Chemical Technology
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Module - 08
Polymer
Lecture - 04
Elastomers: Styrene Butadiene Rubber (SBR)
Polybutadiene Nitric Rubber

We are discussing the module 7 of the organic chemical technology course and we discuss about the polymer industry different type of the polymers. Today, we will be discussing about the elastomer means the natural rubber and the synthetic rubber. The next 2-3 lecture that will be on the synthetic fiber.

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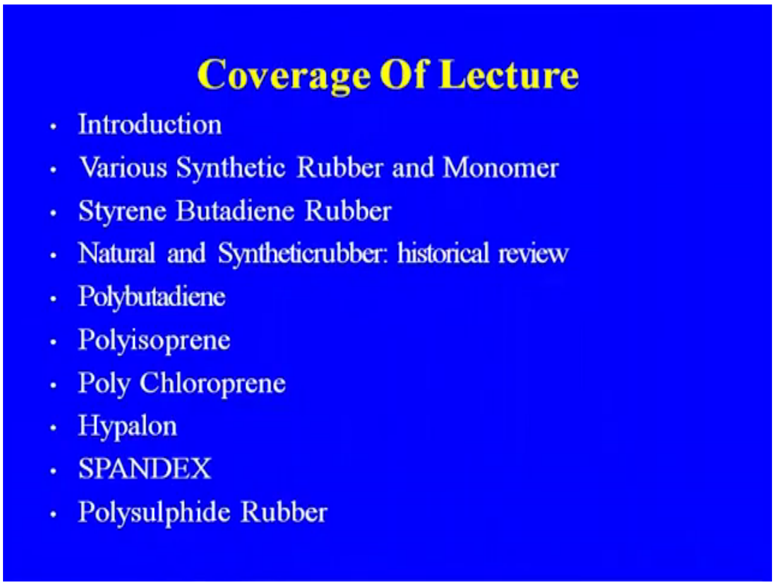

So, the coverage of the lecture that will be the introduction various synthetic rubber and monomer styrene butadiene rubber which is the one of the most widely used rubber. Natural and synthetic rubber historical review polybutadiene, polyisoprene, polychloroprene, hypalon, spandex, these are the some of the other synthetic rubber that we are making.

I will go very quickly on these polyisoprene poly chloroprene or the hypalon. We will be discussing in more detail about the synthetic rubber and the polybutadiene. Why the importance of the polybutadiene? You know, the polybutadiene and the petrochemical complexes they are having the cracker plant.

So, the butadiene one of the very important feed stock for making or for the which we are getting from the sea forest steam of the your cracker plant, and this is the reason why the reliance and the even the earlier refinery where they are naphtha cracking. They are recovering the butadiene and in case of the reliance hazira, they are having the polybutadiene plant and I O C panipat refinery, they are going to have the S B R plant. This lecture 4 will be on the elastomers styrene butadiene rubber polybutadiene nitrile rubber and some of the other.

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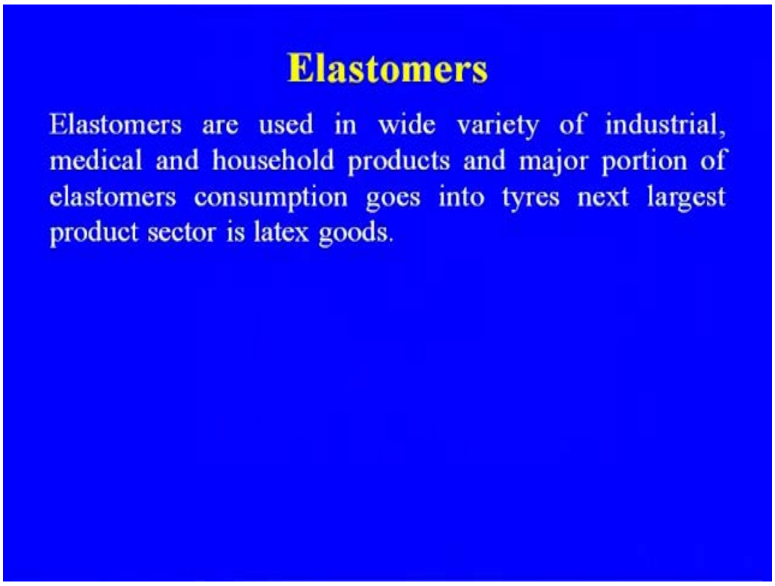

Specialized rubbers which I discuss here, elastomers are used in variety of industrial, medical and household products and major portion of the elastomer consumption goes into tyre next largest product sector is the latex good. You see, the importance of the elastomer or the rubber when a child start walking and playing.

So, first he start playing with the ball and that ball is from the synthetic rubber. So, there has been revolution in case of the synthetic rubber manufacture all over the world because of the coming of the large number of the petrochemical complexes and the availability of the raw material which was earlier through the non petrochemical route.

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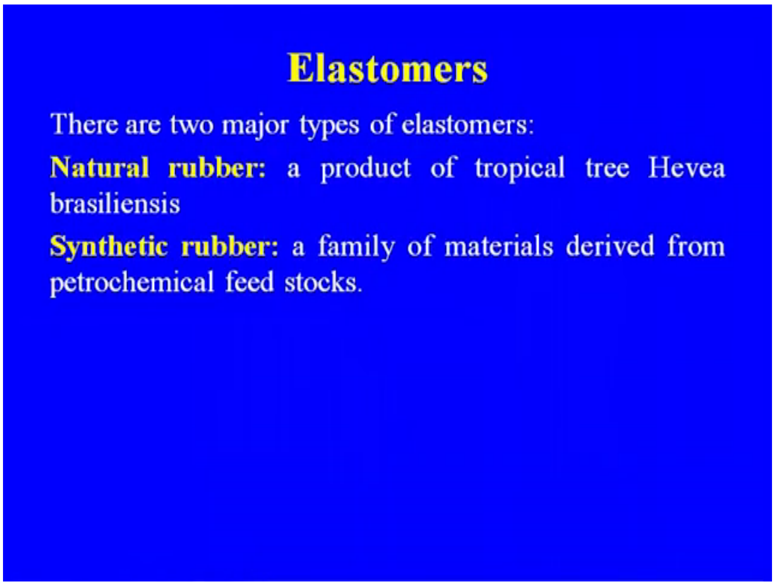

There are two major type of the elastomers, that is the one is based on the natural rubber a product of the tropical tree hevea brasiliensis and the synthetic rubber a family of materials derived from the petrochemical. So, these are the some of the tropical countries they are producing natural rubber. India is also one of the major nature raw producer, but in synthetic rubber that is playing the important rule and that is important part of the elastomers major producer of the natural rubbers are.

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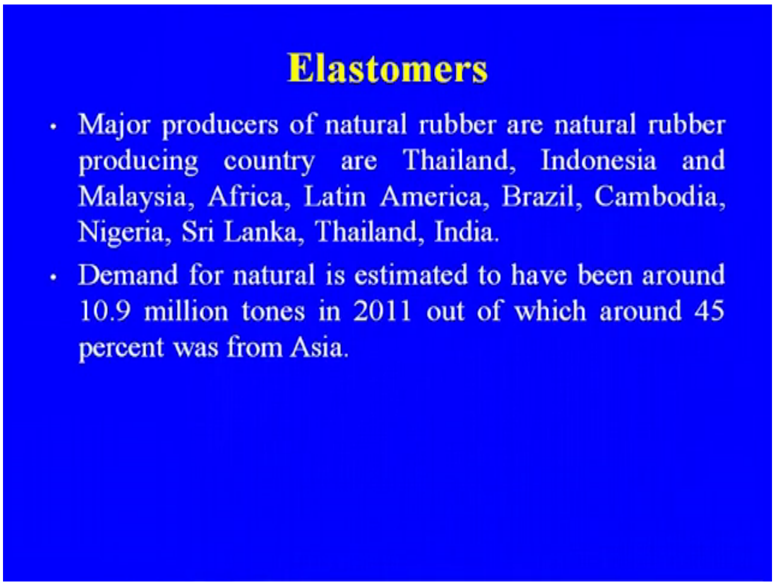

Natural rubber producing country are Thailand, Indonesia, Malaysia, Africa, Latin America, Brazil, Cambodia, Nigeria, Sri Lanka, Thailand and India. Demand for the natural rubber is estimated to have been around 10.9 million tons in 2011 out of which around 45 percent was from Asia. So, this is the you can see, the some of the country which are producing, they are the Asian country which are making huge amount of the this natural rubber.

Let us discuss some of the historical background because this is the, so far the elastomer or the rubber is concerned. This is not the from the ancient time even in the 1525, which is the elastic ball reported by Mexico tribal people that was the 1735 first scientific study of the rubber by Charles de la Condamine and then the 1920 first plant planting of the rubber in India at the Tranvancore that was started 1832.

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Roseburg factory was set up for rubber goods with non vulcanized rubber because the one of the in case of the rubber uses the vulcanization of the rubber which you are doing in case of the tyre. Where the vulcanized rubber, that has been there methyl 8 1914 methyl isoprene rubber in Germany 1845 that was the pneumatic tyre that was introduced first commercial plantation in 1903.

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First large scale commercial production of butadiene rubber that was 19 and 10 1914 to18 methyl isoprene rubber in Germany, and you see the lot of the development earlier also I told you that during the world war one, and the world war one and world war two lot of the development took place. In case of the chemical industry just to the rising demand which were also required from the wall pointer view and, so that lead to the development number of the your petrochemical important petrochemicals. So, methyl isoprene rubber in Germany that was in 1940 1930 organic polysulphide rubber neoprene productions and started in 1932 first synthetic rubber plant.

