# Science and Technology of Polymers

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## Lecture - 19
## Polymer Products (Contd.)

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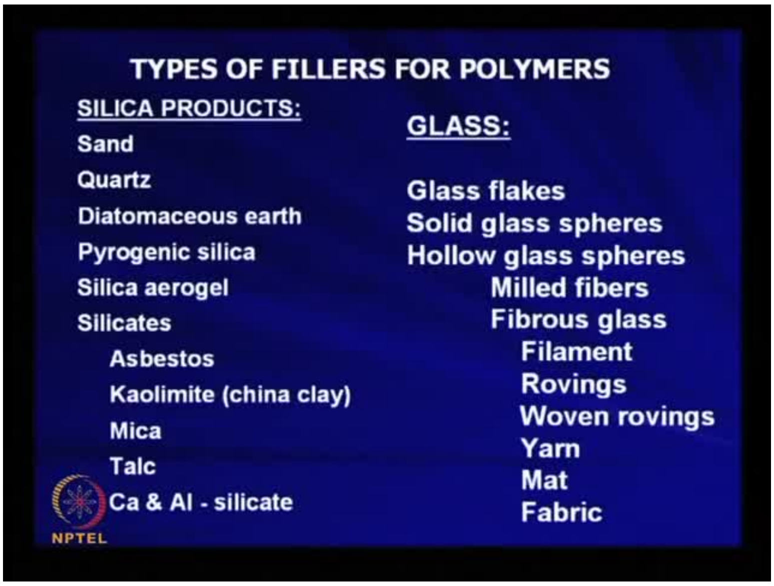

TYPES OF FILLERS FOR POLYMERS

SILICA PRODUCTS:
- Sand
- Quartz
- Diatomaceous earth
- Pyrogenic silica
- Silica aerogel
- Silicates
  - Asbestos
  - Kaolimite (china clay)
  - Mica
  - Talc
  - Ca & Al - silicate

GLASS:
- Glass flakes
- Solid glass spheres
- Hollow glass spheres
  - Milled fibers
  - Fibrous glass
    - Filament
    - Rovings
    - Woven rovings
    - Yarn
    - Mat
    - Fabric

Welcome back. Now, there are other types of fillers for polymers as those of wood base fillers, synthetic fillers or carbon base fillers, say silica based fillers are also available, sand of fine particle size can also used in the polymer as filler, quartz, even if it is very hard, but it can also be used as filler for some product diatomaceous earth, pyrogenic silica, silica aerogel. Then silicates, hydrated silicates are also used in asbestos, kaolimite which is called china clay. Mica in flake form, in particle form, talc, talcum powder, calcium and aluminum silicate; these are used as fillers.

Then glass based fillers say, glass in the form of flakes, glass spheres, glass that may be again, hollow glass sphere, spheres milled fibers means chopped or very sorted glass fibers, fibrous glass in the form of filament, rovings, woven rovings, yarn, mat and fabric. That means glass can also a drawn into thermo fiber, glass fiber and from that glass fiber, glass fiber fabric is also made. Those glass fiber fabrics are used for thermal insulation purpose, for making some composites, glass fiber reinforced composites, glass fiber reinforced polymer composites, these are existing. So, this gives you a picture of different types of fillers used.

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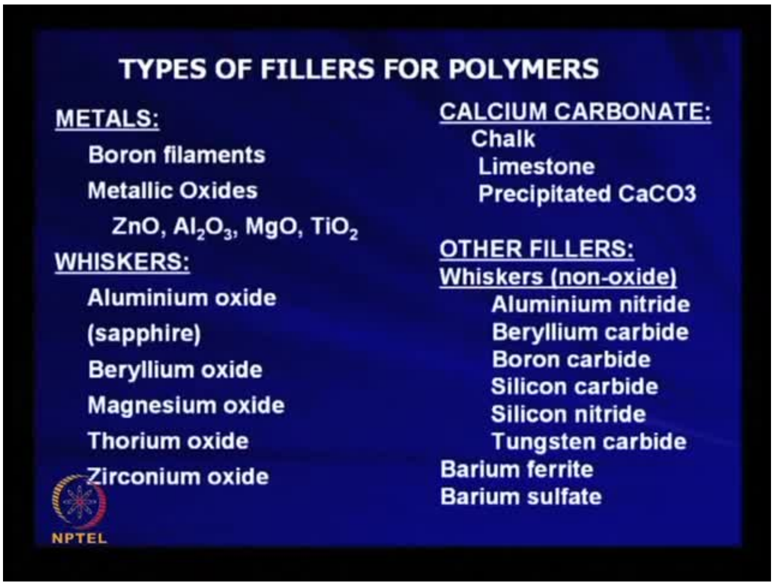

TYPES OF FILLERS FOR POLYMERS

**METALS:**
- Boron filaments
- Metallic Oxides
  - ZnO, $Al_2O_3$, MgO, $TiO_2$

**WHISKERS:**
- Aluminium oxide (sapphire)
- Beryllium oxide
- Magnesium oxide
- Thorium oxide
- Zirconium oxide

**CALCIUM CARBONATE:**
- Chalk
- Limestone
- Precipitated CaCO3

**OTHER FILLERS:**
- Whiskers (non-oxide)
  - Aluminium nitride
  - Beryllium carbide
  - Boron carbide
  - Silicon carbide
  - Silicon nitride
  - Tungsten carbide
- Barium ferrite
- Barium sulfate

There are other than this glass and a silica based etcetera. Then metals say metallic powder, metal powders or metallic fibers also used as fillers, metallic oxides are also used as fillers, say boron filaments. Metallic oxides, zinc oxides, aluminum, magnesium oxide, titanium these are also used as fillers, whiskers, aluminum oxide, sapphire beryllium oxide, magnesium oxide, thorium oxide, zirconium oxide, these are also used as fillers.

Calcium carbonates the chalk, limestone, precipitated calcium carbonate so these are used also used as fillers other fillers, whiskers, fibers are very thin diameter, aluminum nitride, beryllium carbide, boron carbide, silicon carbide, silicon nitride, tungsten carbide, barium ferrite, barium sulfate. So, these fillers or these fibers are used for making high performance composites, very strong and high temperature resistant, heat resistant composites for making heat resistant composites to be used as elevated temperature, these fillers are used.

Suppose, there is a requirement from some motor vehicle company that we have to develop some heat resistant coating, surface coating. For motor vehicles, for engine parts, motor vehicle engine parts or some composites which should a withstand 400 to 500 degree Celsius for some short period of time, it should not degrade, it should not be damaged. For that, then what is the polymer it should be made with polymer and polymers, majority of the polymers burn or degrade beyond 150 or 200 degree on prolonged exposure, but there are technologies available, where even it is made of polymer, but these are very stable to high temperature exposure.

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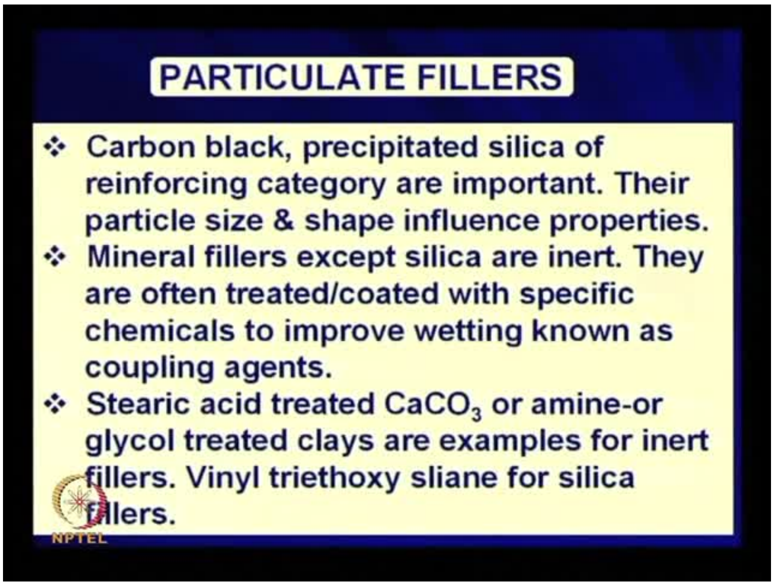

## PARTICULATE FILLERS

- Carbon black, precipitated silica of reinforcing category are important. Their particle size & shape influence properties.
- Mineral fillers except silica are inert. They are often treated/coated with specific chemicals to improve wetting known as coupling agents.
- Stearic acid treated $CaCO_3$ or amine-or glycol treated clays are examples for inert fillers. Vinyl triethoxy sliane for silica fillers.

