Polymer Chemistry
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Lecture - 40
Polymers Additives (Contd.)

Welcome back to this course on polymer chemistry. And, in this lecture, we will discuss about polymer additives.

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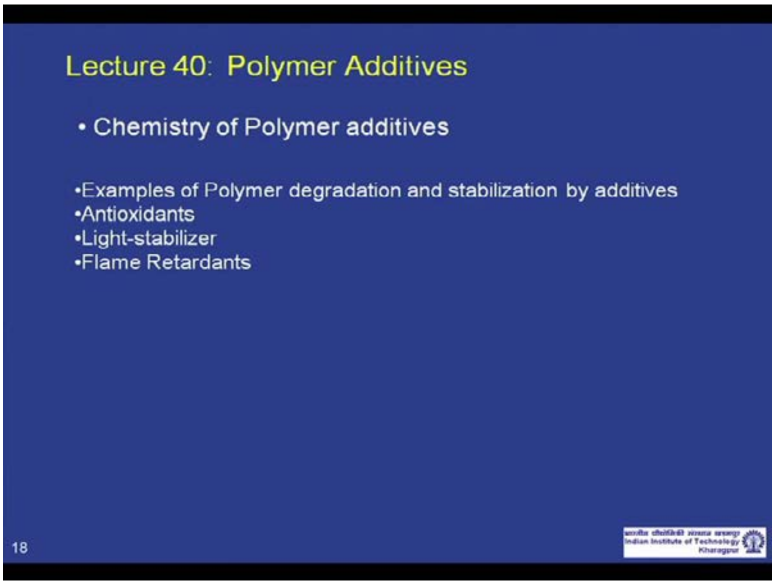

Lecture 40: Polymer Additives

- Chemistry of Polymer additives

- Examples of Polymer degradation and stabilization by additives
- Antioxidants
- Light-stabilizer
- Flame Retardants

We will talk about chemistry of polymer additives, and we will give examples of polymer degradation, and how the stabilization is done using externally added additives. We will talk about anti-oxidants and how they are, how they function in a polymer metrics. We will talk about light stabilizer, and then flame retardants.

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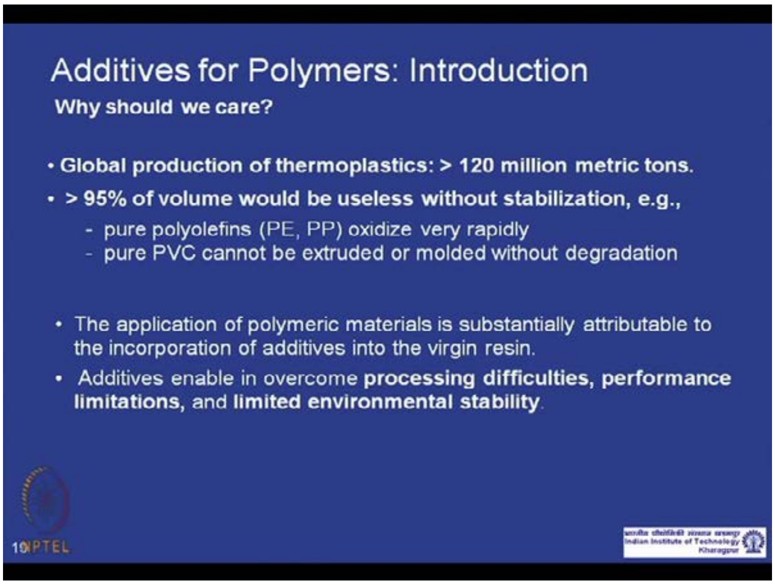

Additives for Polymers: Introduction

Why should we care?

- **Global production of thermoplastics: > 120 million metric tons.**
- **> 95% of volume would be useless without stabilization, e.g.,**
    - pure polyolefins (PE, PP) oxidize very rapidly
    - pure PVC cannot be extruded or molded without degradation

- The application of polymeric materials is substantially attributable to the incorporation of additives into the virgin resin.
- Additives enable in overcome **processing difficulties, performance limitations,** and **limited environmental stability**.

Now, let us first understand, why we need to add additives in polymers? Why should we care at all? Now, if you look at the production of thermoplastics alone, they are over 120 million metric tons. Now, out of this entire volume, 95 percent and more would have been useless without stabilization by adding external additives.

For examples, this pure polyolefins like polyethylenes, polypropylenes, they oxidize very rapidly. So, basically drawing them is very difficult, unless they are stabilized by adding external additives. Pure PVC cannot be extruded and molded in the higher temperature, their processing temperature without degradations. So, if you, if you do not add additives for stabilization, then the polyvinyl chloride, we get out of; the molded part will have very poor mechanical properties, which is, which are not useful for particle applications. So, we require stabilization to have this polymers apply, applicable in the applications, where they are currently used.

So, the application, the successful application of polymeric materials is substantially attributable to the incorporation of the additives into the virgin resin, we just produced from the reactor. Unless, if you do not use the additives in those resins which are coming out of the reactor, they are, will come down drastically. What does additives do? Additives enable the polymers to overcome the processing difficulties; for example, the polyvinyl chloride, we just mentioned; it also help in overcoming some performance limitations, and it also protect, give the protection in a polymer from the environment.

We discussed about the weathering condition with ability, where polymer exports are experienced heavy light and other parameters. So, if we stabilize the polymer, keeping those application in mind, then the applicability will go up. So, basically, by using additives we can enhance or we can overcome the limited environmental stability of the polymers.

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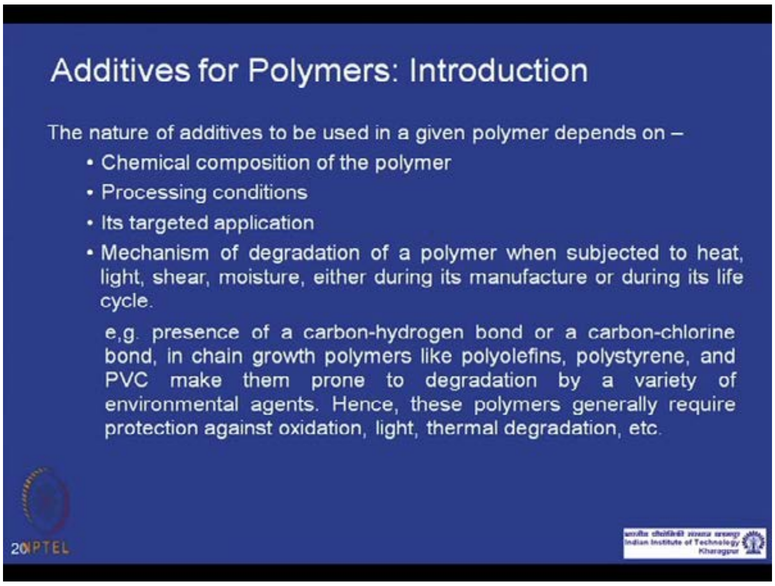

Additives for Polymers: Introduction

The nature of additives to be used in a given polymer depends on –

- Chemical composition of the polymer
- Processing conditions
- Its targeted application
- Mechanism of degradation of a polymer when subjected to heat, light, shear, moisture, either during its manufacture or during its life cycle.

  e,g. presence of a carbon-hydrogen bond or a carbon-chlorine bond, in chain growth polymers like polyolefins, polystyrene, and PVC make them prone to degradation by a variety of environmental agents. Hence, these polymers generally require protection against oxidation, light, thermal degradation, etc.

Now, how do you choose polymers, which polymer, sorry, additives for a particular polymers? Now, the nature of the additives we must use or we use, must be depended on several parameter; for example, composition on the polymer. The additives must be chosen, keeping in mind the chemical composition of polymer; their additive must be comparable; in the sense, that it should not react with the, with the polymer itself or it should not make harm to the polymer itself, which will deteriorate the polymer property.

Processing condition; now, we must know the processing condition of the polymer for which we want to use the additive; now, that will that will give the temperature of use and the amount of share. So, the additives, which we are using, or you planned to use must survive those conditions themselves. So, if we use some additives, which do not survive the condition of the processing of the polymer, which you are interested. Then, obviously, the additives will not function after the molded part or the final part is made.

And, obvious; and also, the interaction between the additives and polymer might be different at that higher condition, higher temperature and higher share rate. So, those things has to be kept in mind. Obviously, the target application has to be kept in mind, which, for which application we want to use that additive. And, we must remember, if you are talking about the stabilizations specifically, you must remember the mechanism by which the polymers are degraded, when subject to heat, light, shear, moisture, either during the processing or during the manufacturer, and during its life cycle.

So, basically, if you want to stabilize or if you want to have a polymer made with the help of, with addition of additives, and we must know the mechanism by which the properties of the polymer deteriorates with the, in presence of light, heat, shear, during the processing or during the use of the polymers in actual application.

Normal chain growth polymers like polyolefins or polystyrene, polyvinyl chloride, they have these carbon hydrogen bond, carbon chloride bonds; these bonds are very prone to degradation by a variety of environmental agents. So, we; so, these are the polymer generally require protection against oxidation, light, and protection again against a UV light and thermal degradation, etcetera. So, these are example about the chemical structure. We need to keep in mind, the chemical structure of the polymer when you design a additive.