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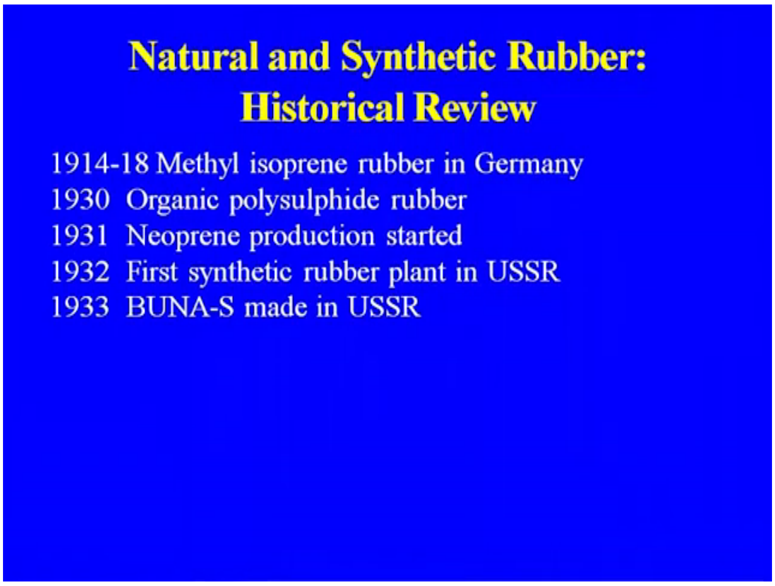

In U S S R and 1930 BUMA-S made in U S S R. As you know, the Dunlop, now there are other pairs are also there we are making the tyre another c 10. So, number of the plants are now then, but first it was in 1936 first automatic tyre factory by Dunlop that was started in India.

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1963 first synthetic rubber plant in India that was the I told you earlier also while discussing. The raw material and the petrochemical because synthetic chemicals and barely that was the first known petrochemical route plant which was started in barely, but due to some other reason that unit is now closed, but that was the first plant where the molasses. That was the molasses to ethanol and ethylene butadiene all those products they were made from the your molasses route 1976 first nitrile rubber by synthetics chemical 1978 first polybutadiene plant in India by I P C L.

Now, reliance at Vadodara that was the because you see, the reliance Vadodara unit earlier it was the I P C L. That is one of the largest you can say, the integrated petrochemical complex where above 18 to 19 plants are there although at that time the capacity that was, but in the now all those capacity are not at the world level and so the plant capacity.

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Less in all those unit reliance industry hazira started manufacturing. The polybutadiene and now the I O C panipat S B R plant in the pipe line and, so shortly they will be, that is the action phase. So, S B R plant that is coming where they will be using the butadiene from the cracker plant. Then, styrene they will be making their ethylene they will be using.

So, that is the new plant that is coming at the I O C panipat refinery. Now, let us discuss about the synthetic rubber, synthetic rubbers have slowly replaced the natural rubber and have undergone various development for application in automotives chemical industry because automotive is the one of the major consumer of the rubber chemical industry.

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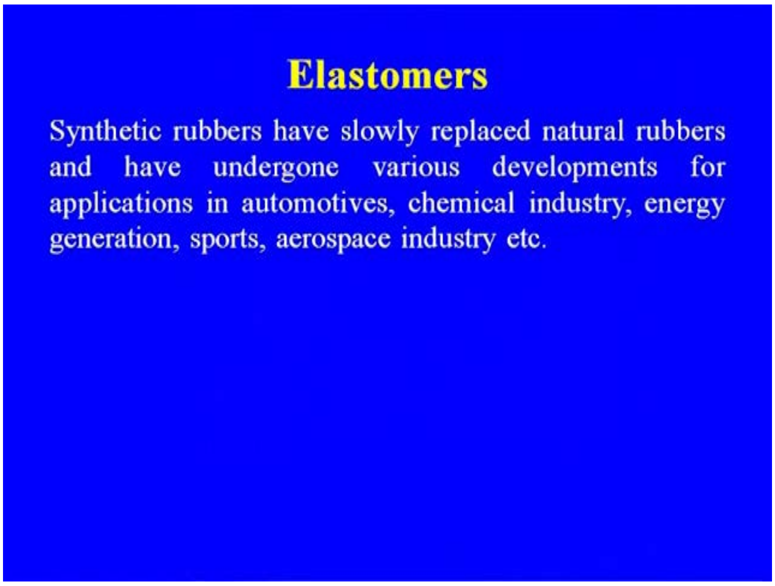

We are having the we are using the rubber landing of the equipment that is being done in various other application appliances also. We are using the rubber goods, so energy generation sports aerospace industry, these are all where we are using the synthetic rubber in some or other form.

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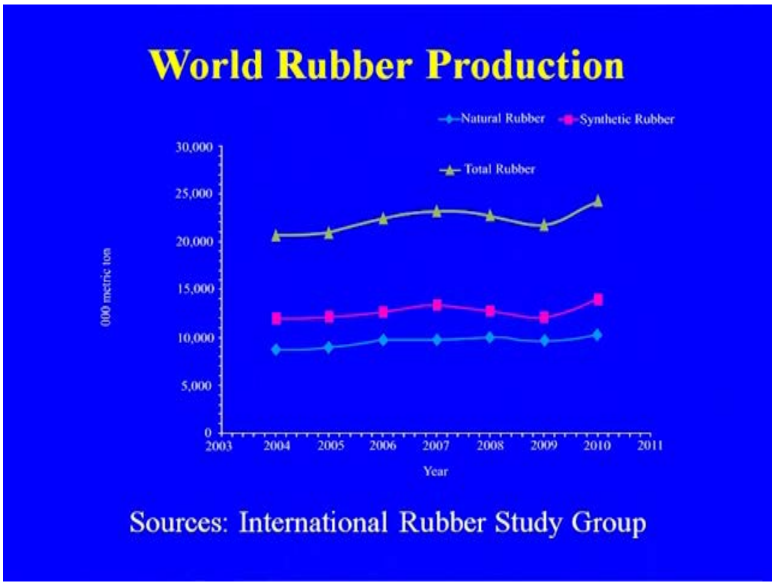

This is the how the development in case of the natural rubber and the synthetic rubber that has taken place. So, let us discuss the what are the various type of the synthetic rubber that is available so first is the major is the styrene butadiene rubber the second is the polybutadiene rubber because in case of the S B R we need the ethyl benzene and ethyl benzene to styrene.

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Various Synthetic Rubbers

Styrene butadiene rubber SBR	Butyl rubber and Chloro butyl rubber
Polybutadiene rubber BR	Polyisoprene
Nitrile rubber(Butadiene, acrylonitrile rubber) NBR	Vinyl pyridine butadiene Rubber
Vinyl pyridine styrene butadiene	Nitrile chloprene

So, they in case of the because the polybutadiene also one of the very important your rubber. So, the reliance they are making the polybutadiene not the S B R. Another important that was the nitrile rubber with the were the butadiene acrylonitrile rubber, because that was again requirement of the time during over cealen, because the oil resistant resistance towards the oil.

So, this was the one of the very important development during that with nitrile rubber vinyl pyridine styrene butadiene rubber butylrubber and the chlorobutylrubber, polyisoprene that is because the isoprene. Now, the as I while discussing the C 4 C 5. I discussed the isoprene about 8 to 10 percent that is available from the C 5 steam of the cracker plant.

So, the or the F C C, so that can be recovered and that isoprene can be made available to the synthetic rubber use. So, that is the how the otherwise the natural resource is of course, there vinyl pyridine, butadiene rubber, nitrile chloroprene various combination of the your monomers are.

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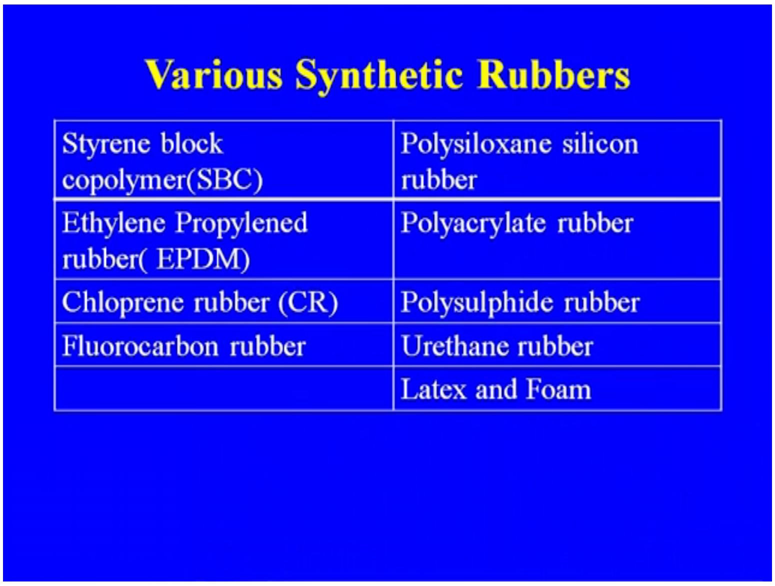

There, then the styrene block copolymer S B C that is also one of the very important outlet for the styrene ethylene propylene rubber E P D M chloroprene rubber fluorocarbon rubber and the polysiloxane silicon rubber. That is also one of the very important class and the polyacrylate rubber polysulphide rubber urethane rubber latex and foam.

So, these are the some of the god range of the synthetic fiber that we are making, but among all these S B R polybutadiene and the nitrile rubber these are the very important synthetic rubber. That is being that has having the wide application in the industry these are the some of the monomer that we are using ethylene propylene butadiene isobutylene.