Examples of for particulate fillers, carbon black, precipitated silica, reinforcing category. I shall discus later when I shall discus the rubber products about the details of carbon black, on those things and silica fillers and again to increase the to increase the interaction between a fillers and the polymer. Sometimes these fillers are little bit modified, say calcium carbonate, it is inorganic in nature can it be miscible with organic polymer, no if it is not miscible, then it is inert.

Then, if it is inert again to incorporate and disperse in a polymer matrix is a difficult task. It is not so easy, it is very difficult task because you have to disperse these fillers in fine particle form, then you have to go for milling in a mixture machine or a blender machine at elevated temperature. So, it needs huge power consumption for mechanical milling as well as thermal input, heat input.

Now, that can be improved if you can coat give a thin very thin coating to a filler particle say, here is a example of this stearic acid treated calcium carbonate. Calcium carbonate is a inert filler, but you can easily disperse in a hydrocarbon or or a organic polymer more easily. If you can make a thin coating of organic material, stearic acid you know, stearic acid, fatty acid. Can you tell me source of fatty acid source of fatty acid, vegetable oil. Vegetable oil is a glyceride esters of fatty acids, triglyceride is a fatty acids. So, those fatty acid can be taken from or extracted from oil and that fatty acid can be dissolved in a solvent, dilute solution then make a spray coating on this filler particles, what will happens solvent will evaporate out and there will be thin coating of stearic acid or this fatty acid on filler particle. So, it will be organically modified filler and that can easily the blended with polymer.

Now, here you are referred to one aspect of miscibility and solubility parameter. Miscibility, two component can be miscible provided there are of identical nature is not it. Two friends can remain in one room if they are of identical mind, identical habits. If the habits are different then they cannot stay for a long of period, you have to change the room. Here also, here also if the two things are identical then only they can have a friendship that is interface, friendship.

One cannot remain without the other that is the interface. Now for that interface bonding sometimes middle man or middle man is invited, some coupler is invited, marriage maker is invited. This marriage is nothing but coupling agent coupling agent this coupling agent has got two hands of two different properties. One hand with one person another hand with other person. In matrimonial effects what happens some middle man is there he tells all the (( )) of brides on one side or all the (( )) of grooms on the other side.

So, this way what happens they, all the (( )) or all the good things keeping your hidden the bad things. So, he makes the marriage, this way coupling agent, middle man. So, here also in case of this filling, filler, if the filler is not compatible, if the filler is not miscible with the polymer take a coupling agent. Say for example, silica silica feeler is a very good reinforcing filler for polymer, but it is inorganic in nature. It is not miscible with this organic polymers, what is done.

Normally, some silent derivatives are used silent coupling agent is used, say phenyl triethoxy silane, vinyl triethoxy silane, please note down, vinyl triethoxy silane vinyl triethoxy silane. So, this vinyl triethoxy silane, it contains vinyl site, means organic sight and ethoxy silane s i o, on the other side. So, it will make a coupling between silica filler and the polymer, where also stearic acid being organic in nature it has got one carboxyl group polar site. That will be oriented towards the calcium carbonate site and the organic site organic chain will remain on the other site that will mix with the polymer so this is the basis principle.

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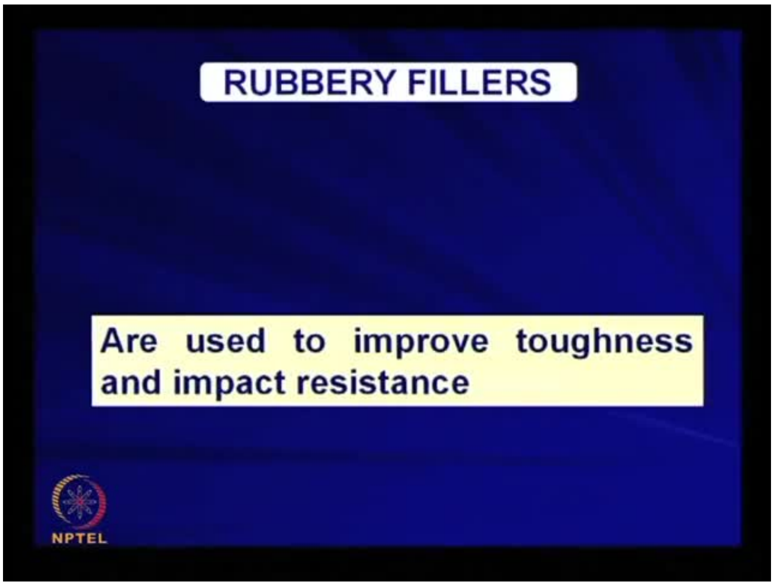

RUBBERY FILLERS

Are used to improve toughness and impact resistance

Rubbery fillers are used to improve toughness and impact resistance because you know rubber are flexible, soft. So, they will increase the toughness increase the flexibility etcetera and impact resistance will be more.

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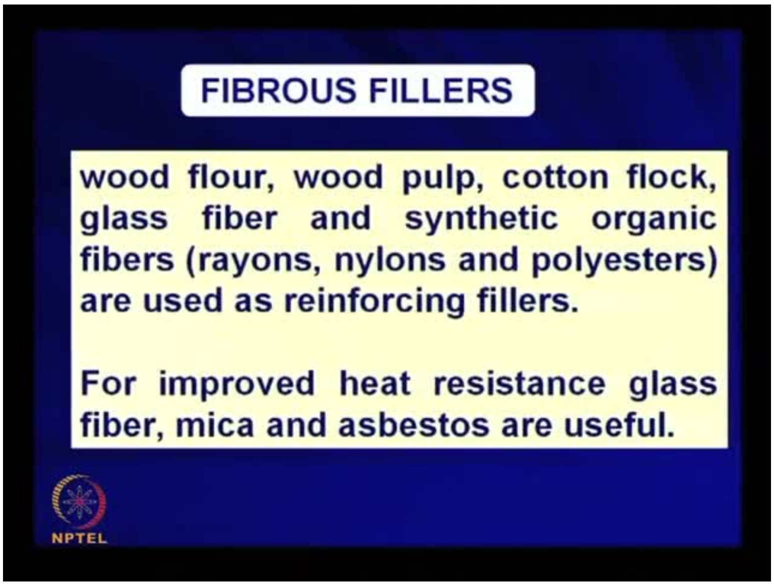

FIBROUS FILLERS

wood flour, wood pulp, cotton flock, glass fiber and synthetic organic fibers (rayons, nylons and polyesters) are used as reinforcing fillers.

For improved heat resistance glass fiber, mica and asbestos are useful.

Fibrous fillers again examples are there.

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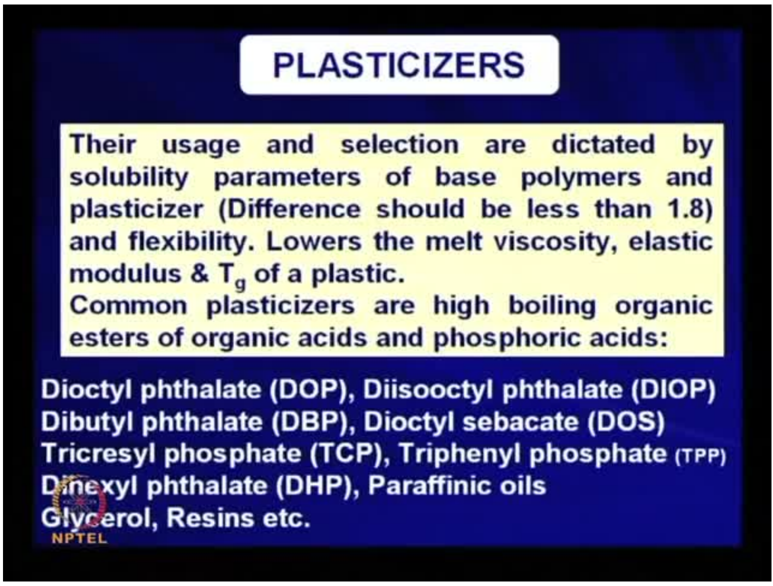

## PLASTICIZERS

Their usage and selection are dictated by solubility parameters of base polymers and plasticizer (Difference should be less than 1.8) and flexibility. Lowers the melt viscosity, elastic modulus & $T_g$ of a plastic.
Common plasticizers are high boiling organic esters of organic acids and phosphoric acids:

Dioctyl phthalate (DOP), Diisooctyl phthalate (DIOP)
Dibutyl phthalate (DBP), Dioctyl sebacate (DOS)
Tricresyl phosphate (TCP), Triphenyl phosphate (TPP)
Dihexyl phthalate (DHP), Paraffinic oils
Glycerol, Resins etc.