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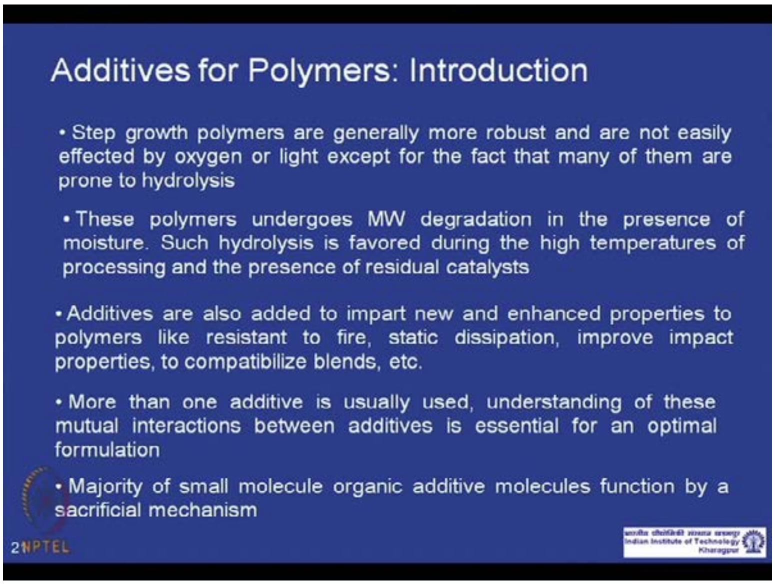

Additives for Polymers: Introduction

- Step growth polymers are generally more robust and are not easily effected by oxygen or light except for the fact that many of them are prone to hydrolysis
  - These polymers undergoes MW degradation in the presence of moisture. Such hydrolysis is favored during the high temperatures of processing and the presence of residual catalysts
- Additives are also added to impart new and enhanced properties to polymers like resistant to fire, static dissipation, improve impact properties, to compatibilize blends, etc.
- More than one additive is usually used, understanding of these mutual interactions between additives is essential for an optimal formulation
- Majority of small molecule organic additive molecules function by a sacrificial mechanism

Step growth polymers, generally do not have these bonds which are very prone for degradation, but they do have the functional groups which are prone to hydrolysis, like this ester groups, amide groups, or carbonate groups. They are, these groups typically hydrolyze very easily, and specially in presence of impurities, metal impurities, and acids and brushes.

So, this polymers actually undergo molecular degradation in process, presence of moisture. And, these hydrolysis, such hydrolysis is favored during high temperature processing. And these are accelerated by, this hydrolysis is accelerated by the presence of residual catalyst. So, you must have, this you keep in mind, when you design additives for step growth polymers.

And, additives are also added to import new and enhanced properties like, in the polymer like, fire resistants, static dissipation, improvement in mechanical properties, to compatibilize blends and so on. So, there are many more examples, where the property of the polymers are enhanced by use of adding external additives.

And, typically in a polymer formulation, more than one additives are used. And, so, a understanding of the mutual interaction between this additives are essential for making an optimal formulations. And, generally, this small organic additives, they worked by sacrifices, sacrificial mechanism; by meaning, by terms sacrificial mechanism meaning, that they do destroy themselves and protect the polymer, the main polymer which you want to maintain or retain. So, basically they destroy them self by doing some chemical reaction, and sacrifice them self to protect the main polymer in concern.

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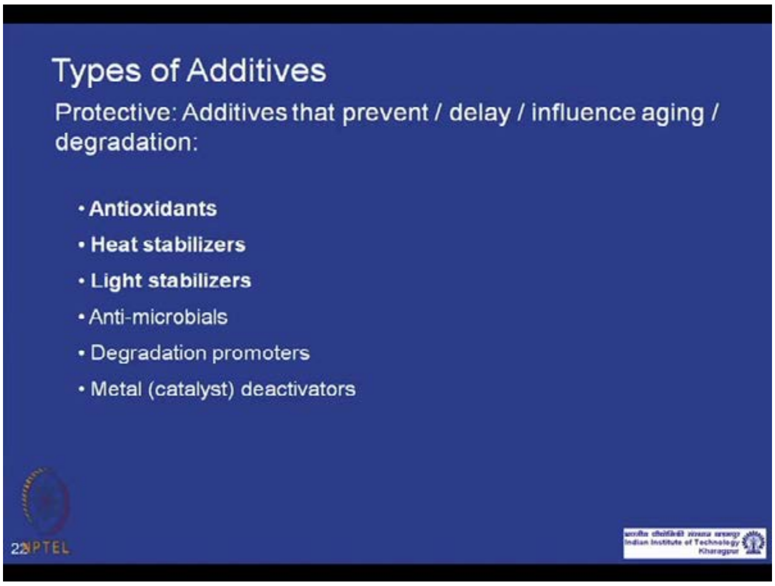

Types of Additives

Protective: Additives that prevent / delay / influence aging / degradation:

- **Antioxidants**
- **Heat stabilizers**
- **Light stabilizers**
- Anti-microbials
- Degradation promoters
- Metal (catalyst) deactivators

So, that, they, we can classify the polymers in several ways. And, we can, for example, we can classify them as a protective, protective additives; which, they are the additives which prevent, or delay, or in or influence, the ageing process or degradation process in the polymers. And, some of the additives used are antioxidants, which basically prevent against oxidation; heat stabilizer, which prevents degradation of polymer under heat; light stabilizer, which basically protect the polymer from UV radiation. Anti microbials, which protect polymer from microbes, bacterias, and so on; metal deactivators, which basically deactivate the catalyst residues or metallic impurities residues, which basically help in, or which basically degrades the polymer, during its use or in processing time.

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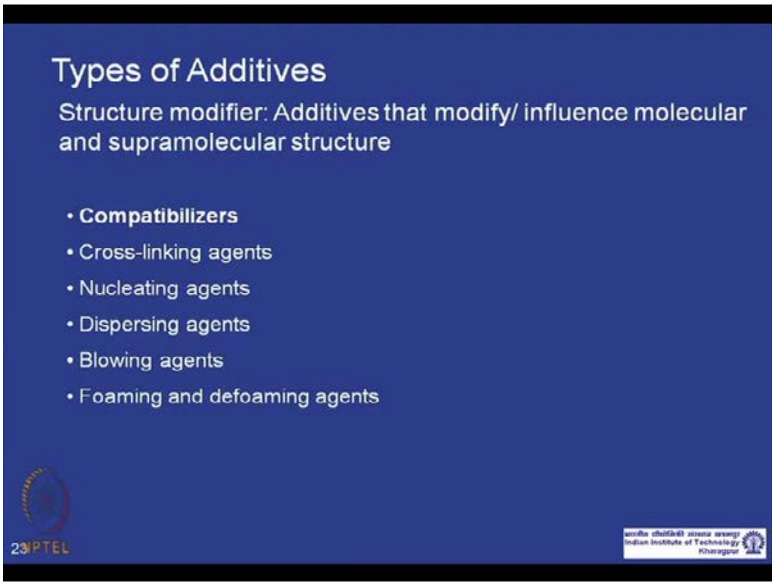

Types of Additives

Structure modifier: Additives that modify/ influence molecular and supramolecular structure

- **Compatibilizers**
- Cross-linking agents
- Nucleating agents
- Dispersing agents
- Blowing agents
- Foaming and defoaming agents

Structure modifier: the additives which modify or influence the molecular or super molecular structures, like compatibilizer, they help in making compatibilized blend; cross linking agents, which obviously, introduced or added to bring cross linking between polymer chains; nucleating agents, they basically added to increasing, increase the crystanality; dispersing agents which are used for dispersing some fillers in the polymer metrics; foaming and defoaming agents, which are added to make foamed polymer product.

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Additives that assist in processing, fabrication, assembly:

- **Lubricants**
- Processing aids
- **Mold release agents**
- Adhesion promoters
- Scavengers and acid neutralizers
- Catalyst quenchers

There are additives, which are used in polymer formulations, which basically assist in processing and fabrication, or in assembly, like lubricants, mold release agents which basically help in reducing the mold from after the brat is formed processing head, adhesion promoters, scavenger and acid neutralizer, catalyst quenchers; they are some other examples, general examples of this type of additives.

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Additives that provide enhanced properties:

- **Flame retardants**
- Impact modifiers
- **Antistatic agents**
- Antiblocking agents
- Antifogging agents
- Optical brighteners
- Pigments and colorants
- Coupling agents
- Plasticizers
- **Reinforcements**

As I said earlier, that there are numerous, numeron additives are added to increase the property, or they enhance the properties of polymers. And, there, there could be list of many such additives; for example, flame retardants which help in reducing the flame flame ability of the polymers, impact modifier, antistatic agents, antiblocking agents, anti fogging agents, optical brighteners, pigment and colorants, coupling agent, plasticizers, reinforcements, so many things can be added to enhance the property. And obviously, you cannot add all these for every polymer. And, it depends upon the final applications; if your applications required a flame, a polymer which is flame resistant, then you must add a flame retardant to it.