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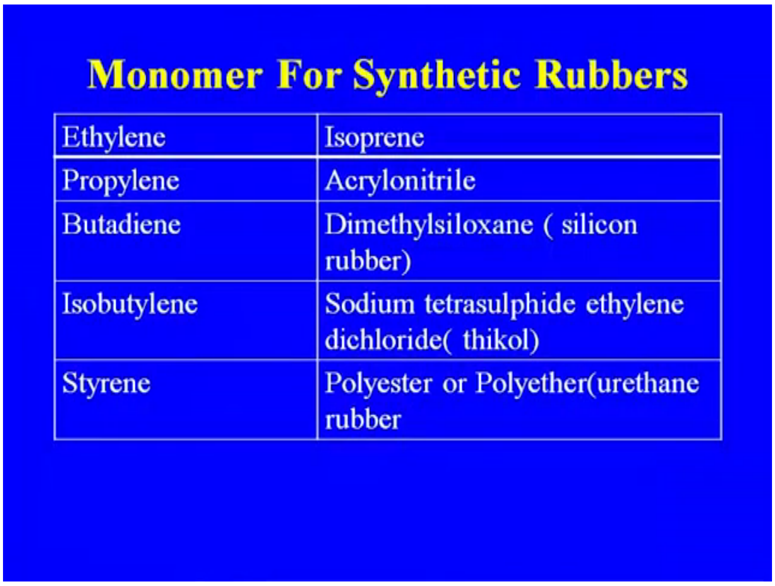

So, these are all the products you see the you are getting through. Now, with the petrochemical isobutylene, also that is while discussing C 4, I told you the M T B. The that can be cracked or the your hydration that was the another routes that will be just we will be getting the isobutylene the for the rubber gate polymerization gets high purity also get from the cracker plant from the C 4 steam of the cracker plant or the F C C.

So, that is also, all these 4 again the styrene also we need the ethyl ethylene benzene. These all that you can get from the even in case of the cracker form itself. You can get the benzene and the ethylene and then ethyl benzene and then again the development of the alkylation process. The development in the catalyst earlier to the manufacturing more and more manufacturing of the styrene. Another important feedstock that is the acrylonitrile isoprene of course, and that I told you that the isoprene that is one of the again it is available from the C 5 steam acrylonitrile because.

You see, the acrylonitrile earlier it was made from the acetylene route which I told you the while discussing the petrochemical, but acrylonitrile now that is available through the propylene route which is being now the most of the acrylonitrile. That is being, so that has also played important role in providing the feedstock for the synthetic rubber industry.

This is the another the varying for the silicon rubber dimethylsiloxane that is the another for the silicon rubber sodium tetrasulphide, ethylene dichloride thikol. There were using and the polyester or the polyether for the urethane rubber, so these are the some of the important monomer for this synthetic rubber industry. This is the importance of this rubber which I told you in the automotive because huge amount of the rubber that.

We are using in case of the automobile industry, so one of the major consumer is the tyre you see the whether it is the 2 wheeler, 3 wheeler or the 4 wheeler you need the tyre. So, the tyre and even in the tyre. Now, we are having the tubeless tyre or the earlier it used to be tube in the tyre all the cases that we need the rubber.

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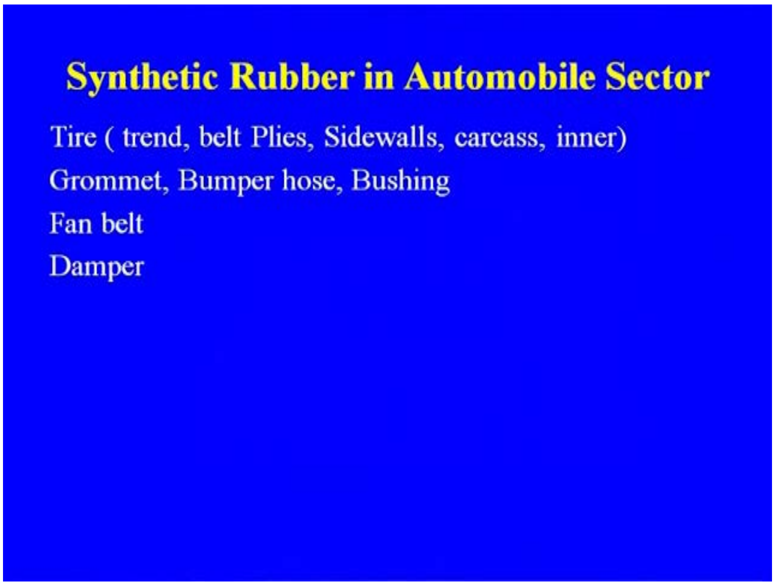

So, that was the one of the major and the trend belt plies sidewalls, carcass, inner grommet bumper hose bushing fan belt damper. So, these are the some of the actually the, so far the automobile sector where the application of the rubber is there. Now, let us discuss about the styrene butadiene rubber which is one of the most widely used elastomer in the world because of the availability, because of the flexibility in the raw material either from the molasses route or from the petrochemical route.

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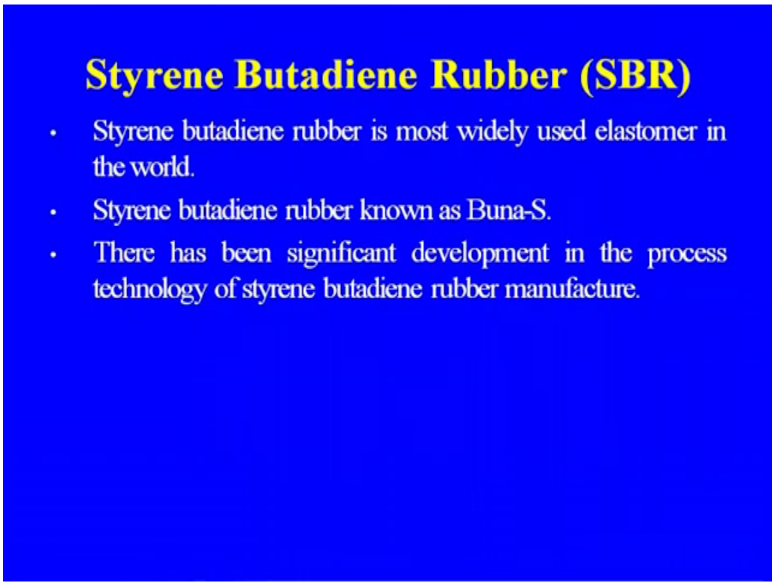

So, styrene butadiene rubber is known as BUNA-S, also there has been significant development in the process technology of the styrene butadiene rubber manufacture. Amongst the various processes which we are using emulsion polymerization of the styrene butadiene rubber is most commonly used method.

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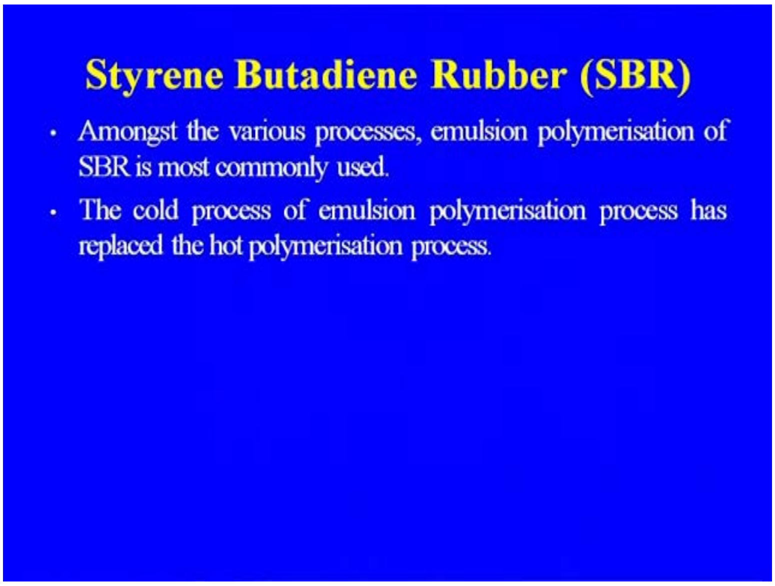

The cold process of the emulsion polymerization has been replaced with the hot polymerization process.

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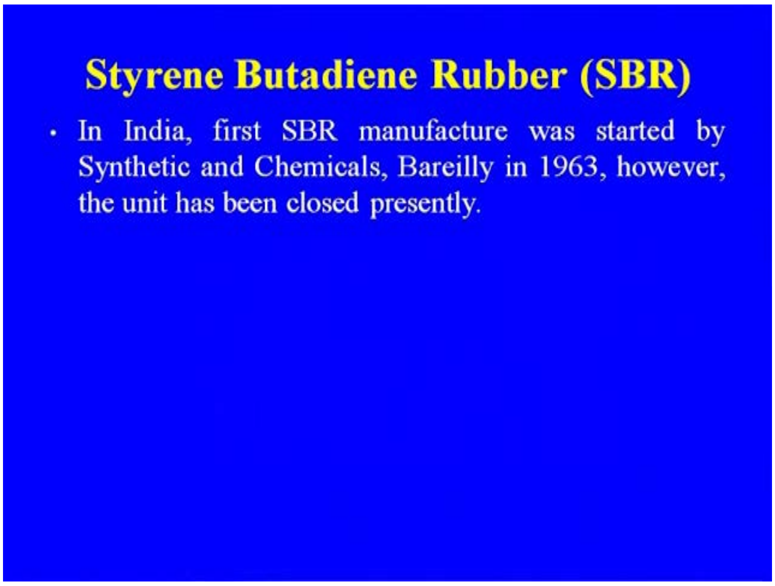

In India, the first S B R styrene butadiene rubber manufacture was started by Synthetic and Chemicals Bareilly in 1963. The unit is now closed because of the their own problem. The although the butadiene because the another important for the styrene butadiene is the rubber is the butadiene raw materials.