Plasticizers, this is most important thing. I told what is plasticizers these are low molecular weight, low molecular weight organic esters and provided the solubility parameter of the plasticizer are very close to those polymers then only, particular compound particular ester compound can be useful as a plasticizer, for one particular polymer. So, there are various large number of example say dioctyl phthalate, dibutyl phthalate, tricresyl phosphate, dihexyl phthalate, triphenyl phosphate, dioctyl sebacate etceteras glycerol, resins. Now, you have seen some… When this you are on a frying pan, some dosa or something like that is made, some lubricant or some plasticizer, some oil is spread over the surface then this is put and spread and again it can easily come out of the surface otherwise it is to stick to this thing.

The principle of this plasticizer is almost similar, same type. Here the dioctyl phthalate, dibutyl phthalate, some, even some oils even some oil etcetera or say, say paraffinic oil. Here you see glycerol or some resins these increase the softness of the polymer, increase the flexibility of the polymer, decrease the hardness of the polymer. I gave you the example of that plasticized PVC, but being small molecular weight or small molecular size, molecular weight is low, what happens.

Whereas, the polymer is of high molecular weight, it may be miscible and while the product is made, what happens. Slowly this plasticizer will diffuse to the outer surface because it is soluble in the polymer matrix it is mobile in the polymer matrix. So, continues diffusion will be there and the polymer will be will be will be on dynamic stressing, dynamic loading.

Sometimes, sometimes this surface is being wiped out, what happens. It is coming to the surface and surface is wiped out, that is that plasticizer molecule, which is comes to, which comes to the surface, blooms to the surface, migrate to the surface that is lost this way the slowly and slowly what happens. There will be loss of plasticizers from the product and the product will become hard and brittle.

You have experience this thing in on your cycle seat cover that is plasticized PVC, when you buy it, it is very soft when it is new. In winter season it becomes stiff, in summer it becomes soft and after 6 months or 1 year of use it develops cracks. It becomes brittle, softness goes because of what, because of this plasticizers which are present inside comes out. Similarly, it happens to the footwear also, footwear’s become, footwear is a PVC footwear that becomes rigid, and brittle and cracks and breaks after 6 months or 1 year use.

That is due to loss of this plasticizers because this dioctyl phthalate, write the formula of this phthalate phosphate compound, you will see the size of this molecules are low and when these are blended with polymer, so this can easily come out of this come out or bloom to the surface or migrate to the surface, these are lost. So, initial purpose is subbed, but in the long run, long run it, it is not stable within the polymer matrix.

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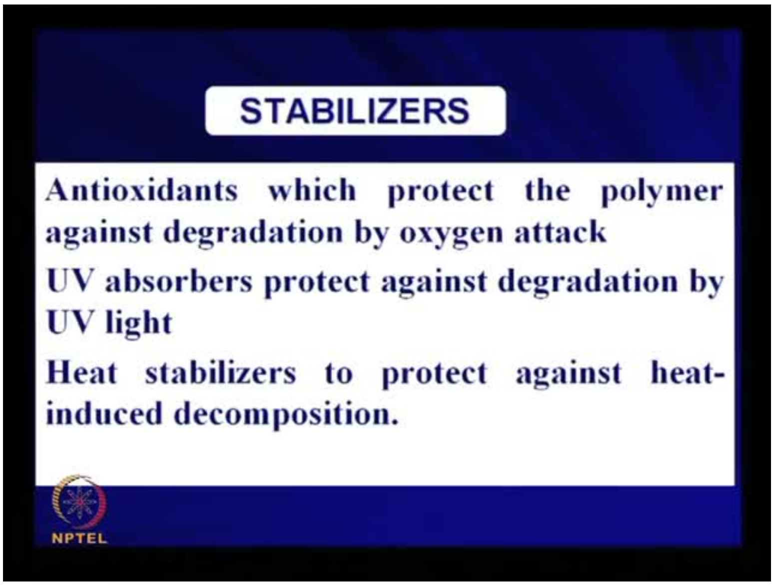

STABILIZERS

Antioxidants which protect the polymer against degradation by oxygen attack

UV absorbers protect against degradation by UV light

Heat stabilizers to protect against heat-induced decomposition.

Then stabilizer I told you the necessity of using stabilizer as ingredient in the polymer. The agencies are oxygen in air, ozone in air, ultraviolet light of sun ray, ultraviolet radiation of sun ray or some chemical agency or microbial attack or thermal environment. So, these are the agencies to which if the polymer product is exposed then that undergo the degradation, that undergo degradation. What kind of degradation means those energies attack this bonds chemical bonds carbon carbon, carbon hydrogen, carbon nitrogen, carbon oxygen, carbon halogen, carbon phosphorus.

Those bonds are present over there so those bonds will be exposed to these energies, these agencies and they can (( )) the bonds. If they break this bonds so the molecular weight of the polymer will be reduced and the ultimate properties of the product will gradually decrease. So, that means the stability of the products are at stake so what you have to do, you have to increase the stability, so that the product is durable, so that the product is durable.

Nobody wants that every 6 months you have to replace your cycle tire, do you want it, do you want it that every 6 months you will be replacing your cycle tire, no. It should be durable more than one or 2 years or after certain mileage, say four-wheeler tires, what is the durability, do you know. 3 years, not through the years time only, but it is mileage also should be counted 60, 40000, 50000, 60000 kilometers. After that it will old out, it will abraded out or it will develop crack so there will shrinking out of the thread portion or, there will be catastrophic failure, bursting of this tire and even to prevent those failure, you have to use certain stabilizers.

Now, while rolling a tire through a road surface the temperature goes high, temperature goes high, due to friction and inside there is air, so huge oxygen is there. Outside there is oxygen so inside, outside there is oxygen and the temperature is high so there will be thermo oxydity degradation, under mechanical stressing, mechanical as well as dynamic, periodic of cyclic, rolling of the tire. So, under cyclic stress, under this oxygen stress, under thermal stress so under all this stress this product is performing. So, its life has to be increased that means you have to prevent this thermo, it is thermo oxydity degradation. You have to prevent its physical your breakdown also for those we need anti degradants, means which will fight with the degrading agencies.

What happens when this products are exposed to those degrading agencies that breaks a bond or containing two electrons so if it is hemolytic breaking so two free radicals will be created. You know these free radicals are highly active, energetic, once the, once a few free radicals are created on the product surface or within the product bulk, what happens. If it get access to other agencies or it is process will be accelerated and it will break more and more number of bonds and ultimately it will start a chain of reaction.

Chain of breaking reaction, bond breaking reaction, a chain of bond breaking reaction, you know and there will be first degradation, first breakdown of the polymer chains, that means degradation process. So in order to prevent that, if there is some anti-degradant, stabilizer so it will just capture, it will scavenge, it will hold it like some defense person. If there is some miscreant going to do some crime, if there is some defense person so he will catch it, catch him like this to prevent, to do any crime, like that. So, it will not allow it to further degrade, it is stops it activity there that is called stabilization.

So, degradation and stabilization ,degradation agencies, degrading agencies as those are those I have mentioned and stabilization, for stabilization you have to use some anti degradants which will fight with this agencies and stop their activities. So, UV absorbers, ultraviolet absorbers there will be some ingredient which should be blended with the polymer that will absorb the ultraviolet light. That means, it will make a sealing effect suppose, it will not allow the polymer to absorb the UV. So, that ingredient will absorb the UV it will convert it to energy of higher wavelength that means less harmful. So, from harm harmful to harmless situation that can be done by some UV absorbers if the product is expose to UV light, heat stabilizers to protect against heat-induced decomposition.