And, if you are making a polymers, which will be like a packing film for food trapping application; then if you, if he is having anti fogging additives, then it will prevent fogging a condensation of the water moister in the packing film, which will basically allow the customers to look through that film. If the anti fogging agents, so, additives were not present, it will condense, and the customers could not be able to look through that film; so, that will basically be a bad property of the film.

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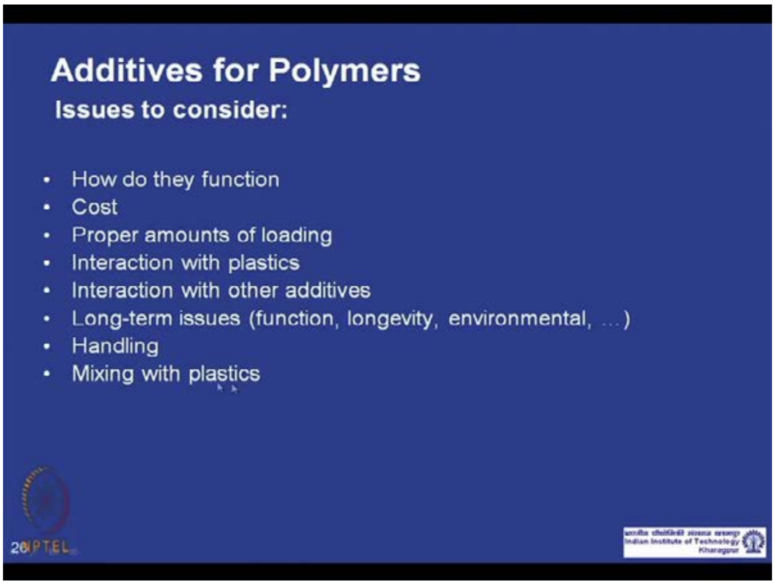

Additives for Polymers

Issues to consider:

- How do they function
- Cost
- Proper amounts of loading
- Interaction with plastics
- Interaction with other additives
- Long-term issues (function, longevity, environmental, ...)
- Handling
- Mixing with plastics

Now, before we discuss; in the chemistry, there are some issues about the additives we must consider is, how do they function, the mechanism; obviously, chemistry plays a major role in this. And, cost, though the amount of additives are added in small quantity, but typically they are much costlier than the base resin. So, basically, one must remember or must consider the cost of the additives used. Even though the amount of the additives used are less, but because of their higher cost compared to the base resin, the cost of the polymer formulation would be higher. So, the cost for the particular application must be kept in someone, in mind of the, in mind of the manufactural.

Proper amount of loading: sometimes this additives function for a particular level of loading; too less loading or might not be bring about the advantage which are the manufacturer looking for; and too much of addition of the additive might destroy the polymer itself, and obviously, the cost of the formulation will go up. So, the optimum loading of the additives is what required. And, you must know the interaction of the additives with the plastics; what is the, how they interact with plastics, interacts with other additives; as I said, the multiple additives are used; same times interaction with other additives are also be important.

And. long term issues: like, how they function, there long term longevity, and they are effect in the environment; they must, this should be considered; for example, if you are using some the packaging film for food application, then the additives should not leak out and contaminate the food. For example, if you are adding some additives for some medical application, then the additives should not come out and contaminate the medical devices. So, so that should be considered before the polymer is used.

How it is handling? Handling of the additives also concerned. For example, liquid additives are normally difficult to handle. If you are using a polymer powder, and if you want to add liquid, the dispersing, dispersion of the additives in the polymer powder is difficult. So, how, you must know, how you will handle the additives which you are going to add in the formulation, and how you are going to mix it with the plastics, that is important.

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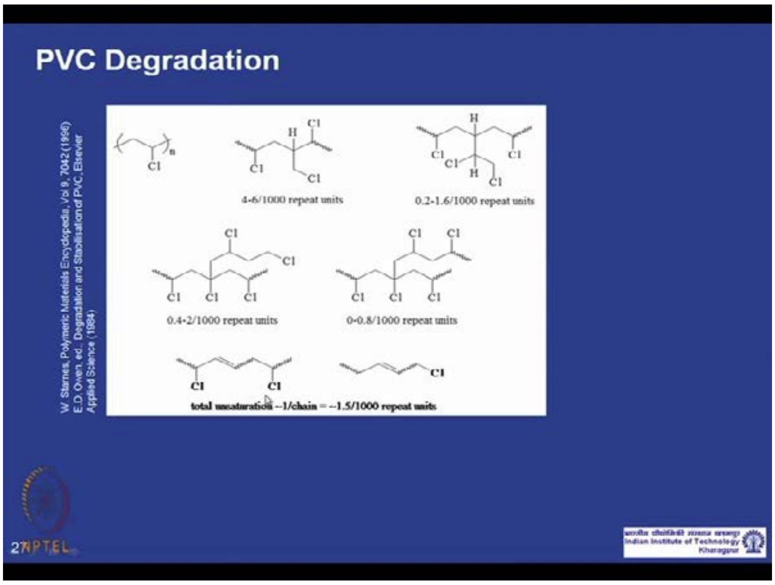

PVC Degradation

W. Starnes, Polymeric Materials Encyclopedia, Vol 9, 7042 (1996)
E.D. Owen, ed., Degradation and Stabilisation of PVC, Elsevier Applied Science (1984)

4-6/1000 repeat units

0.2-1.6/1000 repeat units

0.4-2/1000 repeat units

0-0.8/1000 repeat units

total unsaturation ~1/chain = ~1.5/1000 repeat units

Let us take an example about polymer degradation. We are discussing that polymer might degrade in presence of UV light, or in presence heat or light. Now, let us talk about one of the common example of polymer degradation and the stabilization; and let us take example of polyvinyl chloride degradation. Now, these are the; this is, as you know, this is the structure of polyvinyl chloride, but along with the main chain, there could be some other units in the polymer back bone. They are, the number is very less; it is given 4, 4 to 6 out of 1000 repeat units, 0.2 to 1.6 out of 1000 repeat units. So, basically, these, this irregularities are very less in the polymer chain, but the degradation is mainly caused by this irregularities itself, not the main polymer chain.

So, the unsaturation and the tarcaric chlorines are very bad for thermal stability, for polyvinyl fluoride. And, these unstauration or the terminal chloride, terminal chlorine, resins of terminal chlorine arises due to the chain transfer reaction during polymerization. And, it is very difficult to avoid these reactions. And, these sides serve as chlorine radical source, which basically initiate the degradation.

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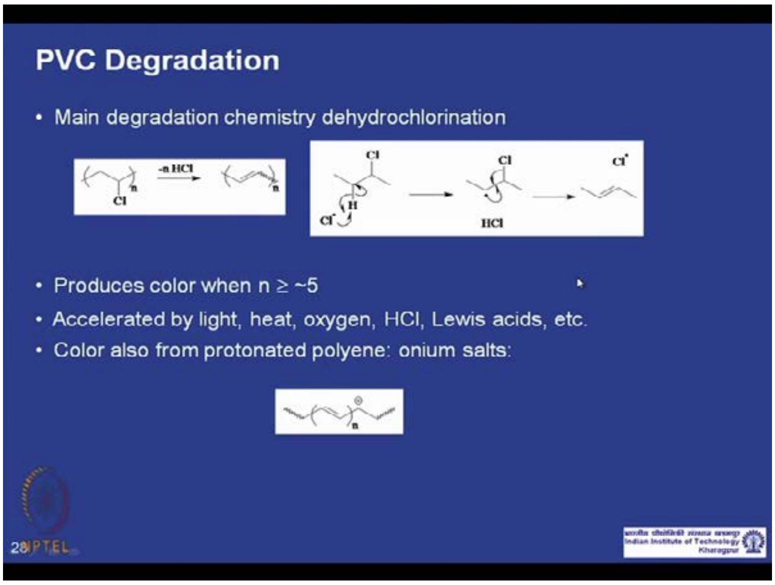

PVC Degradation

- Main degradation chemistry dehydrochlorination
- Produces color when n ≥ ~5
- Accelerated by light, heat, oxygen, HCl, Lewis acids, etc.
- Color also from protonated polyene: onium salts:

So, the main degradation happened by dehydrochlorination as shown in this figures. The main degradation of polyvinyl chloride happened due to the dehydrochlorination at higher temperature, and that starts with chlorine radical. And, if you have these consecution over 5, 5 carbon atom or 5 double bonds basically, then it will produce colour. And, these degradation is accelerated by, in presence of light, heat, oxygen and presence of acids. And, colour may form, also from these protonated polyenes as it is shown in this figure.

So, basically, if you want to stabilize polyvinyl chloride, you basically want to have a mechanism by which you can trap chloride chlorine radical, or you can destroy this allophonic or arylic double bonds which is producing, getting produced during the degradation process.