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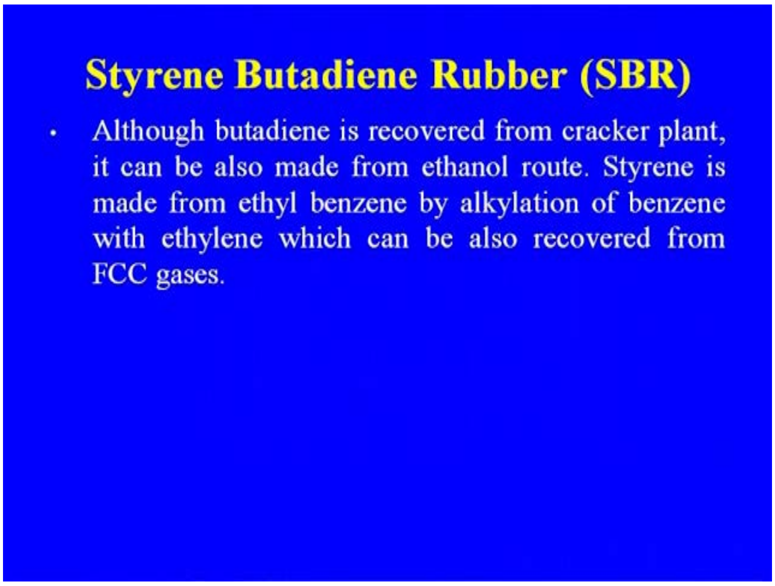

Although butadiene again is recovered from the cracker plant it can be also made from the ethanol route styrene is made from the ethyl benzene by alkylation of benzene with ethylene which can be also recovered from the F C C gases. I told you that the now the interest is there why not to recover that ethylene which is available in the F C C gases .

Although they the amount of the ethylene that is less. It is below 10 percent, but still that can be used for the alkylation process and now the technology available for the direct F C C gas. You can containing ethylene that can be used for the making of the styrene butadiene rubber means the styrene means the ethyl benzene. It will be first and then the styrene, so styrene butadiene.

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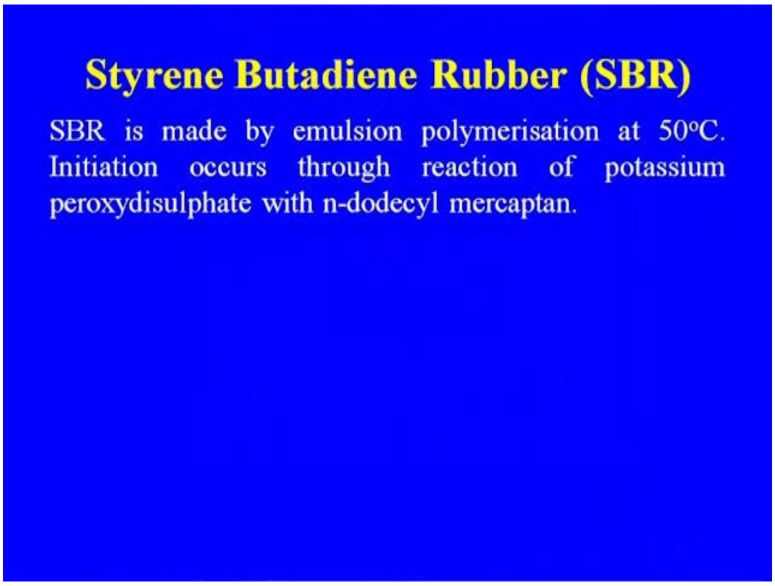

Rubber is made by emulsion polymerization at 50 degree centigrade initiation occurs through reaction of potassium peroxydisulphate with n-dodecyl mercaptan. Unit, so the chain propagation occurs by growing chain free radical of mercaptan attaching either butadiene or styrene.

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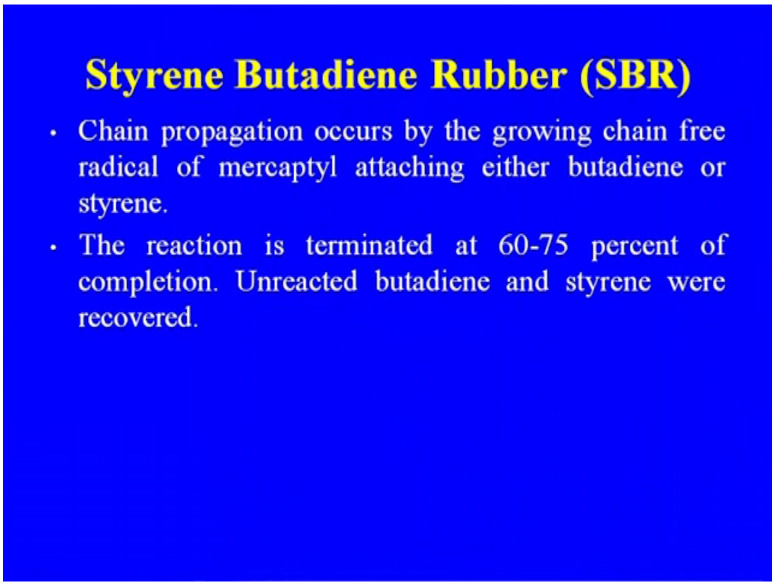

The reaction is terminated at around 60 to 75 percent of the completion of the reaction unreacted butadiene and the styrene are recovered.

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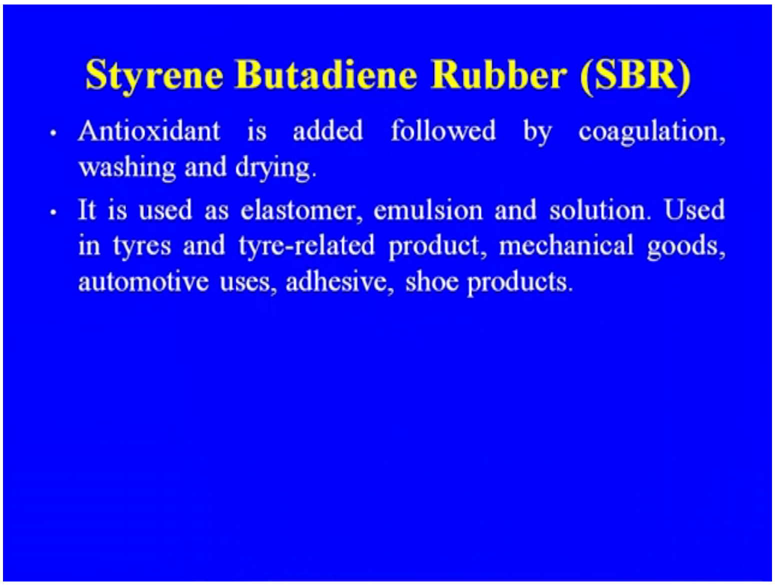

So, other actually additives are also added antioxidant is added followed by coagulation washing and the drying. It is used as elastomer emulsion and solution used in the tires tyre related product mechanical goods, automotive use, adhesive and the shoe products another important ethic under the polystyrene butadiene.

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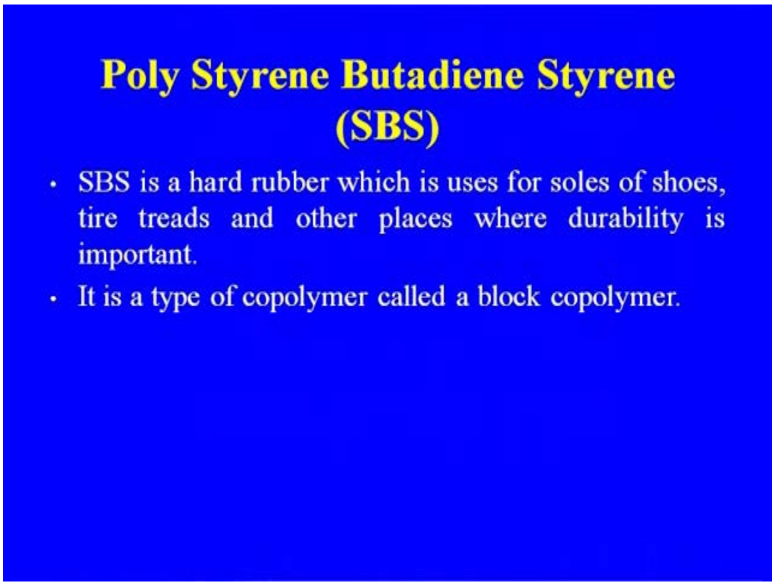

That is the S B S is a hard rubber which is used for the soles of the shoes, tire tips and other places where durability is important. Now, you see the earlier we used to have the shoe soles made of the leather. Now, with the coming of the synthetic rubber and the urethane rubber especially the lot of the durability of the earlier we used to have the cracking. So, durability is much longer of the shoe, so this is one of the another actually the advantage in case of the synthetic rubber. It is a type of the copolymer called a block copolymer.

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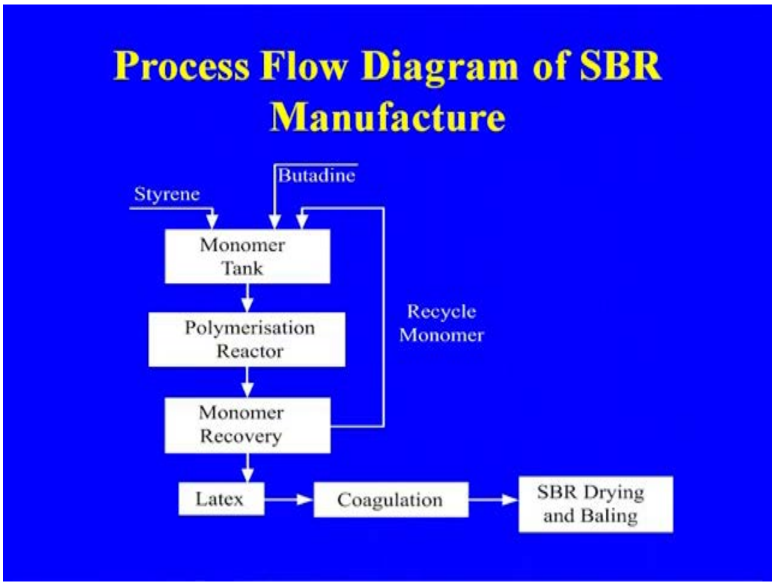

This is the process for the manufacture of S B R. The styrene butadiene that is going to the monomer tank mixing and the polymerization reactor where the reaction that is taking place and as I told you the after the completion 60 75 percent of the completion, that is going to the monomer recovery where the monomer again. It is recovered here. That is going to recycling and we are getting the latex as such it can be used or it will go for the coagulation.

