but they start participating in the quenching of the free radicals that have been generated during the combustion process. For example if you have a polymer which had gone through this process of hydrogen abstraction and there was a polymer radical.

Let us say the polymer radical can react with the gas which is the Hcl for that matter or HBR for that matter can produce halogen free radical alright, if halogen free radical not halogen radical but is a halogen radical alright, but a free radical means the radical ok. So this radical which is

the halogen radical can combine with let us say another free radical which is hydrogen and can produce this gas back or this gas which is there here here can react with hydrogen to produce another free radical.

And this can also react with OH to get H_2O, that means the thing which are trying to quench are these type of things can easily quenched and so the flaming combustion reactions will retard.

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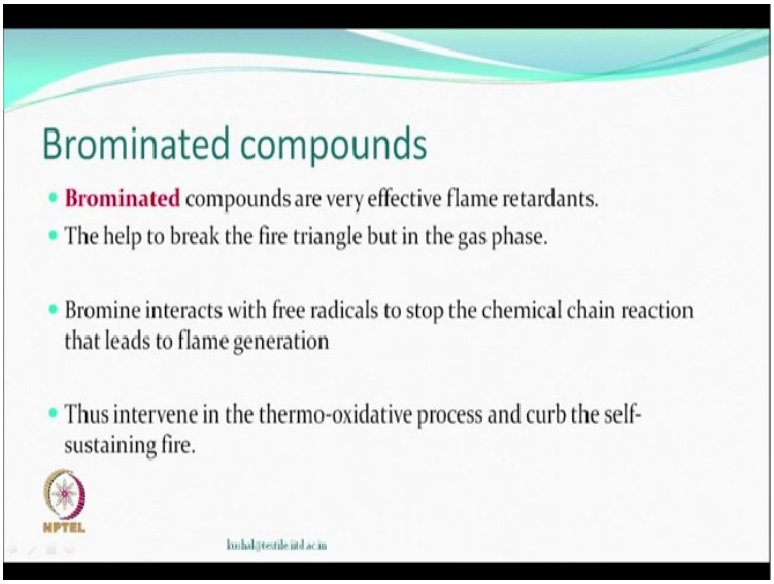

So various types of bromine based compounds are very very successful and they were very successful for synthetic fibers like polyesters, nylons and they could be introduced during the spinning process or they could be applied as finished alright. So whichever way so you can make inherently flame-retardant fibers because they are man-made fibers or you can give a topical finish at a later stage.

So they have a very popular very effective flame retardant which would be working in the gaseous phase or the vapor phase, very effective, so brominated compounds instead of chlorinated compounds were generally used and these compounds could be very effective, they help to break the fire triangle. So the quenching takes place further free radical reactions are inhibited and in the gas phase.

The bromine interacts with the free radicals as we have seen to stop the chain reaction which obviously leads to generation of a flame. So these brominated compounds as we said effective

they help in breaking the fire triangle, they stop the chemical reactions and therefore they intervene in the thermo oxidative process and the tendency of the self sustenance of the fire.

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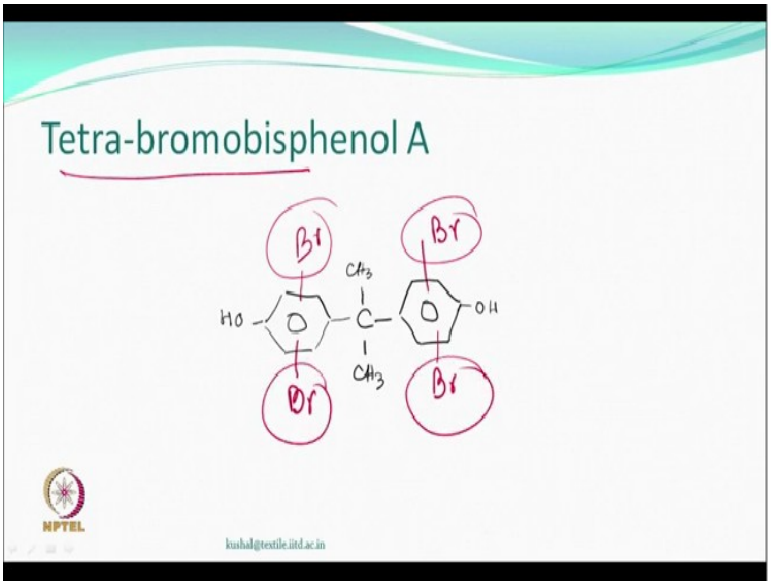