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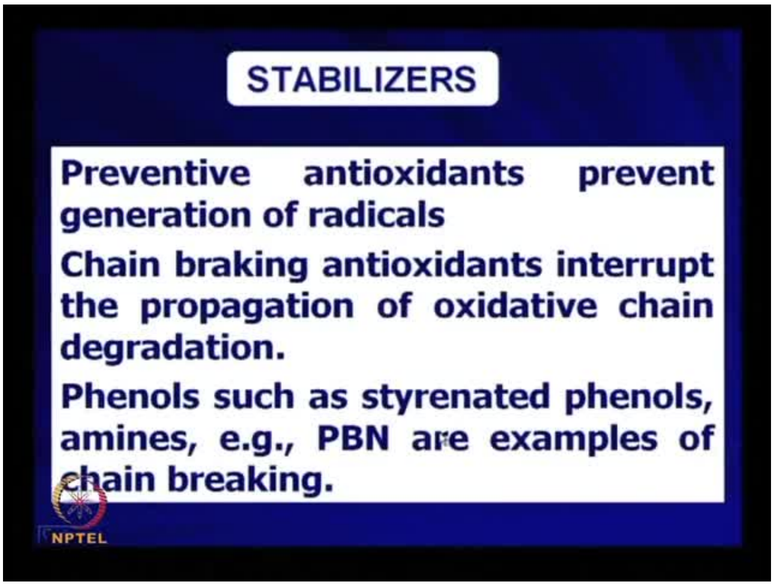

**STABILIZERS**

Preventive antioxidants prevent generation of radicals

Chain braking antioxidants interrupt the propagation of oxidative chain degradation.

Phenols such as styrenated phenols, amines, e.g., PBN are examples of chain breaking.

Now preventive antioxidants prevent generation of radicals. So, what happens, if I show you in general.

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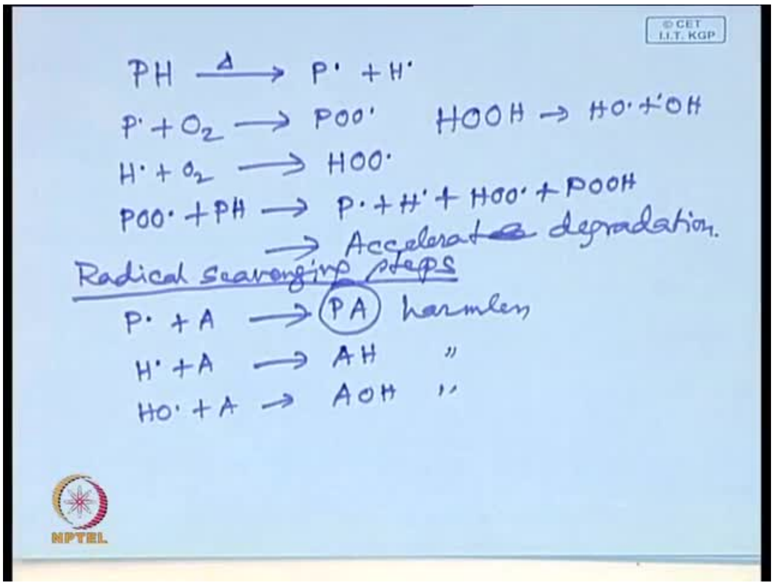

$PH \xrightarrow{\Delta} P^{\cdot} + H^{\cdot}$

$P^{\cdot} + O_2 \longrightarrow POO^{\cdot}$ $\quad HOOH \rightarrow HO^{\cdot} + {}^{\cdot}OH$

$H^{\cdot} + O_2 \longrightarrow HOO^{\cdot}$

$POO^{\cdot} + PH \longrightarrow P^{\cdot} + H^{\cdot} + HOO^{\cdot} + POOH$

$\longrightarrow$ Accelerates degradation.

Radical scavenging steps

$P^{\cdot} + A \longrightarrow \boxed{PA}$ harmless

$H^{\cdot} + A \longrightarrow AH$ "

$HO^{\cdot} + A \rightarrow AOH$ "

Suppose this is a polymer, some agency suppose is it is heat will produces free radical, polymer radical and hydrogen radical. Now, this polymer radical if it gets access to oxygen, peroxy radical. Hydrogen radical gets to oxygen, access oxygen it will form hydroperoxy radical. So, this POO radical will further react with this polymer forming

PH and even HO and POOH, large number of product will be formed. So, that will accelerate accelerate degradation, this way.

Now, to prevent this if you take some anti degradant A, it will PA harmless, this is harmless or it can react with A, this hydrogen radical can react with A or be AH, this is also harmless. Here, you see this hydroperoxy radicals harmful, this also can react with that means. So, these are radical scavenging steps. I will show you, show you in detail this degradation and stabilization of polymers later not today, just I have mention here.

Chain breaking, here the spelling is wrong b r e a, chain breaking antioxidants, chain breaking not it is it should b r e a. Chain breaking antioxidants means it will break the chain reactions, degradation reactions, chain chain like reaction, nonstop reaction that is called chain reaction. That chain will be broken, that degradation chain will be broken by such kind of radical scavenging steps. (( )) is going to have a radical scavenging steps, radical scavenging that is called chain breaking reactions and interrupt the propagation of oxidative chain degradation.

I will tell you one example, you see wood, hard wood say used for making furniture’s. Now, those furniture’s are stable, does not degrade highly stable even it can it can remain undeformed, undegraded after 100 years or even 200 years would live why because it contains lignin. Lignin contains some phenolic units this phenolic units phenol you know what is phenol. Phenol it can form quinone structure also, phenol to quinone.

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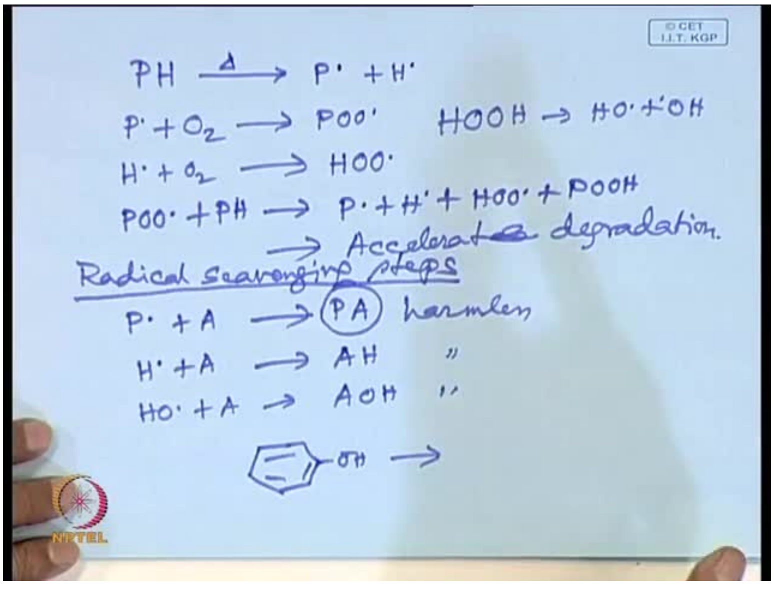

$PH \xrightarrow{\Delta} P^{\cdot} + H^{\cdot}$

$P^{\cdot} + O_2 \longrightarrow POO^{\cdot}$ $HOOH \rightarrow HO^{\cdot} + {}^{\cdot}OH$

$H^{\cdot} + O_2 \longrightarrow HOO^{\cdot}$

$POO^{\cdot} + PH \longrightarrow P^{\cdot} + H^{\cdot} + HOO^{\cdot} + POOH$

$\longrightarrow$ Accelerate degradation.

Radical scavenging steps

$P^{\cdot} + A \longrightarrow \boxed{PA}$ harmless

$H^{\cdot} + A \longrightarrow AH$ "

$HO^{\cdot} + A \rightarrow AOH$ "

So, this this your phenoxy radical through reigniting structures so it can it do phenoxy radical, that phenoxy radical can be give some stable radical. That stable radical will scavenge those degrading free radicals. So, you see phenol formaldehyde products, phenol formaldehyde composites are stable that does not degrade. Oxidative degradation of phenolic composites are almost nil, minimum.

So, wood products woods which contains lignin that is stable because lignin contains phenolic units. Here, you see phenols such a styrenated phenols, amines say, amines. Amines are also anti degradants, amines, amine derivatives, derivatives of ammonia, NH3. You replace one hydrogen of ammonia by a phenyl ring by aliphatic radical or aromatic radical you will get aliphatic or aromatic amines. Again you can have amine derivatives say phenyl beta naphthylamine PBN, here it is written PBN.