Then, the styrene and butadiene rubber drying and the baling that may be done, so this the process for the manufacture of S B R. I was talking about the S B S it is backbone chain is made of 3 segments, first segment polystyrene second polybutadiene and third is the polystyrene.

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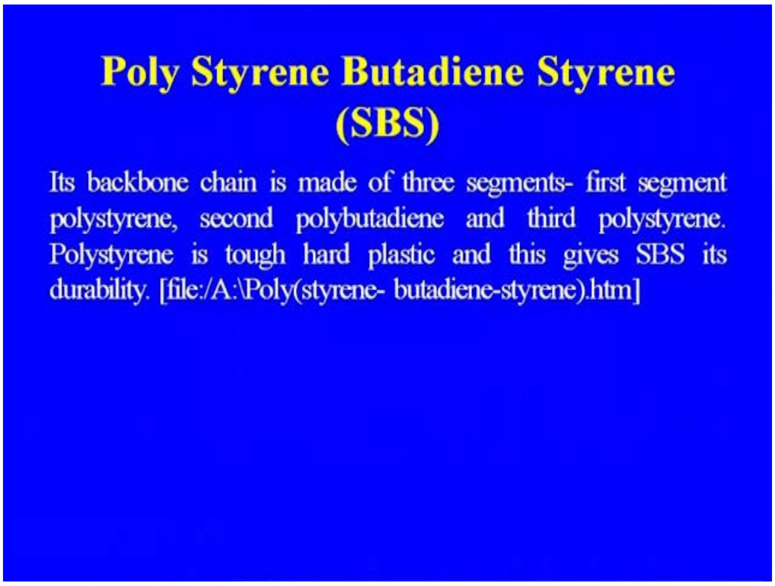

So, this is the combination of styrene butadiene polystyrene butadiene styrene though a polystyrene is tough hard plastic and this gives S B S, it is durability. Now, let us discuss about the polybutadiene because this is another important derivative of the butadiene also and at the same time one of the important poly your synthetic rubber. So, before going for in detail about the polybutadiene process further. Let us discuss about the sources of the butadiene, although I have discussed this while discussing the petrochemical.

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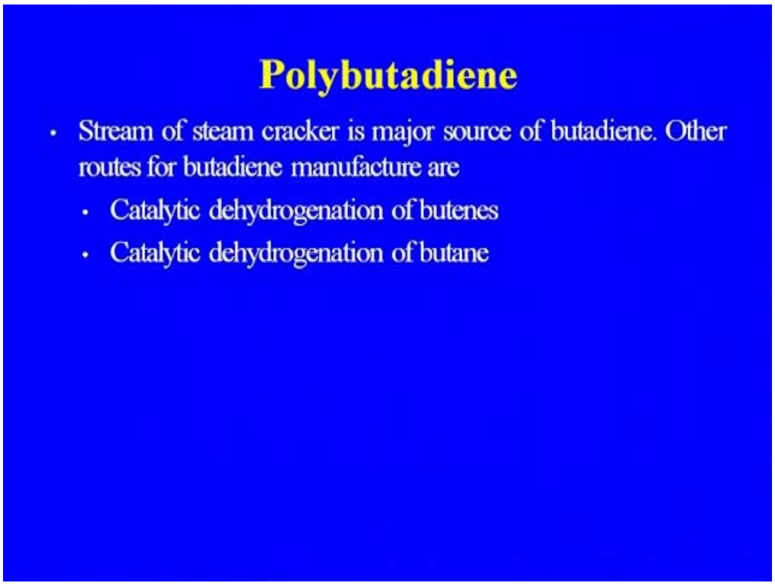

The butadiene steam cracker is major source of butadiene, other routes for butadiene are catalytic dehydrogenation of the butane, that butene catalytic dehydrogenation of the butane. So, these are the 2 other way and this because these two, we can recover from the F C C gases, the C 4 gases. This is the reason why the C 4 gases of the cracker plant as well as the F C C. They are they have become very important source for the value addition to the refinery or the petrochemical complex which was not being done earlier.

So, in future you may have the more and more utilization of the C 4 and C 5 especially some of the raw material which is, which will play important role in the development of the synthetic rubber industry.

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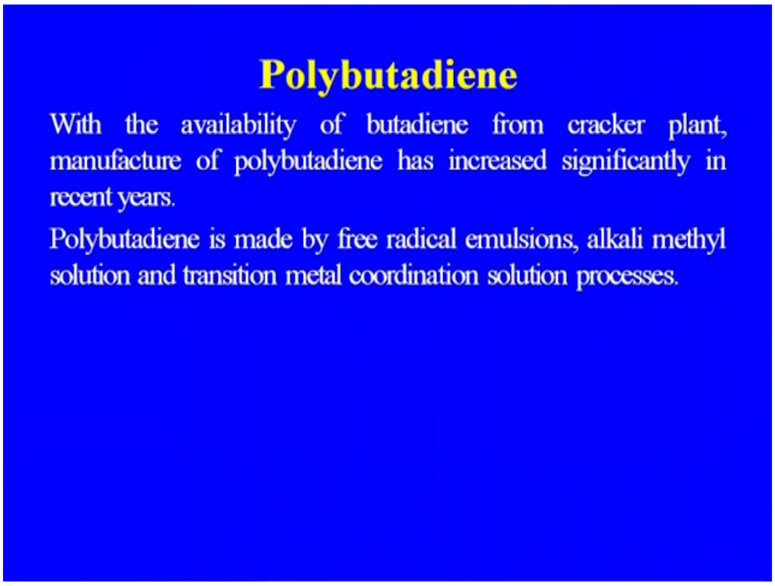

So, with the availability of the polybutadiene as I told you the in the cracker plant manufacture of the polybutadiene has increased significantly in the recent year because we are having now the large capacity cracker for naphtha. Earlier which as I told you during the naphtha cracking we started the only 2000 20000. Now, we are having 800000 tons plus 800000 tons capacity naphtha cracker plant. So, amount of butadiene that is generated very high and so that has lead to the development of the either S P R or the polybutadiene interval.

So, for the process mechanism polybutadiene is made by free radical emulsion alkali methyl solution. The transition metal coordination solution processes most process are based on the solution process large volume use of polybutadiene rubber has been primarily in blend with the other polymers.

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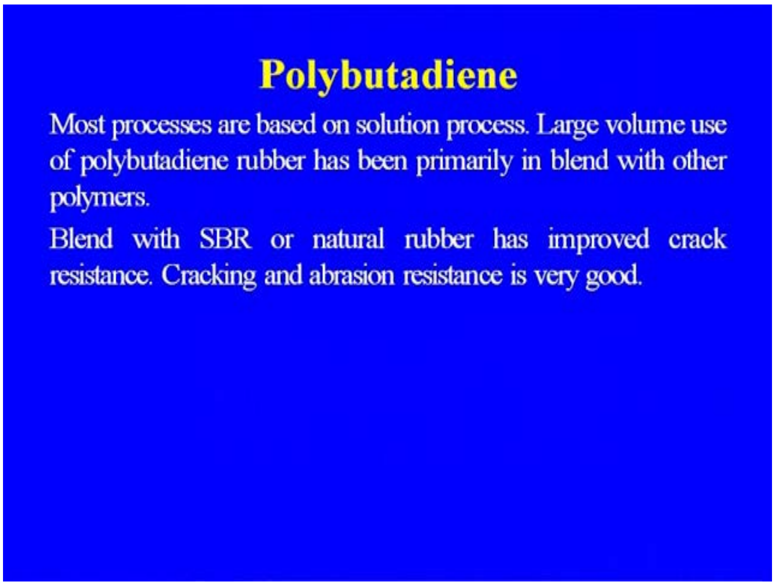

Blend with S B R or natural rubber has improved the crack resistance cracking and abrasion resistance is very good in case of the polybutadiene. It is characterized with a high abrasion and crack resistance better resistance to heat degradation and the blowouts, good hysteresis properties, large scale use in the tyre cord modification of the plastic conveyor.

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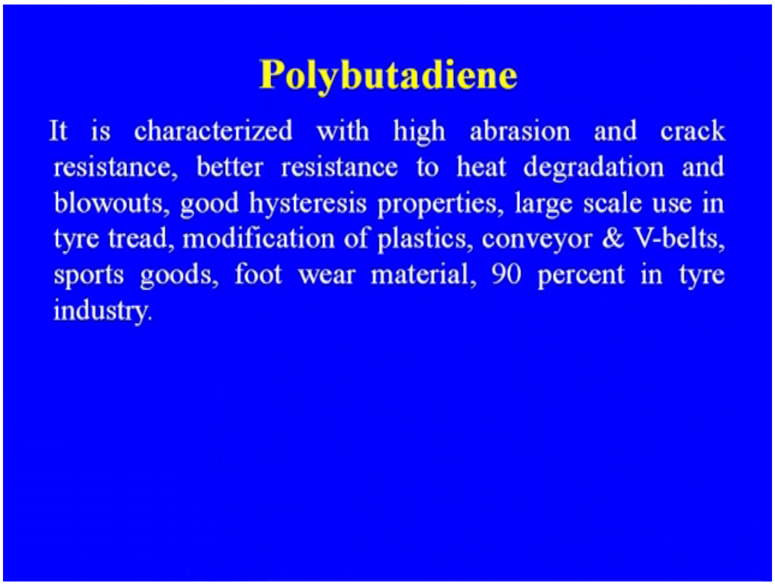

The V- belts again the conveyor and the V-belt is now for the transmission of the raw material in the industry lot of the number of the belts converts. You are having and many equipments, we are having the V-belts sports code because it is also one of the major consumer of the amount that might be less if you compare with the other user, but that is also one of the, and even the sports from the if you see the sports. I mean the football which you are saying or the balls which you are getting. Now, there will be lot of the changes in the raw material contribution food severe that is also one of the important consumer of the polybutadiene and the of course, that is the tyre industry.