One of the example is tetra-bromobisphenol A alright, so this is the group which is interesting, this is the group which will break off from here and make HBR. Now this bromine could be attached on ortho para positions, so here it is represented they could be anywhere so different compounds will be generated as you know if the bromine is in ortho or para positions. So irrespective of that if bromine is available it will work.

Remember there is no phosphorus here, they are still very effective because they are acting now in the gas phase, they are not going to change the burning behavior of let us say the polyester or nylon or any other synthetic material, what they will do is once they were on some gases are coming and the flame during the flaming and combustion process whatever free radical reaction takes place there these will work very effective.

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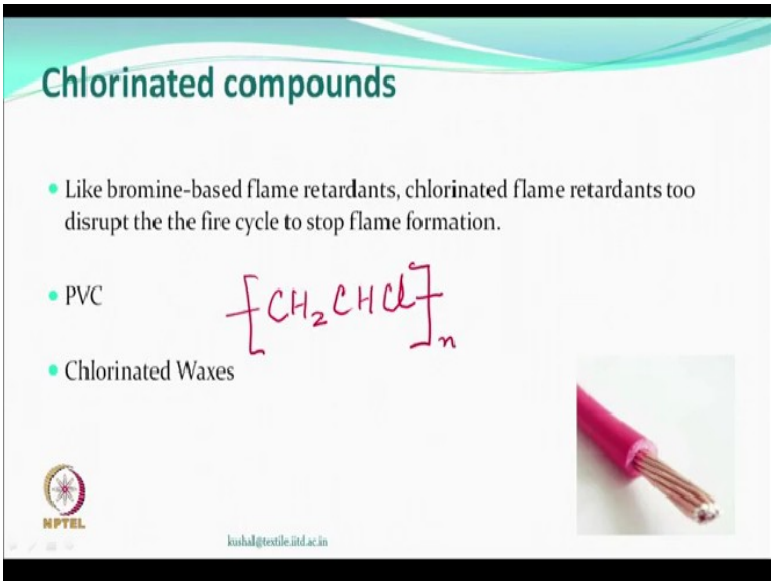

We had already talked about the halogen, so chlorine compounds are also been told you know used as a flame retardant, you may have seen the electrical wire most of the electrical wires have a coating with a copper or aluminum whatever you have, this coating is PVC, what is PVC it is a chlorine based hydrocarbon polymer alright and it acts exactly in the same mechanism by the same vapor phase mechanism.

The chlorine is going to get into the HCl and HCl will participate in the free radical mechanism by quenching ok, the other type of compounds are chlorinated waxes and so on so forth. So whenever chlorine or bromine are available they are going to be doing the quenching of free radicals.