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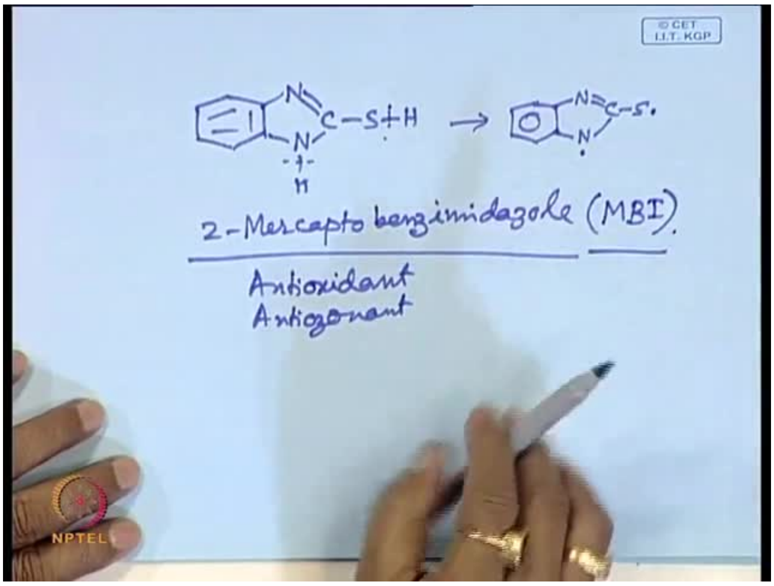

What is PBN, phenyl beta naphthyl amine. So, beta naphthyl group, phenyl amine big derivative of beta naphthol, beta naphthalene. So, this way phenyl beta naphthylamine or other say alkyl, alkyl derivatives of amines say aniline, aniline those are all antioxidants anti degradations and say 2 mercapto benzimidazole 2 mercapto benzimidazole. Now, here you see two bonds are there NH and SH these bonds can break forming radicals S radical and N radicals here. So, these are stable radicals that is why this is known as anti, good antioxidant as well as antiozonant. Ozone is much more reactive then oxygen so it can prevent, this kind of compound can prevent degradation by the action of oxygen as well as ozone, 2 mercapto benzimidazole. This is a buyer germany product, commercially available product MBI or it is known as MBI.

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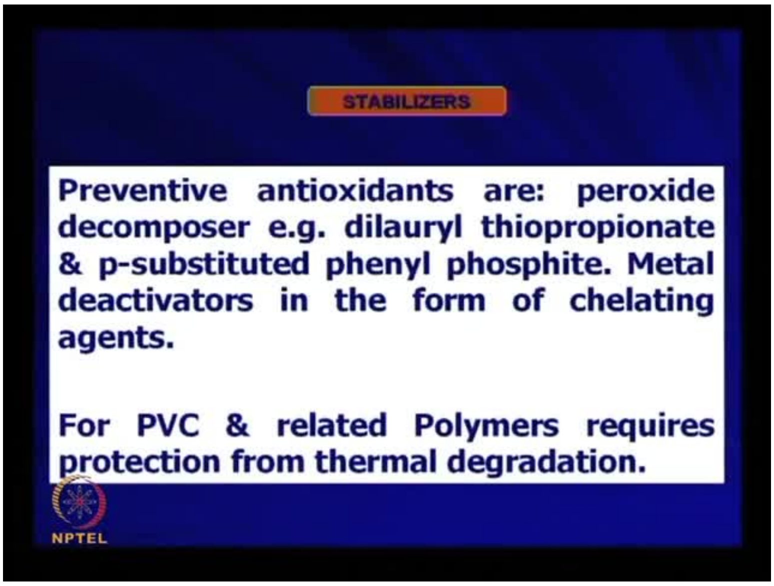

STABILIZERS

Preventive antioxidants are: peroxide decomposer e.g. dilauryl thiopropionate & p-substituted phenyl phosphite. Metal deactivators in the form of chelating agents.

For PVC & related Polymers requires protection from thermal degradation.

Other stabilizers are preventive antioxidants and peroxide decomposer, dilauryl thiopropionate, para substituted phenyl phosphite, metal deactivators in the form of chelating agents. Phosphorus derivatives, phosphoric acid derivatives or thiol derivatives, amine derivatives, say thiol compounds, amine compounds phosphorus base compounds these are used as stabilizers for polymers in general. PVC, now in rigid PVC technology in rigid PVC technology there is in plasticizer. I told PVC is a hard and harden polymer. How to make a product, how to fabricate a product, it is to melted, but before melting it decomposes before melting it decomposes. What is decomposition product of PVC, you know can you, can anybody tell.

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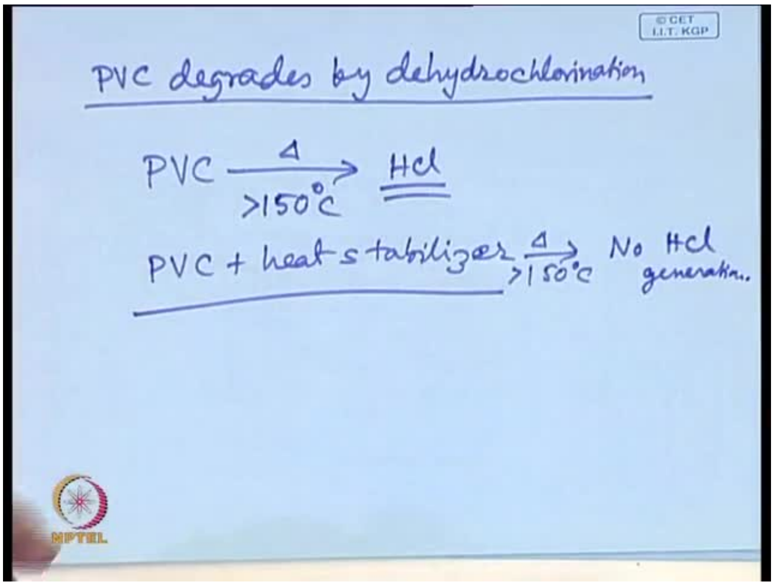

PVC degrades by dehydrochlorination

PVC $\xrightarrow[>150^\circ C]{\Delta}$ Hcl

PVC + heat stabilizer $\xrightarrow[>150^\circ c]{\Delta}$ No Hcl generation..

That means PVC degrades by PVC degrades by dehydrochlorination. So, PVC, heat hydrogen chloride vapor, hydrogen, Hcl vapor, hydrogen chloride vapor that is generated, this is dangerous thing. So, PVC degrades at say this temperature beyond 150 and for making rigid PVC product, one has to heat beyond 150. So, it can be done if some heat stabilizers, which are add to the PVC and then heat is at greater than 150 degree Celsius, no HCl generation. So, here using some heat stabilizer PVC can be protected, PVC degradation can be protected, prevented.

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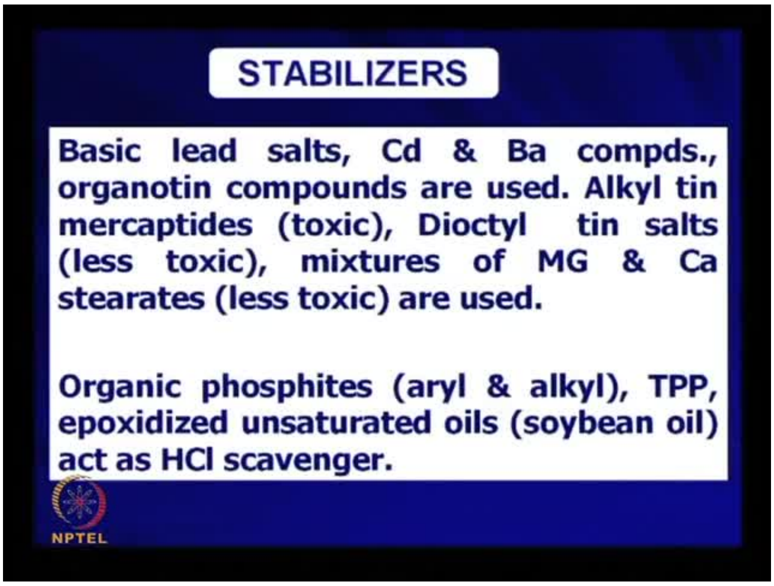

STABILIZERS

Basic lead salts, Cd & Ba compds., organotin compounds are used. Alkyl tin mercaptides (toxic), Dioctyl tin salts (less toxic), mixtures of MG & Ca stearates (less toxic) are used.

Organic phosphites (aryl & alkyl), TPP, epoxidized unsaturated oils (soybean oil) act as HCl scavenger.

So, these are basic lead salts, cadmium and barium salts, organo tin compounds, these prevents dehydrochlorination of PVC. Actually, prior to your, this development of plasticizer till 1975 means mid 70s there was no flexible PVC technology. Rigid PVC technology was there and this stabilizers are, where used, where all these stabilizers are lead, cadmium, barium, tin compounds this metallic compounds are highly toxic, highly toxic. So, these were banned, although these are good stabilizer for these PVC polymers they are banned.