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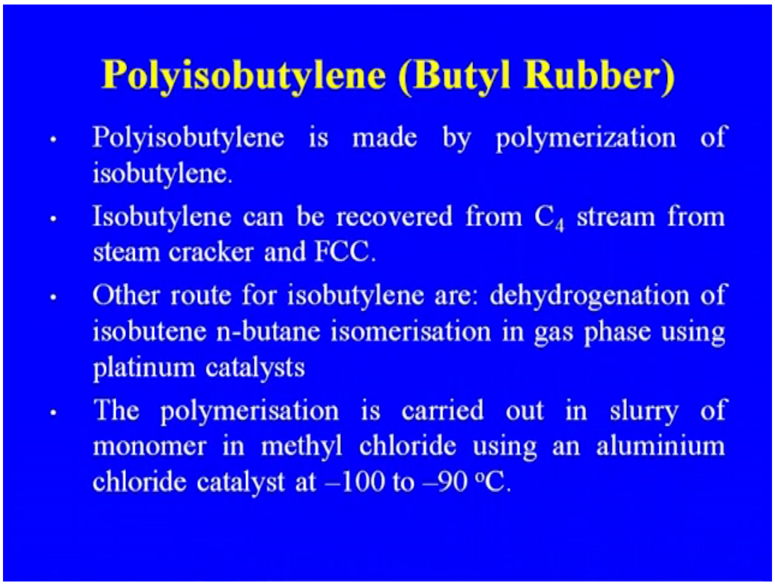

Polybutadiene level is made by the polymerization isobutylene as I told you the isobutylene can be recovered from c 4 steam from steam cracker and the F C C. Other route for isobutylene are the dehydrogenation of isobutene and n butane isomerisation in gas phase using the platinum catalyst. The polymerization is carried out in slurry of the monomer in methyl chloride using an aluminum chloride catalyst at 100 degree to 90 degrees.

The rubber is precipitated by adding water and finally washed and dried. Butylrubber has unique elastomeric qualities low rate of gas permeability thermal stability good ozone and weathering resistance vibration damping and higher coefficient of friction chemical and moisture resistance.

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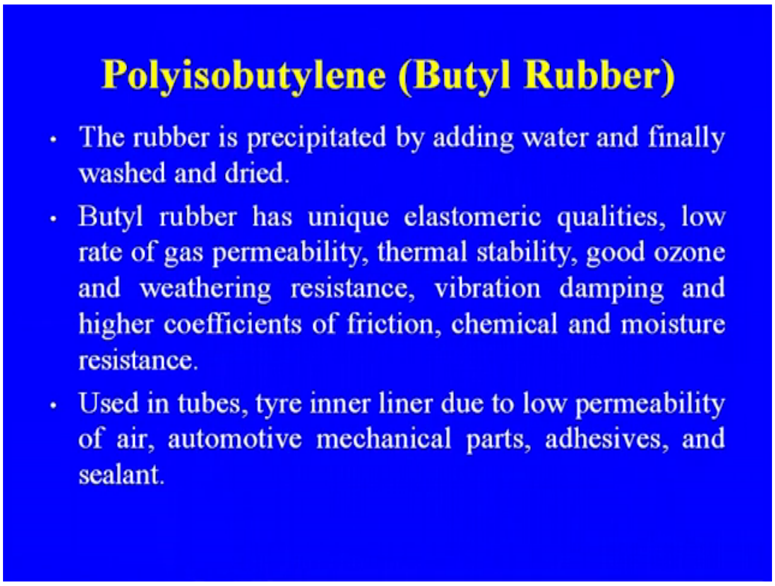

Used in the tubes, tyre inner linear due to low permeability of air automotive mechanical parts adhesives and sealant. So, these are the some of the major application of the polybutadiene level about and, so this is one of the very important property is the low permeability of the air. Another important class of the synthetic rubber is the nitrile rubber which I told you that is the communication of the acrynitrile and butadiene. The both earlier as I told you the starting phase of the nitrile about that was through the non better chemical route.

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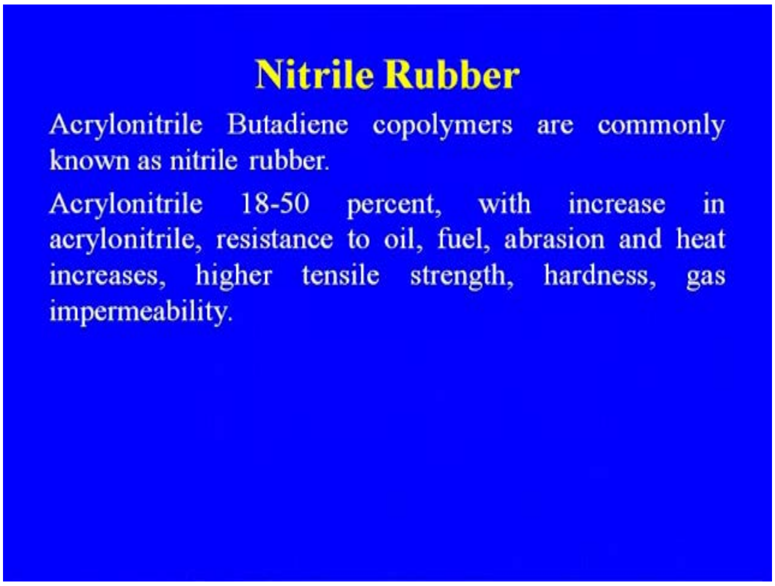

So, acrylonitrile and Butadiene copolymers are commonly known as the nitrile rubber. Acrylonitrile 18 to 50 percent with increase in the acrylonitrile resistance to and this I was telling the oil scene because the oil leakage resistance to the oil leakage in case of the nitrile load is very high. So, the resistance to oil fuel abrasion and heat increases higher tensile strength hardness gas impermeability.

So, these are the, if you are increasing the acrylonitrite content. So the effect will be the more resistance to oil fuel abrasion and heat. Low temperature resistance resilience plasticizer compatibility decreases requires less sulfur more accelerators than S B R highly oil resistant.

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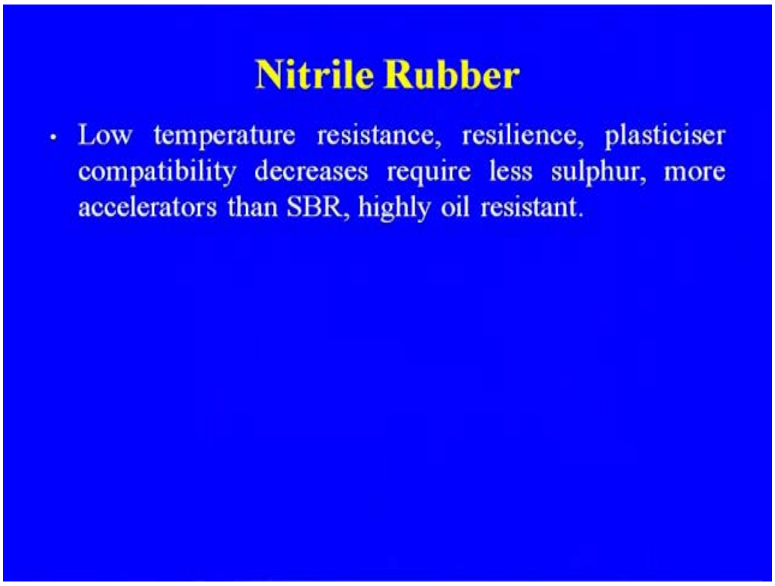

These are the some of the characteristic of the nitrile rubber application fuel hoses collapsible containers nitrile rubber may be reinforced by phenolic resins and P V C.

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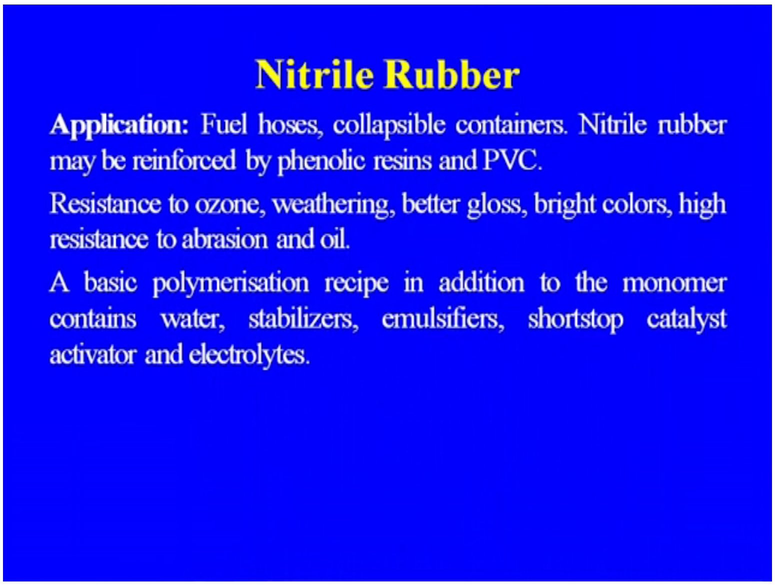

Resistance to ozone weathering better gloss bright color high resistance to abrasion and oil. A basic polymerization recipe in addition to the monomer contains water stabilizer emulsifier shortstop catalyst activator and electrolytes free radical generating catalyst is added.