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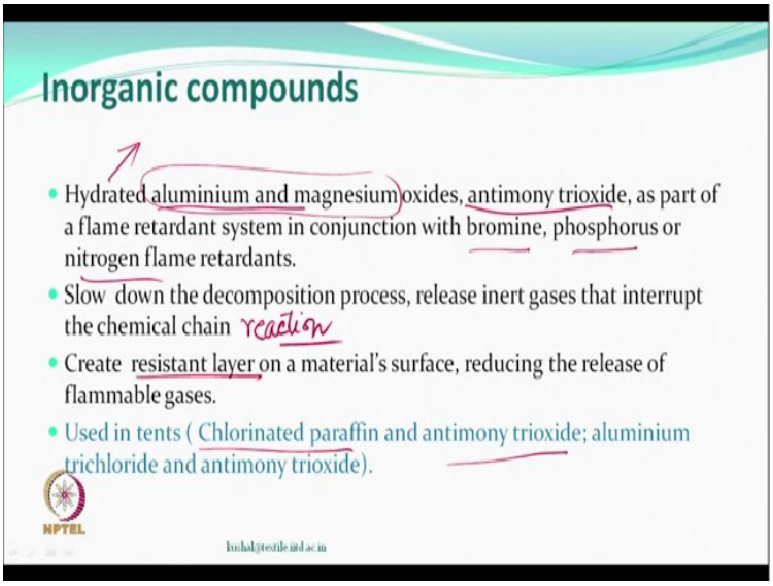

There are some other inorganic compounds also which have been suggested which can be very effective, like the aluminum, magnesium oxides, antimony oxides. So these are important inorganic compounds, hydrated means they contain water of crystallization, antimony trioxide in conjunction with bromine, phosphorus or nitrogen compounds can be used. Of course they will do exactly the same thing which is slow down the decomposition process.

Release of inert gases, that can interrupt the chemical chain reaction which is the free radical reactions, they can also help in creating a layer flame-resistant layer like these type of compounds and reducing the release of the flammable gases, so and if they are used some of them as chlorinated paraffin waxes, the antimony compounds or along with aluminum trichloride and antimony trioxide.

These type of compounds can be used for example the entities like canvas which is used for tents is coated with chlorinated waxes and if it is along with an antimony trioxide acts as a water repellent, water proofing agent, if you fill it up completely to a certain extent and also together with that flame.

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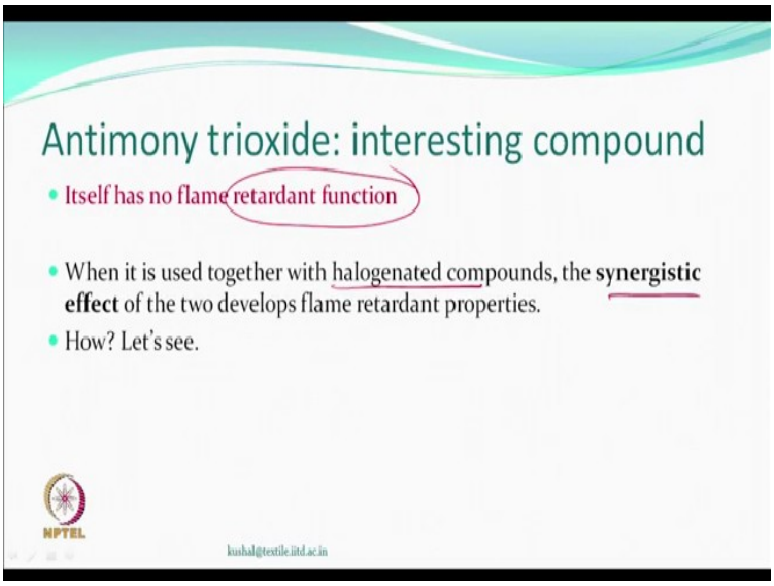

Antimony trioxide is very interesting compound although by itself it cannot do any retardant function, but when it is used with halogenated compound like we talked about PVC or we talked about the chlorinated waxes then it becomes very very effective and that gives a synergistic flame retardancy.