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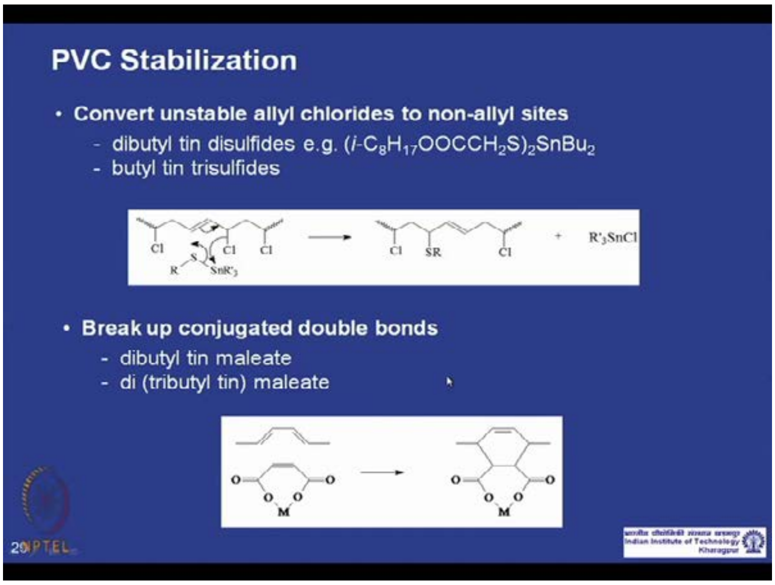

PVC Stabilization

- **Convert unstable allyl chlorides to non-allyl sites**
  - dibutyl tin disulfides e.g. $(i\text{-}C_8H_{17}OOCCH_2S)_2SnBu_2$
  - butyl tin trisulfides

- **Break up conjugated double bonds**
  - dibutyl tin maleate
  - di (tributyl tin) maleate

So, how the stabilization is done? One example, there are many, many additives can be used; one additives, one type of additives are shown here. They convert these unstable arylic, allyl chlorides to non allic, non allyl sites; and example dibutyl tin disulfides, and their chemical reaction with the allylic double bond is shown here. So, they form this arylic, allyl chloride to non allylic sites and prevent degradation. And, there are additives like dibutyl tin maleate, which basically break up the conjugated double bond, and prevent the degradation further.

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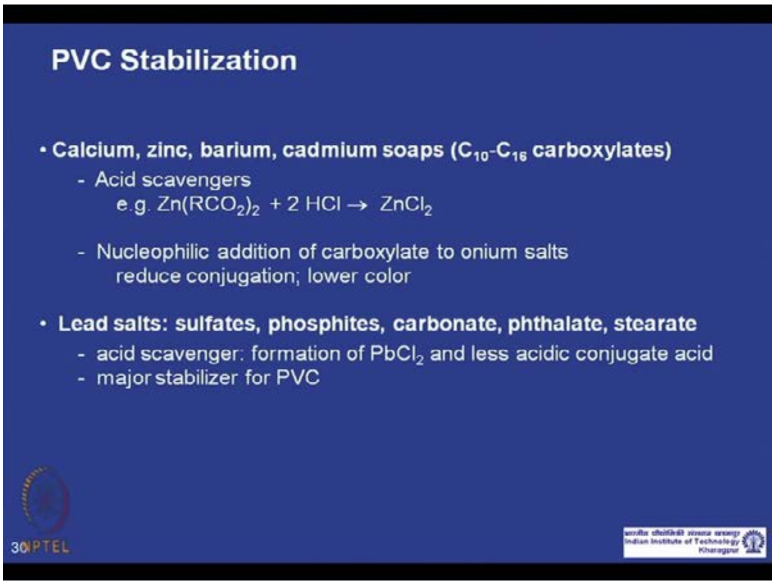

PVC Stabilization

- **Calcium, zinc, barium, cadmium soaps (C_{10}-C_{16} carboxylates)**
  - Acid scavengers
    e.g. $Zn(RCO_2)_2 + 2\ HCl \rightarrow ZnCl_2$
  - Nucleophilic addition of carboxylate to onium salts
    reduce conjugation; lower color
- **Lead salts: sulfates, phosphites, carbonate, phthalate, stearate**
  - acid scavenger: formation of $PbCl_2$ and less acidic conjugate acid
  - major stabilizer for PVC

The other additives used for PVC stabilizations, like soaps of cadmium, zinc, barium salts; and, they act as acid scavengers. Lead salts also act as acid scavenger; and, they, basically are one of the major additives used in PVC industry. So, this is one example, we just discussed about PVC. And, PVC is a very prone to degradation under processing. So, this one example; is a very good example to discuss about polymer degradation and stabilization.

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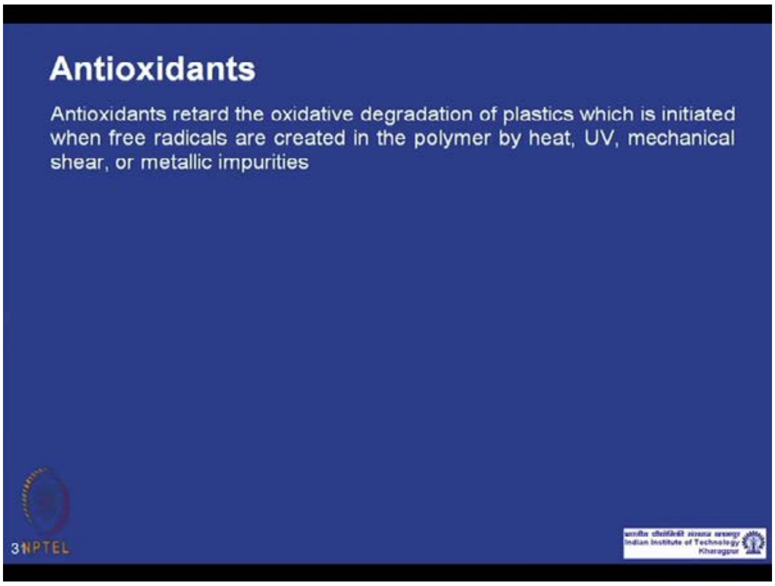

Antioxidants

Antioxidants retard the oxidative degradation of plastics which is initiated when free radicals are created in the polymer by heat, UV, mechanical shear, or metallic impurities

Now, let us talk about one more class of additives- anti oxidants. The anti oxidants basically retard the oxidative degradation process of polymers, which is initiated, the oxidative degradation is initiated, when free radicals are created in the polymer material by, either heat, UV, mechanical shear, or metallic impurities. So, anti oxidants basically retard the oxidative degradation process. Now, to know the anti oxidant additives which are used, let us discuss the basic autoxidation scheme for a minute.

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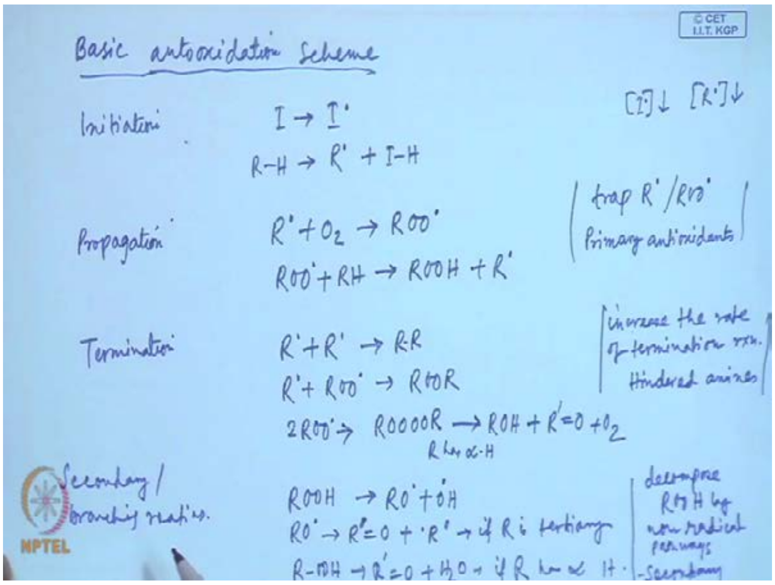

Basic autooxidation scheme

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$[I^\cdot]\downarrow$ $[R^\cdot]\downarrow$

Initiation

$I \rightarrow I^\cdot$

$R{-}H \rightarrow R^\cdot + I{-}H$

Propagation

$R^\cdot + O_2 \rightarrow ROO^\cdot$

$ROO^\cdot + RH \rightarrow ROOH + R^\cdot$

trap $R^\cdot / ROO^\cdot$ Primary antioxidants

Termination

$R^\cdot + R^\cdot \rightarrow R{-}R$

$R^\cdot + ROO^\cdot \rightarrow ROOR$

$2ROO^\cdot \rightarrow \underset{R \text{ has } \alpha\text{-H}}{ROOOOR} \rightarrow ROH + R'{=}O + O_2$

increase the rate of termination rxn. Hindered amines

Secondary / branching reactions.

$ROOH \rightarrow RO^\cdot + {}^\cdot OH$

$RO^\cdot \rightarrow R'{=}O + {}^\cdot R' \rightarrow$ if R is tertiary

$R{-}OOH \rightarrow R'{=}O + H_2O \rightarrow$ if R has α H.

decompose ROOH by non radical pathways -Secondary

So, let us go through and look this basic. The first step is basically initiation. So, you have a initiator forming a initiator radical which might abstract hydrogen from polymer backbone, forming a radical in the backbone. Now, these R, R dot can be produced by the hemolytic cleavage of this C H type bonds, in presence of heat from the polymer itself. Next, normally the propagation happen; propagation step, where it reacts with oxygen forming peroxide radical; and, this radical start the further chain reaction, forming further radical.