Alkyl tin mercaptide toxic, dioctyl tin salts these are also toxic, but less toxicity mixture of this magnesium and calcium stearates these are also used organic phosphites, aryl, alkyl phosphites triphenyl, phosphite or epoxidized unsaturated oils, soybean oil act as HCl scavenger. So, here you see once these, your cadmium, barium, lead compounds are banned then this phosphites, organic compounds or epoxidized unsaturated oil, unsaturated epoxidation of unsaturated oil means unsaturated oils contains fatty acid chains having some double bond and if there is a double bond that can be epoxidized. So, that epoxidized unsaturated oils similarly, natural rubber can be epoxidized. ANR is available commercially, epoxidized natural rubber that means the double bond is epoxidized, epoxy compound so those act as HCl scavenger. So, once some HCl is produced that will be consumed by it so this way this stabilizer is the polymer.

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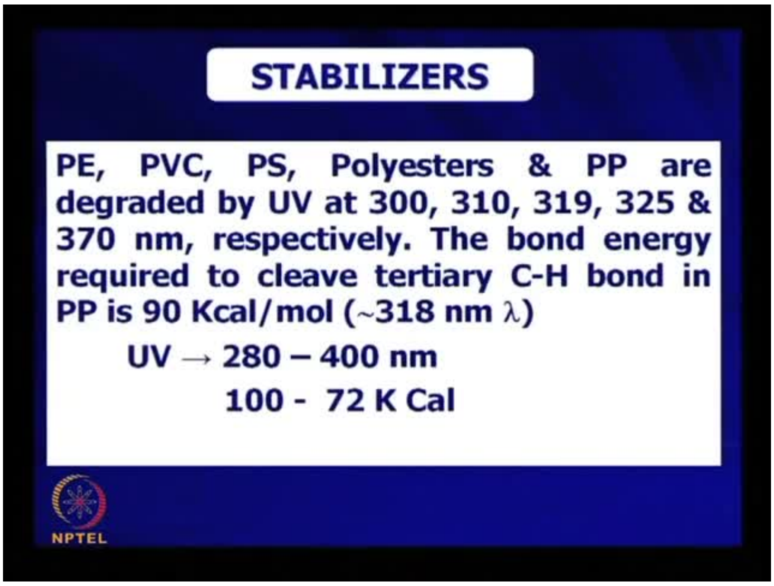

STABILIZERS

PE, PVC, PS, Polyesters & PP are degraded by UV at 300, 310, 319, 325 & 370 nm, respectively. The bond energy required to cleave tertiary C-H bond in PP is 90 Kcal/mol (~318 nm $\lambda$)

UV → 280 – 400 nm

100 - 72 K Cal

So polyethylene PVC polystyrene polyesters and polypropylene are degraded by UV, ultraviolet light at 300 to 370 nanometer range and the polymers which degrade the PE degrades around 300, PVC at 310, PS at 319, polyesters 325 and polypropylene 370 nanometer. So, you see polypropylene degrades at 370 nanometer so polypropylene products are not suitable for outdoor exposure.

You have seen this polypropylene woven sacks, cement bags, fertilizer bags, have you seen those bags, plastic bags. Today fertilizer is packed in polypropylene raffia taps in polyethylene raffia taps. Similarly, cement jute was the only packing material, jute bags were used for packaging of cement and fertilizer. Today almost, jute has been entirely replaced by this polypropylene and polyethylene, but the reuse value of those polypropylene woven sacks today are almost nil, that means after one or after one use it is never used for the second time packing of cement or fertilizer. You have seen some people make tarpaulins, tarpaulin seats using this raffia taps bags, but its life is very short if it is expose to sun light it becomes brittle.

Also, you have some experience of using polymer rope, you say nylon ropes, those are not nylon those are either polyethylene or polypropylene, majority of them are polypropylene rope. Now, if you use that rope expose to sunlight that means outdoor, for your your drying of your clothing’s so after six months it becomes brittle, it goes, it outs, it degrades. Here, you see why this degradation wavelength is 370 nanometer, this is there in sunlight so it degrades.

So, polypropylene is not stable and polyethylene is little brittle because polyethylene degrades at around 300 degree, 300 nanometer which is very small, very less, small fraction than sunlight, but this 3 around 370 there is that is present in sunlight. The bond energy require to cleave tertiary hydrogen bond in polypropylene is 90 per mole, around 318 nanometer wavelength.

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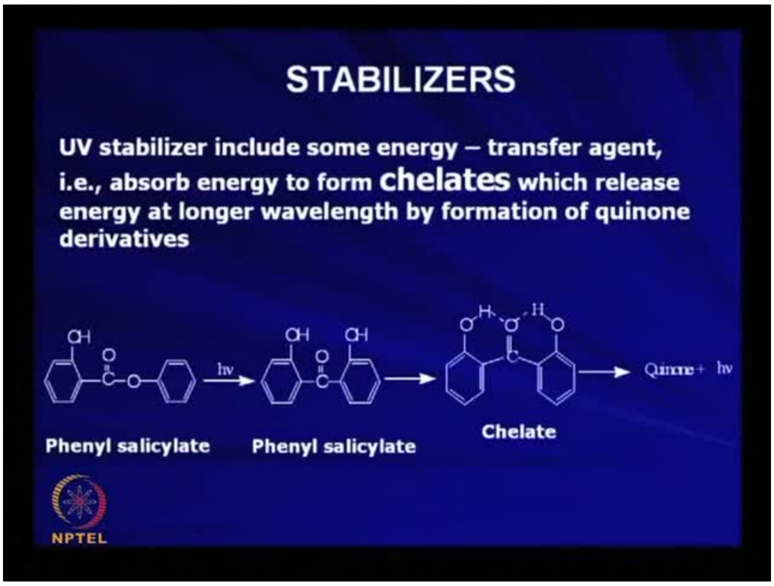

## STABILIZERS

**UV stabilizer include some energy – transfer agent, i.e., absorb energy to form chelates which release energy at longer wavelength by formation of quinone derivatives**

**Phenyl salicylate** **Phenyl salicylate** **Chelate**

Now, you see UV stabilizer include some energy transfer agent that means, say this compounds like phenyl salicylate, what happens, I told that may be many some UV scavenger. So, these additives say phenyl salicylate act as a UV scavenger so if it is present over there then what will happen. It will absorb the UV light and it will converted to energy of visible, in the visible range. That occurs through this chelation, say this chelation this energy converts this compound phenyl salicylate to this structure then this through, this chelation energy is converted from UV to visible range [FL].

One more thing carbon like you see, all most all overhead tanks are black is not it, 2, 1 or 2 percent of carbon black is blended with this plastic, because this carbon black absorbs this UV without any harmful, causing harmful effect on the polymer. So, UV is absorbed by the carbon carbon black before it reaches that carbon carbon and carbon hydrogen bond of polymer, heat absorbs. So, it is stabilize the polyethylene so their carbon black the use of carbon black not as filler, but as UV stabilizer (( )).

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STABILIZERS

Other examples:

Benzotriazoles,

Substituted acrylonitriles,

Nickel dibutyldithio carbonate and

Pigments such as Carbon black (1-5%) also gives protection against UV degradation.

Other examples benzotriazole, substituted acrylonitriles, nickel dibutyldithio, carbonate pigments, carbon black 1 to 5 percent also gives protection against UV degradation. I did quite substituted quantity of research, substantial level of research in my lab on this degradation and stabilization of polymers, earlier. So, my experience is that if you can develop any agency which can break to form free radicals, and if that free radical is stabilized to which it is attached then that can act as a very good stabilizer for your polymer.

Even, there are some plants say moringa oleifera, drumstick plant it contains natural antioxidants. There are many other plants it contains natural antioxidant, medicines we consume those are antioxidants, majority of the medicines are antioxidants because say any bacterial attack, mucus secretion through nose or through rectum due to dysentery etcetera. That is nothing but mucus is nothing but a dead tissue extracts, a was dead. That happens due to attack of tissue by those microbes and that is a free radical process, that is as a degradation process, that is a free radical process.

So, what we do we take some protection by taking some antibiotic those are antioxidants, antidegradants and that process is a free radical process. So, degradation is a free radical process and stabilizer is also free radical process. This drumstick you see it exude some gum and during flowering in the spring session what happens the entire atmosphere actually remains full of opulence of that drumstick flower, that is preventing so that is a natural preventing in the spring time that contains antioxidant.

So, if those things can be extracted from plant and put in polymer it can stabilize polymer, we have seen we have some paper also publish paper on this. So, degradation of polymer by anti degradants, if majority of this degradation process occurs through this free radical process. If it is free radical process then you can think of a chemical compound available in the market or you can extract from nature. Then you put in polymer mix and make a product and that will continue the stabilization.