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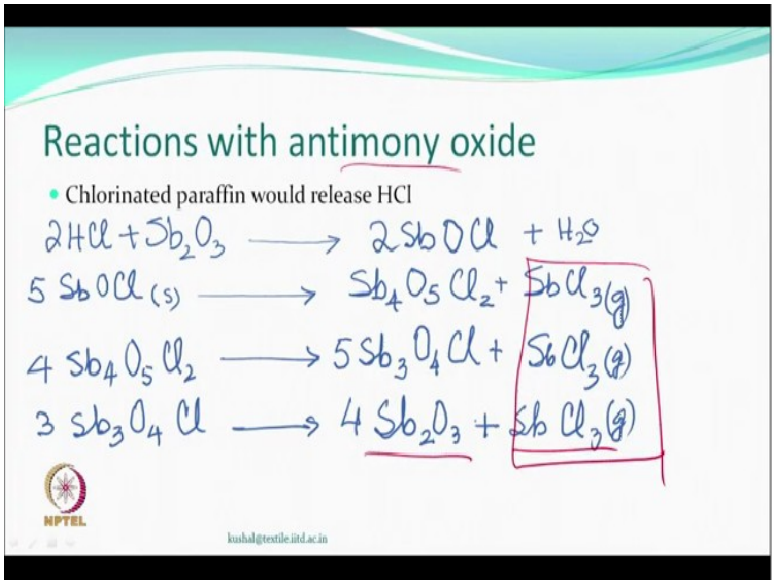

Let us see how does, so they can reduce release HCl and HCl you know can work in the gas phase, but if antimony compounds are present it reacts with these also like the Hcl can react with the antimony oxide to generate compound like oxychloride, antimony oxidechlorides which at different temperatures some reactions of this happen at lower temperature 250 degrees, the others will happen at 300 degrees centigrade.

So this oxychloride in certain proportions can form a gas which is antimony trichloride which is a gas. All these are solid you know solid material, this particular thing which you have used can also with which you have produced by in this previous reaction can further react and produce s SbCl 3 molecule again. This can again further at higher temperatures can get converted to antimony oxide which we had to start with and gas.

Now remember this is gas, it actually is gas, so it is going to be in the vapor form is being produced, this gas which is the antimony trichloride is effective flame retardant exactly in the same way that Hcl but because so much of this can be produced by the antimony itself if it is present then becomes very very effective. So in tents along with waxy compounds chlorinated waxy compounds if you add antimony oxide it can do flame retardant, water repellency, water proofing and so on so forth.

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So interesting, so what have we learned today, we have learned today chemistry of some of the flame retardants.

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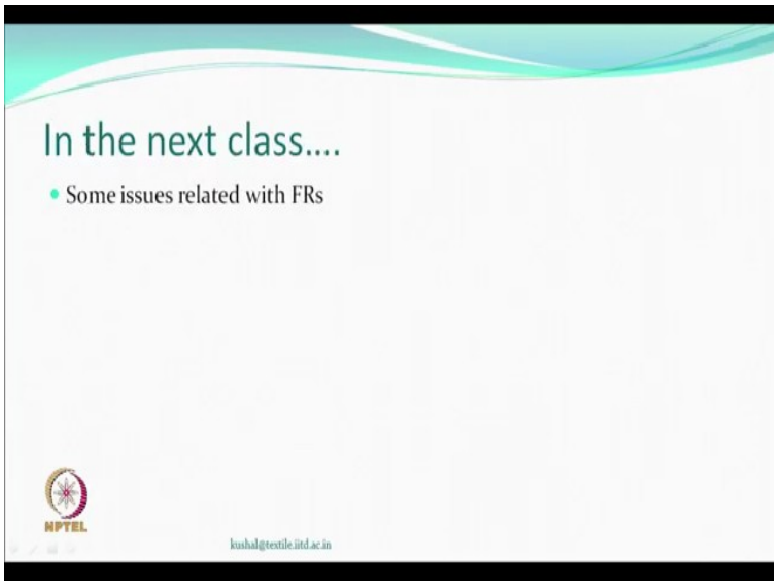

And in the next class we will talk about some other issues related with the flame retardants and maybe flame retardant for some special fibers or flame retardancy of some special fibers that we will talk about ok, till then enjoy see you in the next class.