Termination of this chain might happen by reaction between the radicals; basically, reaction between 2 radicals. Now, if there are, if R has an alpha hydrogen; if R has an alpha hydrogen, it can further form epitomic type moiety. So, this happens, this reaction only happen, that R has alpha hydrogen. The others, other secondary and branching reaction can also happen; secondary and branching reactions, hydro peroxide can give other radical; if R is tertiary, tertiary, if R has alpha hydrogen. So, these are the basic auto oxidation mechanism by which oxidative degradation might happen. It is, as you can see, it is a radical process; now, to prevent these; so, if you want to design an anti oxidant, you basically have to attack or stop all this processes.

Now, anti oxidants are added or designed, which cannot attack or prevent all these steps, but it might prevent some step in between. So, one thing can be possible; if you want to use or stop these auto oxidation, you might reduce the concentration of the I radical or the R dot; you can reduce the concentration of I dot or R R radical; now, that is basically out of our hand, because the processing and the other external conditions we cannot control.

So, what we can do? We can trap this R dot; or, say, peroxide radical, and that is done by primary anti oxidant. So, primary anti oxidant, basically trap this R dot and peroxy radicals. We can increase the rate of termination reaction; and, that is done by addition of hindered amines. Now, we can also do, and decompose the; first stop this step; we can decompose these by non radical pathways. And, this is typically done by use of secondary anti oxidants. So, basically, we know, what are the step in oxidation process or to oxidation processes? Normally, inefficient propagation termination and secondary and branching reactions.

And, to prevent that, what are the things we might do or it is typically done? You can always reduce the radical concentration, but it is not in our hand. So, we can add the additives which can trap this radical R dot or proxy radicals, which is done by adding primary anti oxidant; we can increase the rate of termination reaction, which is done by adding hinder diamine. Or, we can decompose this hydro, hydro peroxides by non radical path ways. And, that is done by adding secondary anti oxidant.

Example of these primary anti oxidants, hinder diamines and secondary anti oxidants, and how they do this trapping or decomposition or increase in the rate of termination, we will discuss briefly now. So, primary anti oxidant, as you said, as I just mentioned, it traps this R dot and proxy radicals.

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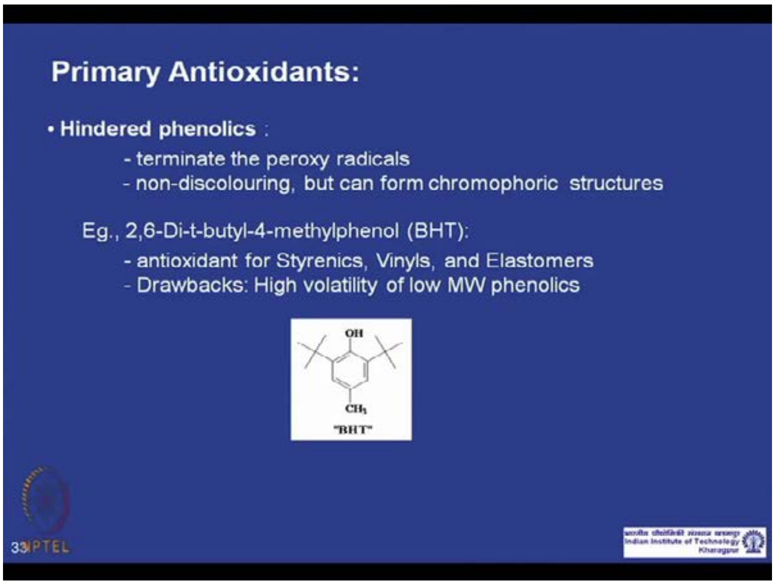

Primary Antioxidants:

- **Hindered phenolics** :
  - terminate the peroxy radicals
  - non-discolouring, but can form chromophoric structures

Eg., 2,6-Di-t-butyl-4-methylphenol (BHT):
- antioxidant for Styrenics, Vinyls, and Elastomers
- Drawbacks: High volatility of low MW phenolics

And, there are several types of anti, primary anti oxidants: one is hindered phenols; they basically terminate the proxy radicals, as I just mentioned. And, they themself are non discolouring, but they can form chromophoric structures, after they, to this hydroxyl, a proxy radical trapping. One example, the common example is BHT, butyl hydroxotolovine; structure is shown here; they are used in this type of anti, primary anti oxidants are used very much for styrenics, vinyls, and elastomers. But, the drawback for these primary anti oxidants, that they form a very volatile low molecular rate phenolics. So, they might get lost during the processing conditions.

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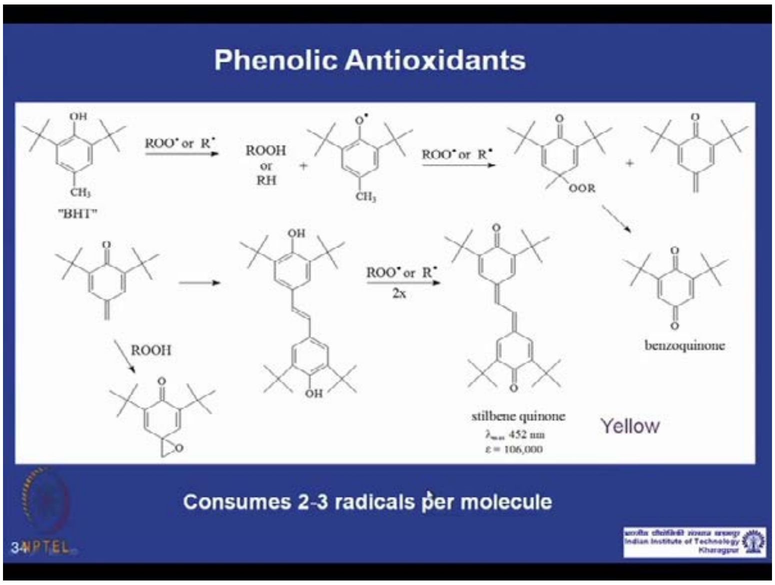

Phenolic Antioxidants

Consumes 2-3 radicals per molecule

So, these are the mechanism by which they work. For example, these are additives, trap this radical, form a radical by themselves, which can rearrange, and react with the other radicals, and form non radical species. And, these final species like stilbene quinine, benzo quinone, they basically are sometimes colour bodies. So, then this additives themself is not, or they would not decolour the polymer, but final compounds, when they form after stabilization, that could generate colour in the polymer matrix, that is the one drawback. And, one each radical, basically capture 2, 3 radicals, and by which they basically prevent these oxidation process.

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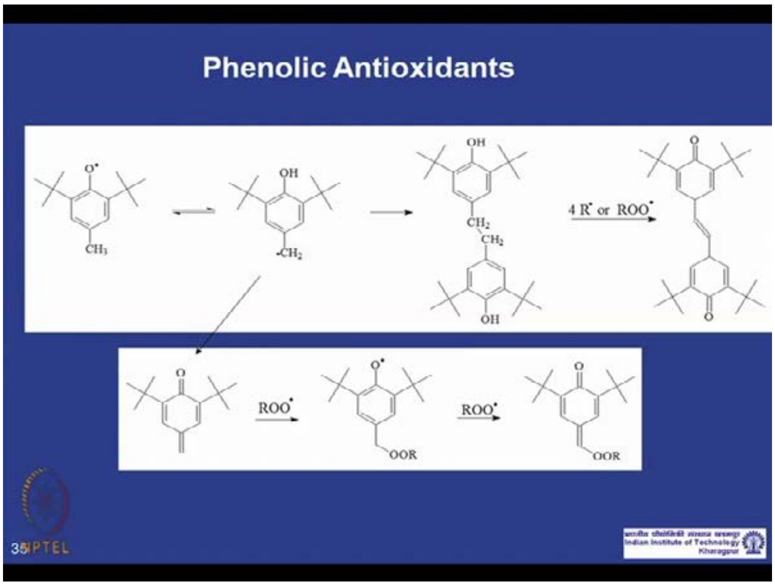

Phenolic Antioxidants

Some other mechanism continuing in the, from the last page, how this type of butane hydroxyl tolovines capture or trap the radicals are shown here. So, basically, they capture or trap the radical produced; and, by doing this, they basically reduce the oxidation process; and, the only drawback is that they sometimes form a coloured compound, in doing that.