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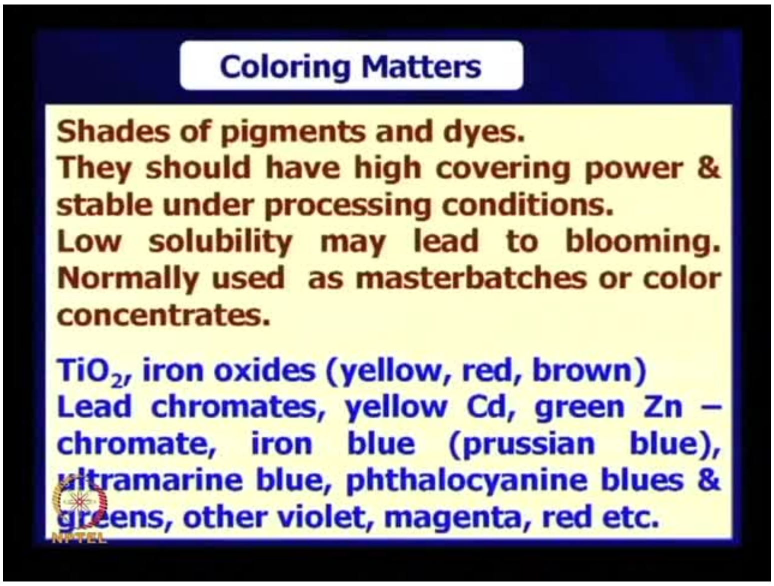

**Coloring Matters**

Shades of pigments and dyes.
They should have high covering power & stable under processing conditions.
Low solubility may lead to blooming.
Normally used as masterbatches or color concentrates.

$TiO_2$, iron oxides (yellow, red, brown)
Lead chromates, yellow Cd, green Zn – chromate, iron blue (prussian blue), ultramarine blue, phthalocyanine blues & greens, other violet, magenta, red etc.

Coloring matters, shades of pigments and dyes pigments are inorganic oxide and salts inorganic oxides and salts. So, this would have high covering power and stable under processing condition. Now, you see for white color, what we use titanium dioxide, zinc oxide good, whitener good white over that you can put a tint of finch of say tint of some other color that may be again some inorganic materials say iron, cadmium, copper, barium, chromium. Compounds or oxides of these elements are good pigments and these pigments are used in fine particle powder with the polymer for coloring purpose today. You see this color, this color, this color all are made from this coloring materials either dyes or pigments.

Normally the organic coloring materials are known as dyes dyes and inorganic coloring materials are known as pigments, pigments and dyes and they, this pigments and dyes are stable under processing conditions, but they are having low solubility and because of this low solubility characteristics they lead to blooming, means migrating to the surface. Normally used as master batches or color concentrate master batch means how to, you see this inorganic particles pigments, how to blend with polymer it is difficult small quantity is used.

That small quantity should be uniformly dispersed in the polymer otherwise the color uniformity will not be available on the surface of the product. It will not be good looking for that say 0.5 pigment is being used in a batch, say 0.5 kg with 100 kg of polymer. So, 0.5 kg of pigment should be properly mixed with the polymer so it needs extensive milling, involving power consumption, it difficult.

Normally what is done a master batch is used means where polymer is less pigment is more so this way you take a stock of pigment and polymer that is master stock a batch known as master batch, where pigment polymer ratio is high. You take few percent of that and since it is already dispersed in that polymer it will be easily dispersed in the final batch. So, what happens during this product manufacture, say master batch is a color, master you can use of this color. Master batch is added along with the base polymer and that will be easily mixed and product will be colored. If you go to some industry you will see that is master batch or color concentrate master batch or color concentrate.

Titanium dioxide iron oxide it may be again yellow iron oxide, red iron oxide, brown iron oxide, lead chromates, yellow lead chromates, yellow cadmium, green zinc chromate, iron blue (( )), blue ultramarine, blue phthalocyanine, blue blue and greens other violets, magenta, red color etcetera. These are available and these are used for coloring of polymers not only that, say colors of paints and surface coatings. Asian paints, Berger paints, they competing with each other for different color shadings you see for coloring of your interior wall outside wall or coloring of any other object. So, those all, all of those content is coloring pigments or dyes.

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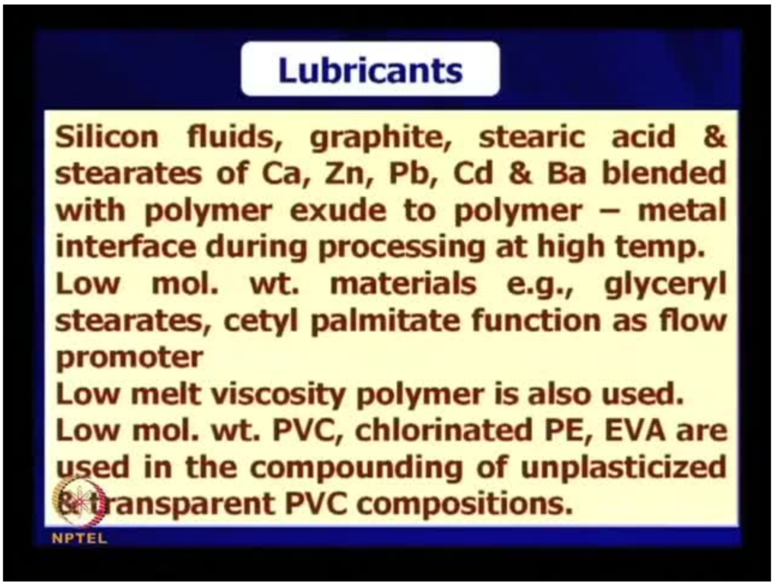

## Lubricants

Silicon fluids, graphite, stearic acid & stearates of Ca, Zn, Pb, Cd & Ba blended with polymer exude to polymer – metal interface during processing at high temp.
Low mol. wt. materials e.g., glyceryl stearates, cetyl palmitate function as flow promoter
Low melt viscosity polymer is also used.
Low mol. wt. PVC, chlorinated PE, EVA are used in the compounding of unplasticized & transparent PVC compositions.

Now, these colors are not actually friendly to living system. For living system, for some herbal color, herbal dyes are used. Herbal dyes are available, herbal dyes are used for coloring medicines, coloring foods. This coloring food should not be made from this cadmium, zinc, barium, iron multiplier using. You do not know these are cheaper instead of using herbal color, herbal color, herbal dyes they are using this inorganic, which are toxic and putting into food, but where some way we are still living, still we are living anyway.

Then lubricants silicon fluids, graphite, stearic acid, stearates calcium, zinc, lead, cadmium, barium and as I told cetyl palmitate chlorinated polymers. Another polymers which are soft low molecular weight, low molecule polymers. Oils, these are used as lubricants there is no big difference between plasticizers and lubricants almost simple paraffin, paraffin oil, paraffin wax. Paraffin wax are also used as lubricants or plasticizers.

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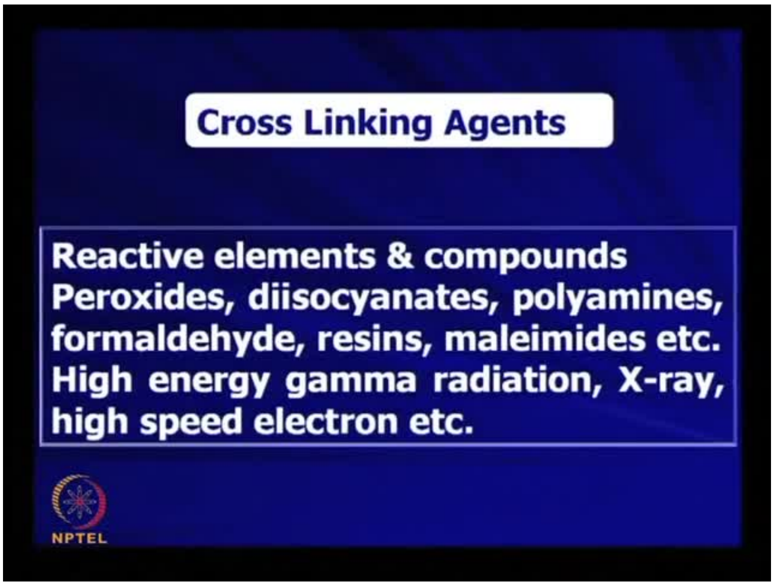

Cross Linking Agents

Reactive elements & compounds
Peroxides, diisocyanates, polyamines, formaldehyde, resins, maleimides etc.
High energy gamma radiation, X-ray, high speed electron etc.