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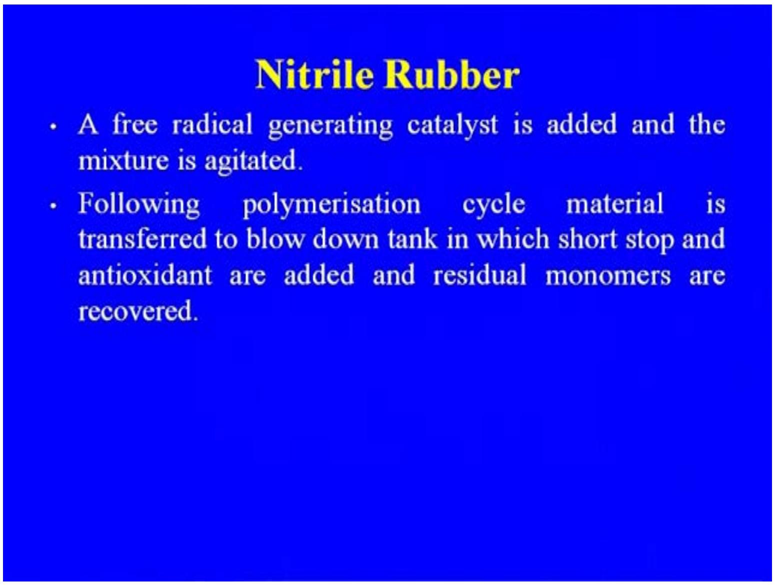

The mixture is agitated following polymerization cycle material is transferred to the blow down tank in which the short stop and the antioxidants which are added and residual monomer are recovered and this is again a recycle to the reactor.

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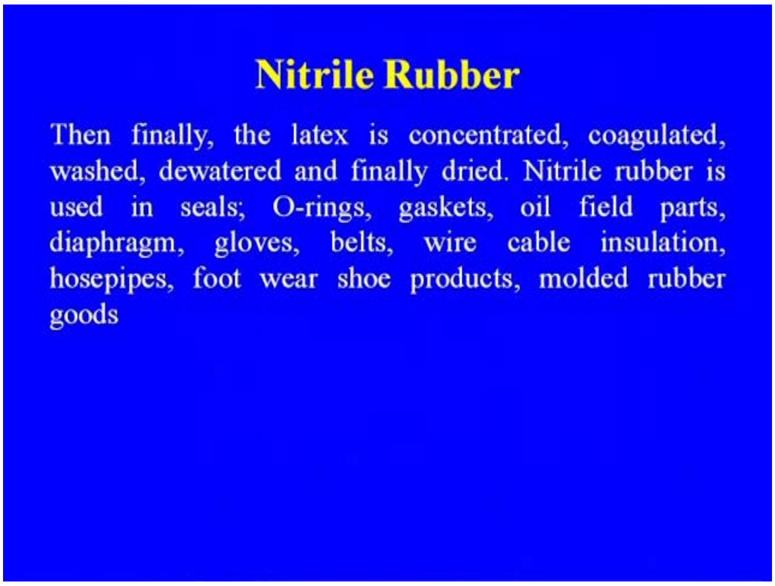

Finally, the latex is concentrated as a others while discussing we discuss the we can have in the latex form which can be coagulated washed dewatered and finally, dried nitrile rubber is used in seals; o-rings gaskets oil field parts diaphragm gloves belts wire cable insulation hosepipes foot wear shoe products molded rubber goods. Now, discuss another important class of the synthetic rubber that is the polyisoprene. That was the actually the importance in case of the recovery of the isoprene from the C 5 gases.

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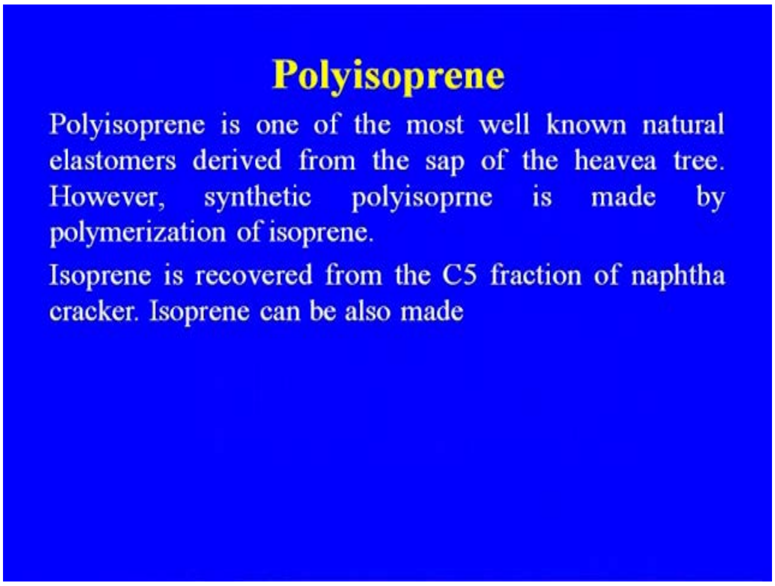

So, polyisoprene is one of the most well known natural elastomer derived from the heave a tree because you see the isoprene. That is, that is the natural rubber, that is the what we are having, but synthetic polyisoprene is also possible. So, that is made by the polymerization of the isoprene which can be recovered from the C 4 C 5 gas from the C 5 gases because after recovery of the C 4 gases that will go to the isoprene. These are actually some problem in separation because of the close boiling point and the liquid extraction that we are separating the isoprene and that is the isoprene that can be used in that from the if you are going from the C 5 float from the C 5 basin.

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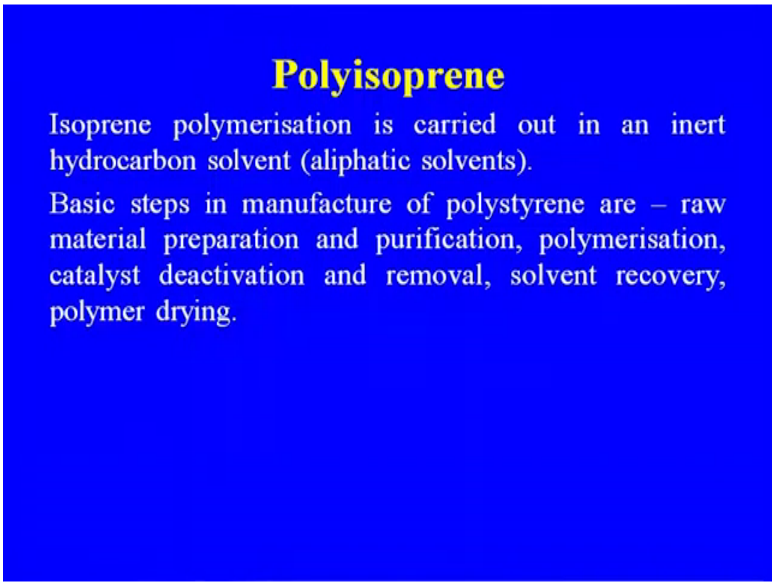

So, isoprene polymerization is carried out in an inert hydrocarbon solvent aliphatic solvent. Basic steps involved in case the manufacture of the polystyrene are raw material preparation purification, polymerization catalyst, deactivation and removal solvent recovery polymer drying. So, these are the basic steps involved in the manufacture of polyisoprene another important class of the synthetic rubber that is the neoprene polychloroprene is made by emulsion polymerization process using resin acid soap emulsifier.

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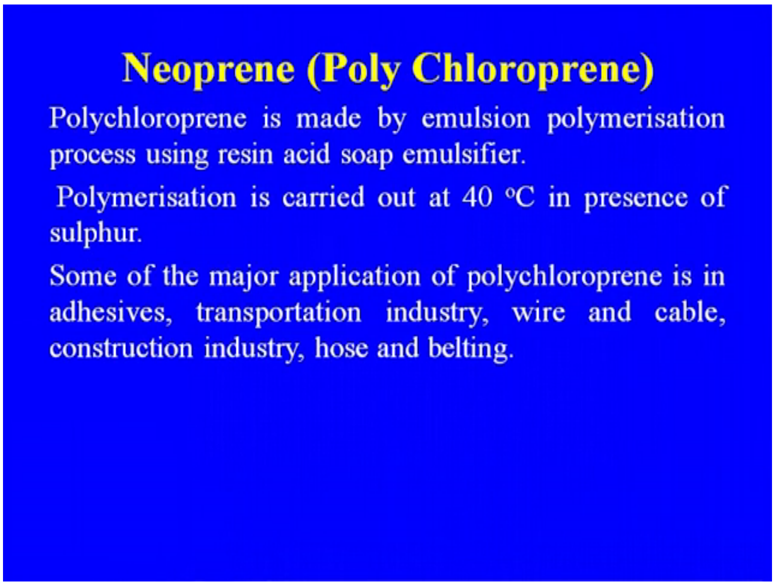

Polymerization is carried out at forty degree centigrade in presence of the sulfur. Some of the major application of the poly chloroprene is in adhesive transportation industry wire and cable construction, industry hose and belting uses adhesive transportation, automotive gaskets, v-belts, shock absorber covers wire, jackets, molded seats, aviation-wire cable, gaskets, seats etcetera rail brake hose track mounting.

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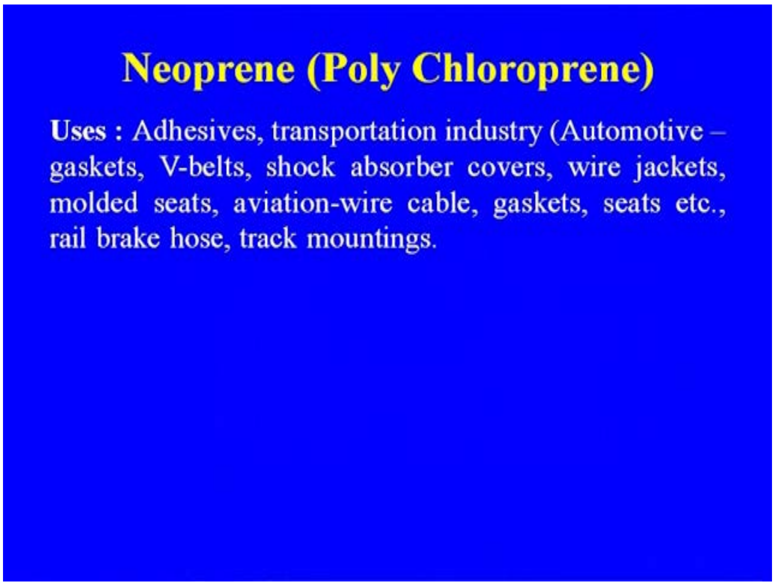

So, these are the some of the major application of the polychloroprene again here also the same acetylene route is available. So, that can be made from the acetylene or the butadiene route because earlier when the butadiene was not from the petrochemical. So, acetylene that was a route for making of the chloroprene, So acetylene route involves dimerization of the acetylene to monovinyl acetylene followed by the reaction of monovinyl acetylene with H C L.