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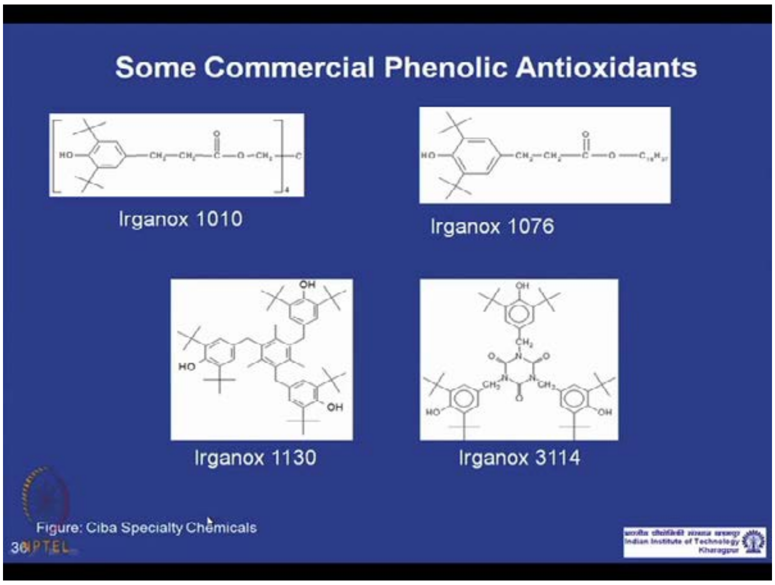

Some Commercial Phenolic Antioxidants

Irganox 1010

Irganox 1076

Irganox 1130

Irganox 3114

Figure: Ciba Specialty Chemicals

NPTEL

Indian Institute of Technology Kharagpur

These are some examples. There are many many phenolic anti oxidants available in the market. These are some example shown here. They are this phenolic anti oxidants. And one thing, it can be noted, not only for this anti oxidant, for all other additives as well that, it is not always a, that all this additives will work for a particular polymer or all polymers.

So, basically there is some trial, and experiments one need to do, to find out the best possible additives for the polymer you are looking for. So, there are some experiments must be done, looking at the mechanism by which the stabilization or the additives; what function you are adding the additives for, that is done.

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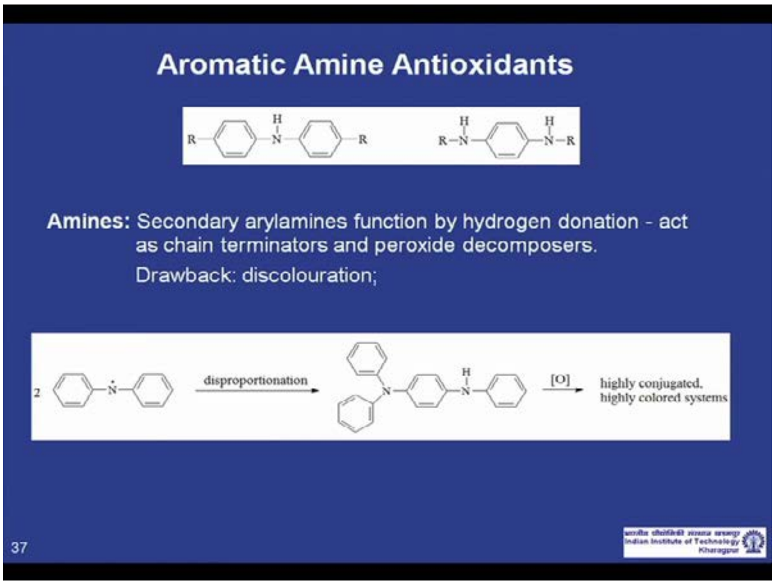

Aromatic Amine Antioxidants

Amines: Secondary arylamines function by hydrogen donation - act as chain terminators and peroxide decomposers.

Drawback: discolouration;

The aromatic amine antioxidants in the diamines, which basically, as we said, increase the rate of termination reactions. So, they are amine, secondary arylamines function by hydrogen donation, and they act has chain terminators of peroxide decomposition, decomposer. The drawback is that they might, it is produced colour bodies, and that will discolour the polymer matrixs. But, these are the some examples, I am keeping on; there could be many many more examples of this type of additives, but this is just for your knowledge that these are the possible way of using additives, and how they actually do their job; for example, primary anti oxidants by trapping the radicals, and these by increasing the termination reaction.

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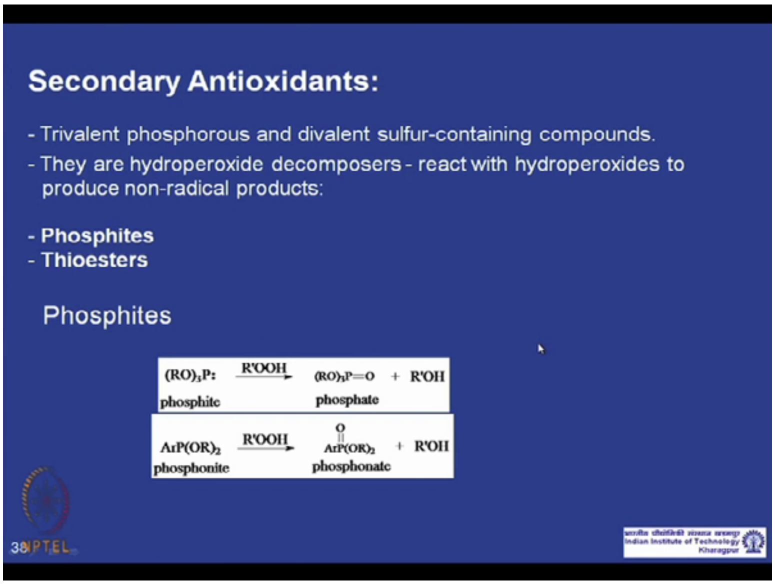

Secondary Antioxidants:

- Trivalent phosphorous and divalent sulfur-containing compounds.
- They are hydroperoxide decomposers - react with hydroperoxides to produce non-radical products:

- **Phosphites**
- **Thioesters**

Phosphites

$$\underset{\text{phosphite}}{(RO)_3P:} \xrightarrow{R'OOH} \underset{\text{phosphate}}{(RO)_3P{=}O} + R'OH$$

$$\underset{\text{phosphonite}}{ArP(OR)_2} \xrightarrow{R'OOH} \underset{\text{phosphonate}}{Ar\overset{O}{\overset{\|}{P}}(OR)_2} + R'OH$$

Secondary anti oxidants, they are hydro peroxide decomposers; react with hydro peroxides and produce non radical products. And, examples are like trivalent phosphorous, divalent sulfur compound, containing compounds, phosphites, thioesters, these are the common examples of secondary anti oxidants. For example, how they work phosphites; they basically decompose these hydro peroxides, and form non radical products, and thereby decreasing the concentration, decrease the concentration of hydro peroxide. Hence, decrease the auto oxidation process.

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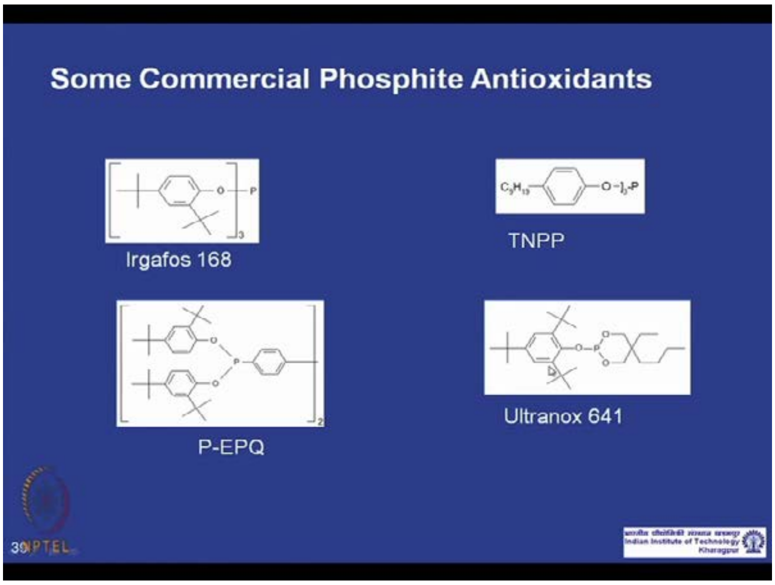

Some Commercial Phosphite Antioxidants

Irgafos 168

TNPP

P-EPQ

Ultranox 641

Some commercial phosphite anti oxidants are shown here. Again, there are many more; and, there is no buyers for these anti oxidants, from my point. These are just examples arbitrarily chosen from the literature.

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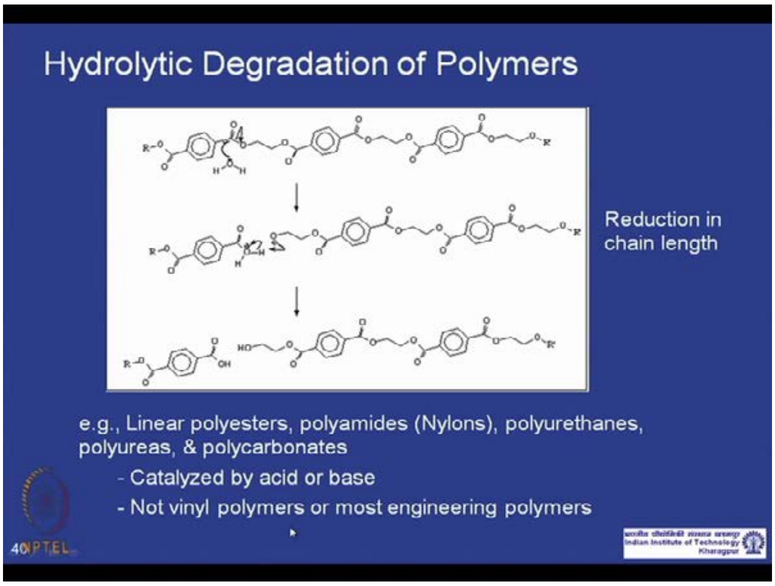

Hydrolytic Degradation of Polymers

Reduction in chain length

e.g., Linear polyesters, polyamides (Nylons), polyurethanes, polyureas, & polycarbonates

- Catalyzed by acid or base
- Not vinyl polymers or most engineering polymers

Now, we mentioned, I mentioned that the step growth polymers are, have those functional groups, like esters, carbonates, or amides. They are proven to hydrolyze. For example, this PET is shown here; polyethylene terephthalate polyester, they can react with water and hydrolyze. And, hydrolysis process, basically reduce the chain length. And, once the chain length is reduced, molecular rate goes down, and the properties of the polymer also go down.