Cross linking agents, no, peroxides. Peroxides are cross linking agents or some functional polymers di functional polymers, say maleimides or diamines. Diamines, for a proxies diamines are cross linking agents, for saturated polymers of polyethylene peroxides are cross linking agents, say (( )) peroxide are cross linking agents. High energy radiations, gamma radiation and X-ray radiations are also cross linking agent because they break the bond, one bond form free radical.

That free radical will interact with another free radical of another chain so forming some carbon carbon linkage between these two free radicals so it cross links. So, if you expose a polymer to high energy radiation it will become cross link and its solubility will be low, loss, decreased because of this thing. So, I hope you have understood what is cross linking we will discuss in little detail while I shall discus with rubber products.

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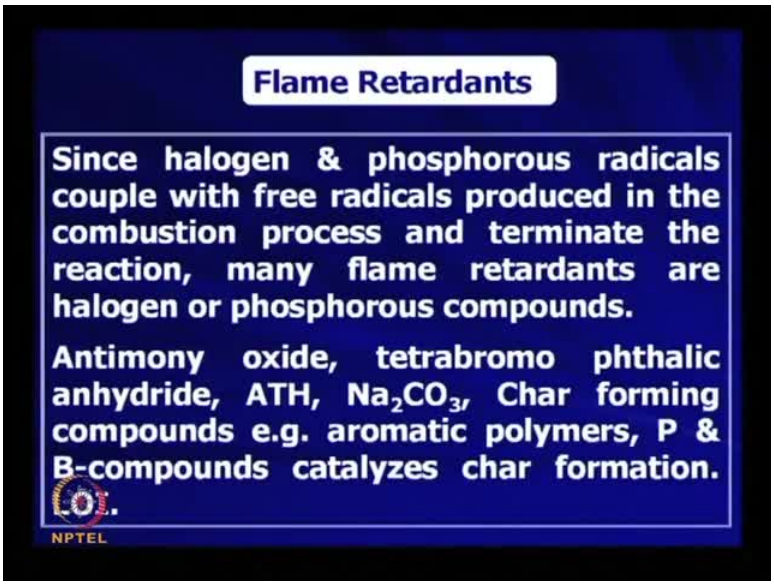

## Flame Retardants

Since halogen & phosphorous radicals couple with free radicals produced in the combustion process and terminate the reaction, many flame retardants are halogen or phosphorous compounds.

Antimony oxide, tetrabromo phthalic anhydride, ATH, $Na_2CO_3$, Char forming compounds e.g. aromatic polymers, P & B-compounds catalyzes char formation.

LOI.

Flame retardants, there is no time today actually each of this ingredient need a whole day for or at least 2, 3 hours lecture. Elaboration flame retardants when I shall discus with these rubber products, there I will discuss this thing.

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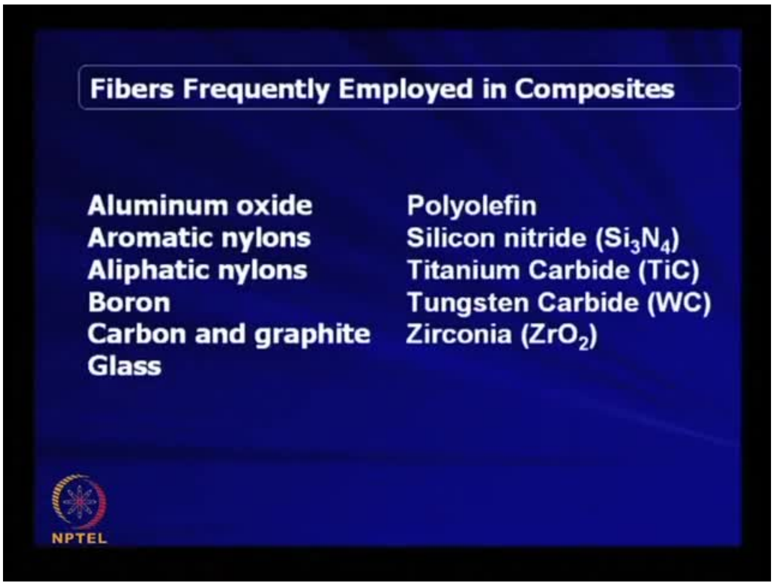

## Fibers Frequently Employed in Composites

Aluminum oxide
Aromatic nylons
Aliphatic nylons
Boron
Carbon and graphite
Glass
Polyolefin
Silicon nitride ($Si_3N_4$)
Titanium Carbide (TiC)
Tungsten Carbide (WC)
Zirconia ($ZrO_2$)

Flame retardants and composites.

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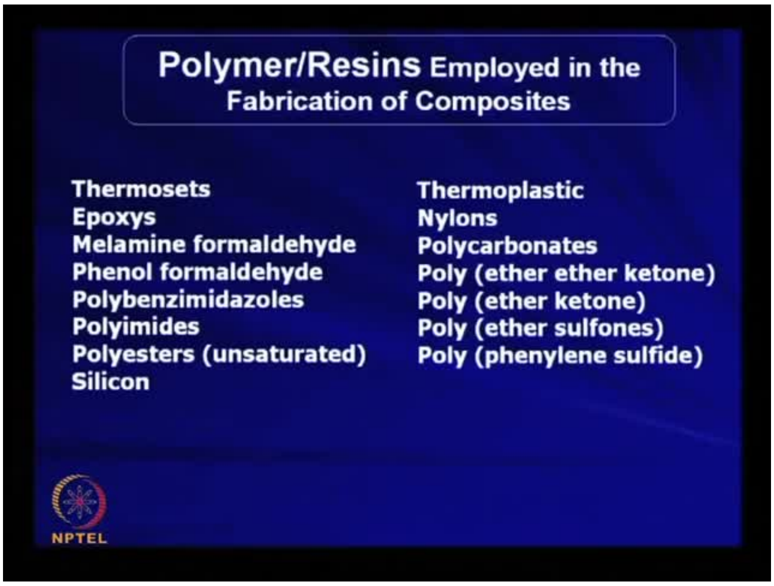

## Polymer/Resins Employed in the Fabrication of Composites

Thermosets
Epoxys
Melamine formaldehyde
Phenol formaldehyde
Polybenzimidazoles
Polyimides
Polyesters (unsaturated)
Silicon

Thermoplastic
Nylons
Polycarbonates
Poly (ether ether ketone)
Poly (ether ketone)
Poly (ether sulfones)
Poly (phenylene sulfide)

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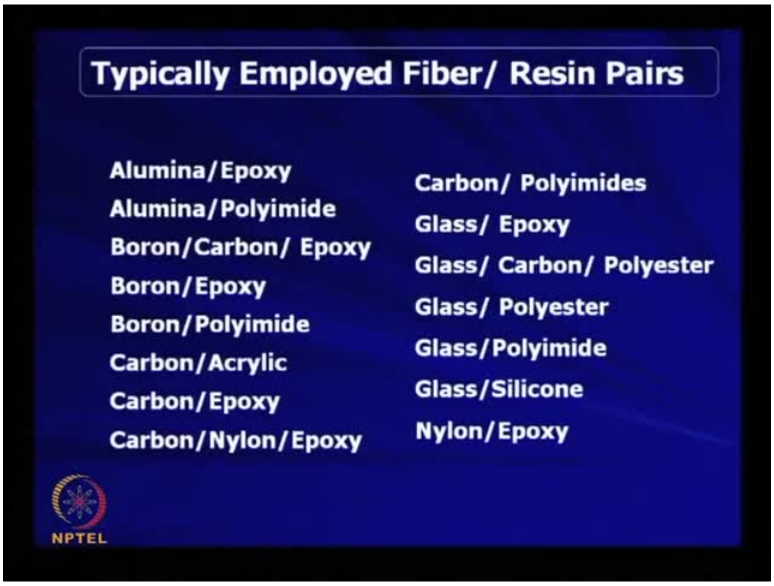

## Typically Employed Fiber/ Resin Pairs

Alumina/Epoxy
Alumina/Polyimide
Boron/Carbon/ Epoxy
Boron/Epoxy
Boron/Polyimide
Carbon/Acrylic
Carbon/Epoxy
Carbon/Nylon/Epoxy

Carbon/ Polyimides
Glass/ Epoxy
Glass/ Carbon/ Polyester
Glass/ Polyester
Glass/Polyimide
Glass/Silicone
Nylon/Epoxy

Resins, I will discuss this thing in that class there, so let us remain here today.

Thank you very much.