And, this happens, as I mentioned this, for linear polyesters, polyamides, polyurethanes, polyureas, polycarbonates, where their functional groups have, groups which are prone to hydrolyze. And, they catalyst by presence of acids or basis we know (()) organic chemistry that hydrolyzes is catalyst by the presence of acid and basis, and vinyl polymers do not usually undergo this type of hydrolysis.

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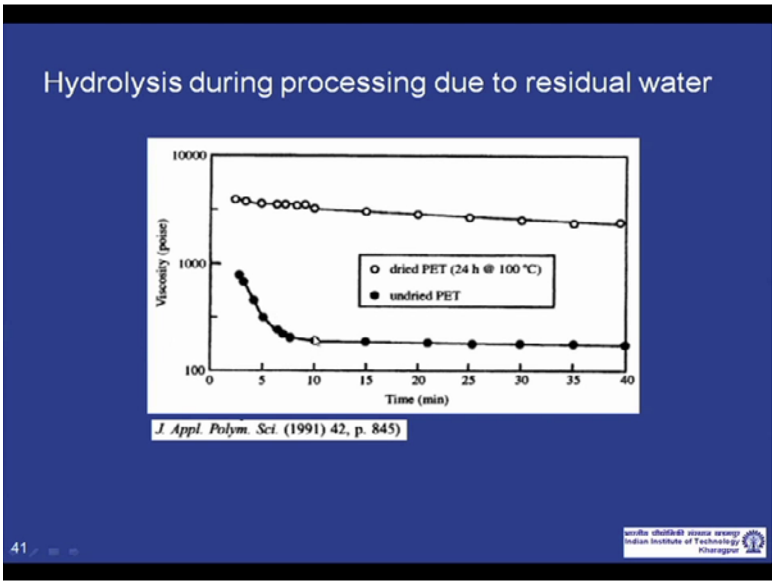

Hydrolysis during processing due to residual water

J. Appl. Polym. Sci. (1991) 42, p. 845)

And, these are the one example of the hydrolysis happening during the processing condition at higher temperature, at higher shear rate. This is for a polyethylene terephalate, which has been dried for 100 degree centigrade at 20 hours; that means, the moisture content in this polyethylene terephalate sample is very less. So, during processing, the hydroxylation, the hydrolysis is less, so the molecular drop. Hence, the viscosity drop is less.

Whereas, if, is take a undried PET, which have significant amount of moisture in the sample, then it actually hydrolysis very soon in that high temperature and high shear condition, during processing as a freezen molecular weight drops, and viscosity of the sample also drops.

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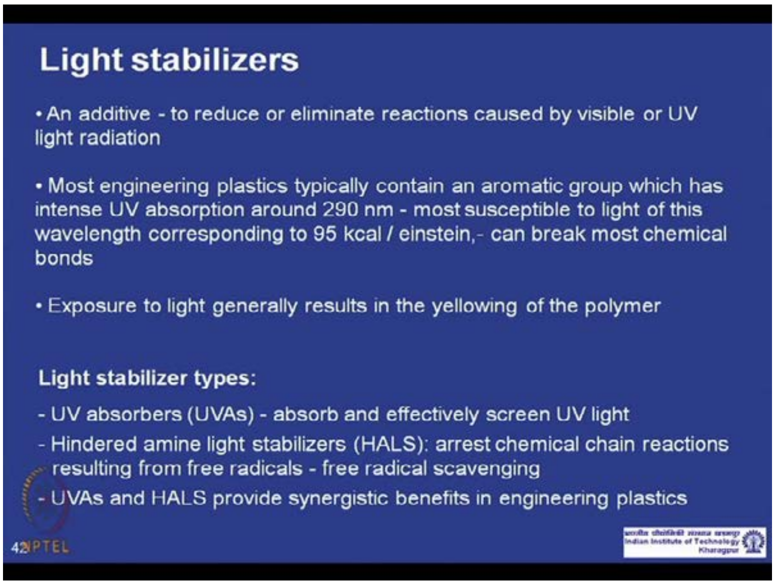

Light stabilizers

- An additive - to reduce or eliminate reactions caused by visible or UV light radiation
- Most engineering plastics typically contain an aromatic group which has intense UV absorption around 290 nm - most susceptible to light of this wavelength corresponding to 95 kcal / einstein,- can break most chemical bonds
- Exposure to light generally results in the yellowing of the polymer

Light stabilizer types:

- UV absorbers (UVAs) - absorb and effectively screen UV light
- Hindered amine light stabilizers (HALS): arrest chemical chain reactions resulting from free radicals - free radical scavenging
- UVAs and HALS provide synergistic benefits in engineering plastics

Let us talk about, next, light stabilizer. Light stabilizers are added as additive to eliminate or reduce the reactions in the polymers caused by visible or UV light radiation. The most engineering plastics or hypo (()) of polymers, they contain aromatic groups, which intensely absorb UV light around 290 nano meter; and, this is most susceptible light in, this wave length corresponds to 95 kilo calorie per Einstein energy; and, that can break most of the chemical bonds. So, basically, absorption of UV light is basically determinant for the polymer molecules. And, once the bond cleavage starts, you can get lots of chemical bodies forming, which absorb the UV, visible near, UV visible range forming yellow colour of the polymer.

So, you can use 2 types of, 2 or 3 types of UV stabilizers. One, UV is UV absorbers which basically absorb and effectively screen the UV light from interactive with bulk of the polymer matrices. Other types of UV stabilizer, hindered amine light stabilizer HALS, which basically arrest the chemical chain reaction resulting from the free radical, which basically are free radicals scavengers. And, this 2 can be added together, sometimes to have a synergistic benefit for engineering plastics.

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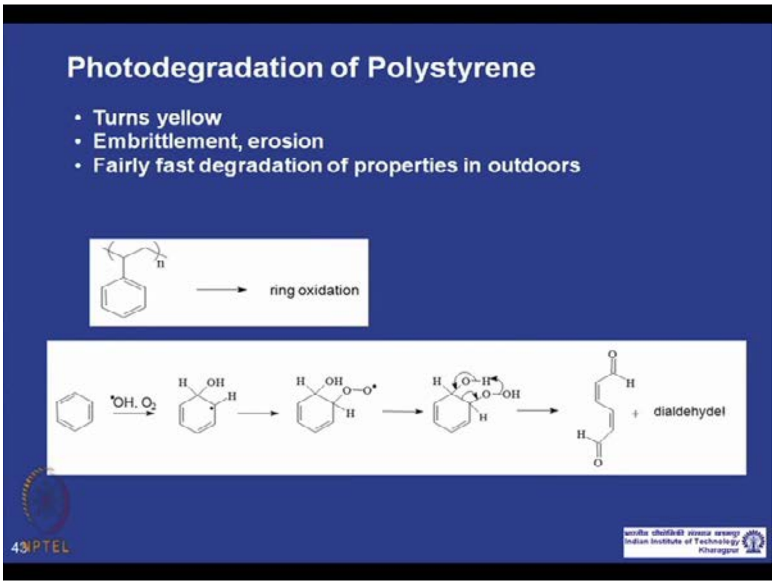

Photodegradation of Polystyrene

- Turns yellow
- Embrittlement, erosion
- Fairly fast degradation of properties in outdoors

Let us take example of photodegradation of one polymer. In this case, we, let us talk about polystyrene. So, with the exposer to UV light, it turns yellow; as a result of that, bond cleavage will be high energy UV light; and, as the result, the polymer becomes embrittle. And, this degradation of molecular happens faster in outdoor conditions, because it has exposed to the UV light, much more extent than indoor conditions.

In case of polystyrene, as we said, that it is the presence of aromatic groups which basically responsible for absorption of UV light, and that actually causes ring oxidation and which can basically initiate the polymer degradation process, as shown in this figure. And, they finally, they can form this (()), which is responsible for the yellowing of the polymer material.

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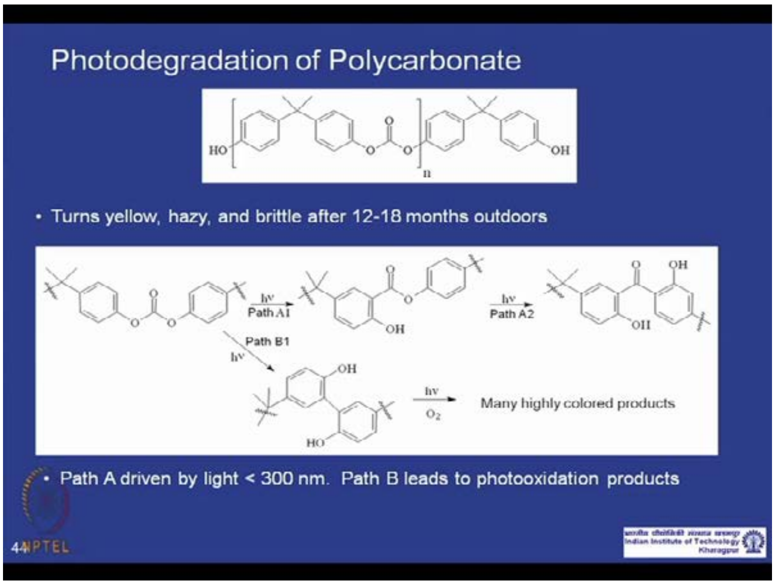

Photodegradation of Polycarbonate

- Turns yellow, hazy, and brittle after 12-18 months outdoors

- Path A driven by light < 300 nm. Path B leads to photooxidation products

And, another example of photodegradation of polycarbonate; if you take BPA polycarbonate and keep it outside, for 1 to 1 and a half hours, it turns yellow and becomes hazy and brittle of that time. And, there 2 path ways by which BPA poly carbonate, discriminate polycarbonate undergo photooxidation. This 2 path is shown here. There could be rearrangement, molecular rearrangement due to absorption of UV light; or, it could be, in this case it could be due to photo oxidation product, and these basically produced highly coloured product.

So, the polymer matrix becomes yellow, and this process also, the polymer property polymer molecular drops, and the property of the polymers become significantly lower compared to what it was originally after the molding.

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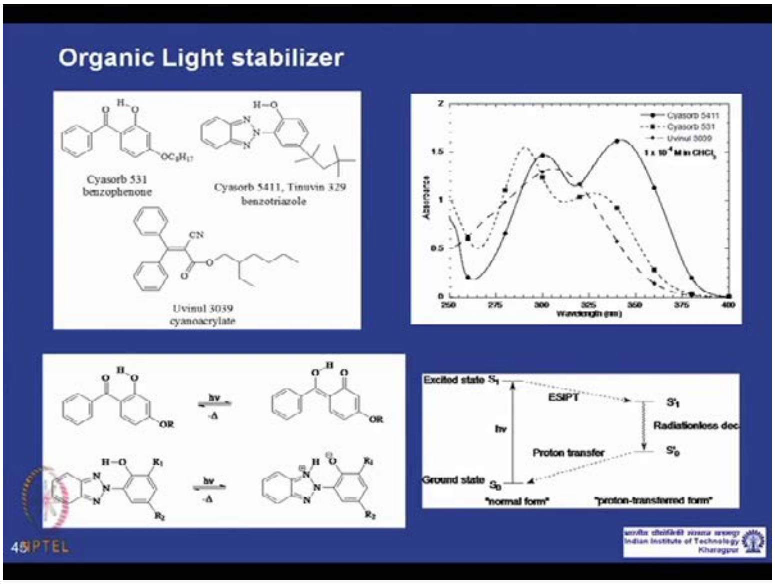

Organic Light stabilizer

So, light stabilizer must; basically we talked about 2 types of light stabilizer- one, which can absorb the UV light and protect the bulk of the polymer from UV light; and second we talked about HALS, which basically prevent the oxidation process or the radical process, and prevent the molecular weight degradation. And, these are the some examples of organic light stabilizers. Again, there are many stabilizers available in the market. I just took few examples.

And, their UV visible spectrise zone, as you can see, from the absorbance, they actually absorb heavily in the UV range, because they absorb; they actually prevent the bulk of the polymer from getting exposed to the UV condition.

Now, the mechanism of these absorption, UV absorption happens that, they basically absorb, and then at excited state, protons transfer happen; and finally, they form a new excited state, which, from which they, by radiation less process they come back to the new ground state.

So, this is example of that photo stabilizer in normal ground state; and, with absorption of UV light they go to a first exited state, where a proton transfer happen; and, finally, a radiation less process bring them back to a new ground state. So, by this mechanism, this is the mechanism by which this organic light stabilizers function as a photo stabilizer.

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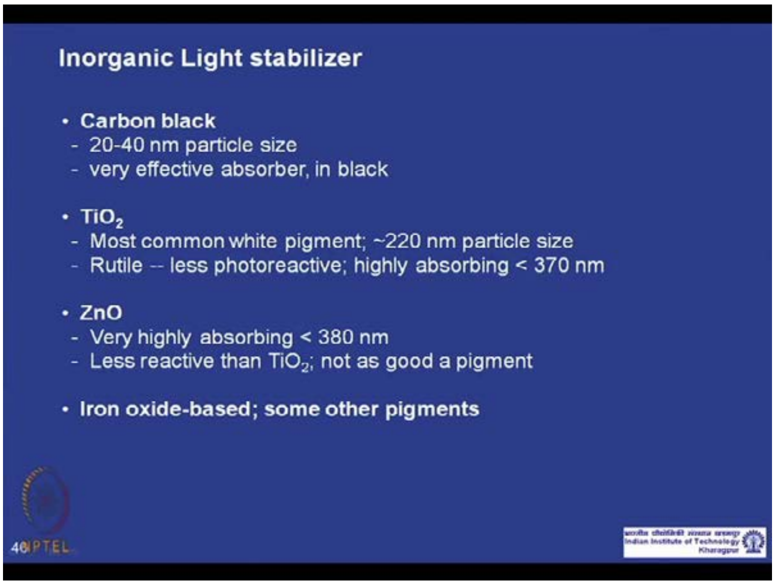

Inorganic Light stabilizer

- **Carbon black**
  - 20-40 nm particle size
  - very effective absorber, in black
- **TiO_2**
  - Most common white pigment; ~220 nm particle size
  - Rutile -- less photoreactive; highly absorbing < 370 nm
- **ZnO**
  - Very highly absorbing < 380 nm
  - Less reactive than TiO_2; not as good a pigment
- **Iron oxide-based; some other pigments**

There could be inorganic lights stabilizer or photo stabilizer as well, for example, carbon blacks; and, they have particle size from 20 to 40 nano meters; and, they are very effective absorber; but, obviously, they can be, all be used in samples, which are meant to be black. Titanium oxides, it is another UV absorber, which absorbs highly below 370 nano meter. Another example could be zinc oxide and iron oxide based, some other pigments also can be used. But, these are not; this is the normanic life steps; there are though, they protect from UV light, but they have some other problems which basically prevent their use in practical applications. So, these are the inorganic light stabilizer; they do not get used very frequently in applications, in real applications.

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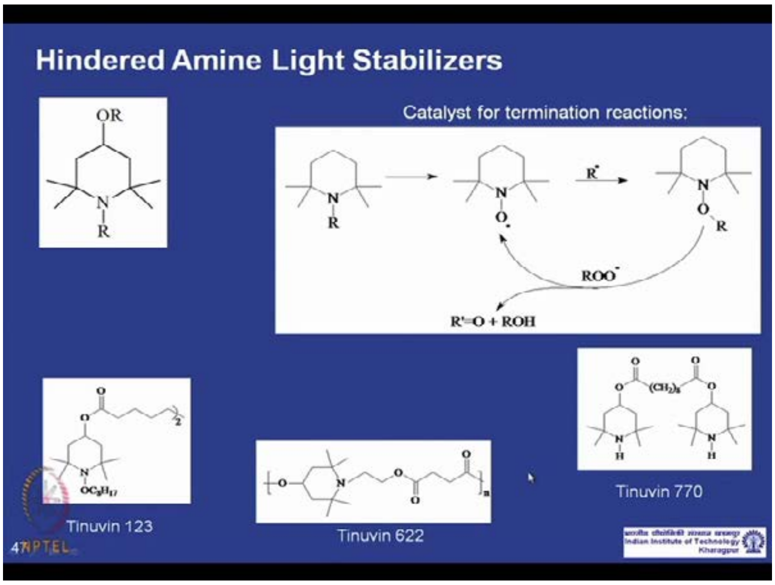

Hindered Amine Light Stabilizers

Catalyst for termination reactions:

Tinuvin 123

Tinuvin 622

Tinuvin 770

The other stabilizers, like hindered amine light stabilizers, we just talked about, which basically prevent the radical process. So, basically, trap the radicals and form non radical process, and by which they prevent degradation of molecular weight, and formation of the yellow colour bodies. And, some of the commercially available hindered amine light stabilizer results are shown here. These are the again represented in examples of some light stabilizers, commonly used in polymers.

Now, what we will do? I will finish of, for this lecture at this moment. And what we will do? I will, in the next lecture, which we will be going to be the last lecture of this course. We will talk about the other types of additives, like this fire retardants, how they work? What is there mechanism and surface migrating of additives? And, we will talk about polymer blends, little bit briefly; and then, go to the concluding remarks for the course. So, let us stop here for this lecture, and we will complete the course in next lecture.