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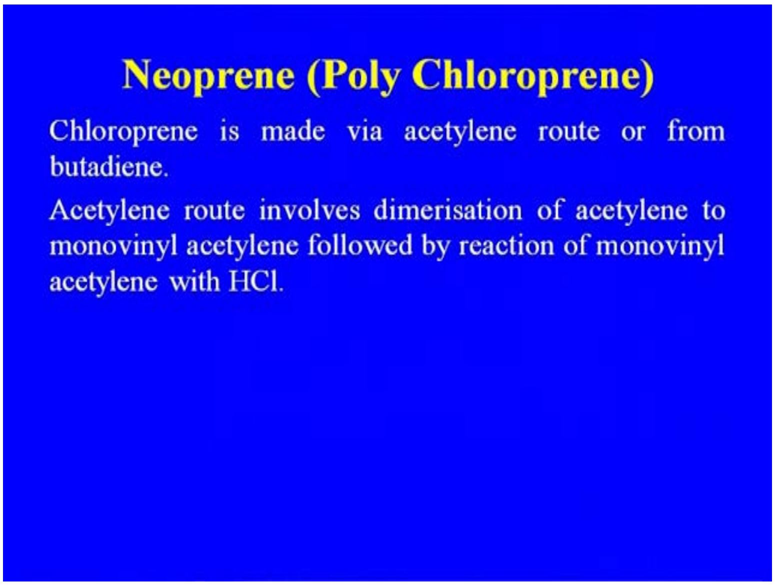

So, this was the method that was developed earlier with the for the acetylene route. So, polymerization in case of the neoprene that is polychloroprene is carried out at 40 degree centigrade in presence of the sulfur.

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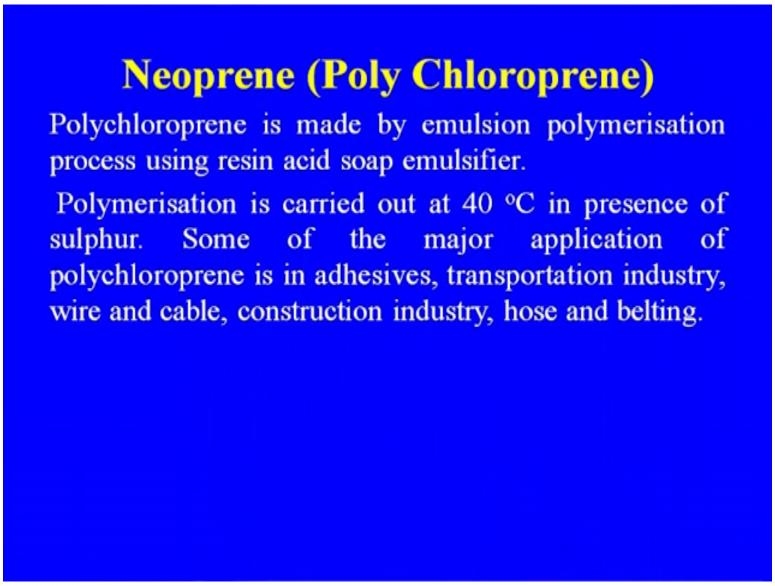

Some of the major application already we discussed about the poly chloroprene that is the adhesive, transportation industry, wire and cable construction hose and belting chlorobutylrubber.

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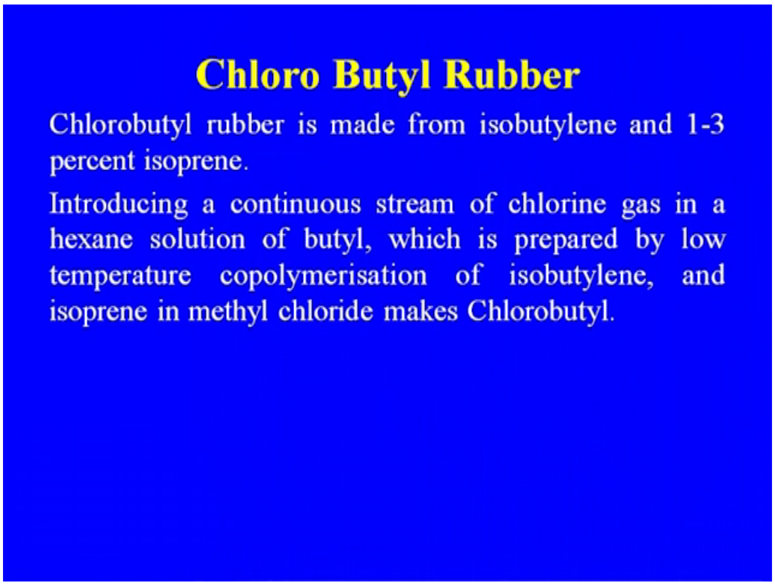

So, here chlorobutylrubber is made from the isobutylene and 1-3 percent the isoprene. Introducing a continuous stream of chlorine gas in hexane because along with isobutylene and isoprene chlorine. So, the introducing a continuous stream of the chlorine gas in hexane solution of butyl which is prepared by low temperature copolymerization of the isobutylene, and isoprene in methyl chloride makes the chlorobutyl. So, this is the process, we are using for making of the chlorobutyl rubber.

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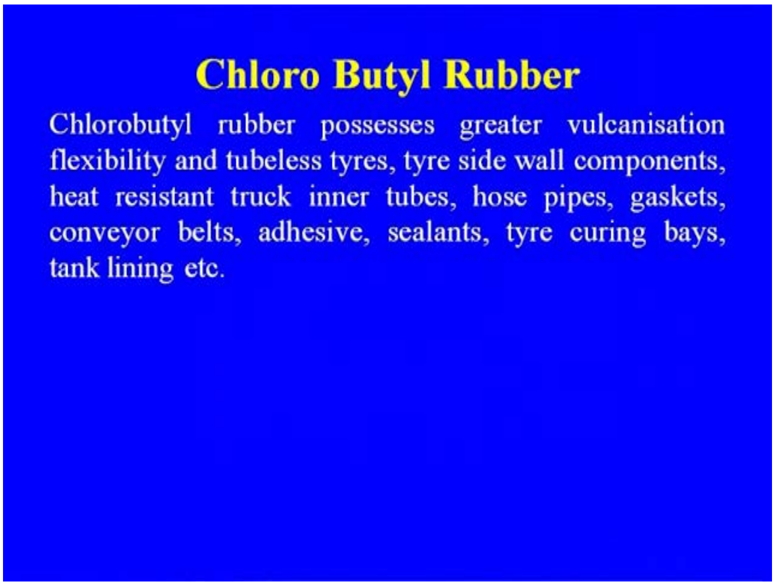

What is the advantage of the chlorobutyl rubber possesses? Greater vulcanization because that is the one of the major part of the process when you are using the rubber and the toluene vulcanization of the rubber that is being carried out. So, the vulcanization flexibility and tubeless tyre. Now, the most of the leo breed of the cars, you will find them, you are having the tubeless tyres. So, tyre side wall components heat resistant truck inner tubes, hose pipes, gaskets, conveyor belts, adhesive, sealants, tyre curing bays and tank lining etcetera.

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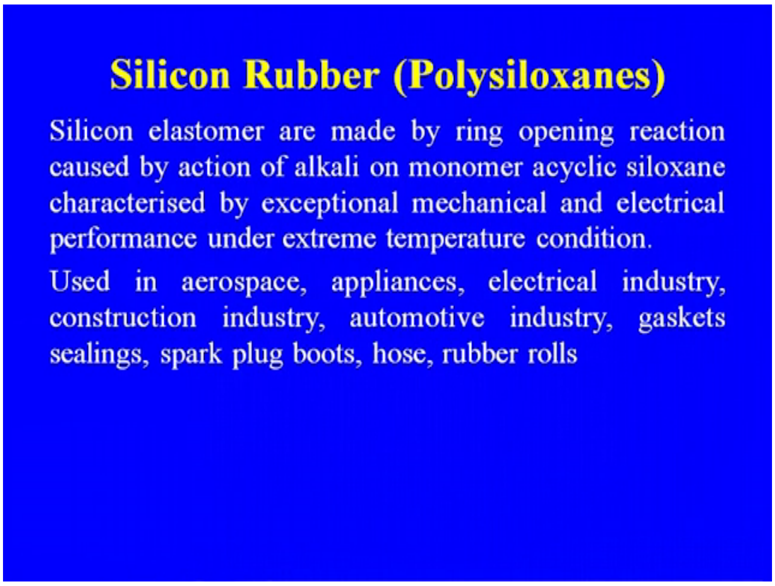

So, these are the some of the uses of the. Now, let us discuss about the silicon rubber that is the poly polysiloxanes. The silicon elastomers are made by ring opening reaction caused by action of alkali on monomer acyclic siloxane characterized by exceptional mechanical and electrical performance under extreme temperature condition. So, the this is one of the various crystallized rubber, you can say and we discuss about the while discussing the polymer elastomer and the synthetic fiber. How we are bring the one is the your special elastomer and another was the which we are using commonly used elastomer.

So, this is coming in case of the specialized elastomer, so because of the exceptional mechanical and electrical components under extreme. It is used in the aero aerospace appliances electrical industry construction industry automotive industry gaskets scalings spark plug boots hose rubber rolls.

So, these are the now one of the another actually I told you the rubber importance of the rubber that is the calendaring. Another this we discussed while discussing the paper the press routes or the final place rolls which there we are using the rubber line. Rolls are there that is applicable, so even in some of the chlorine application. We are doing the lining with the chlorine also of the, so this is the about the not only about silicon, but it was the another major application of the synthetic rubber.

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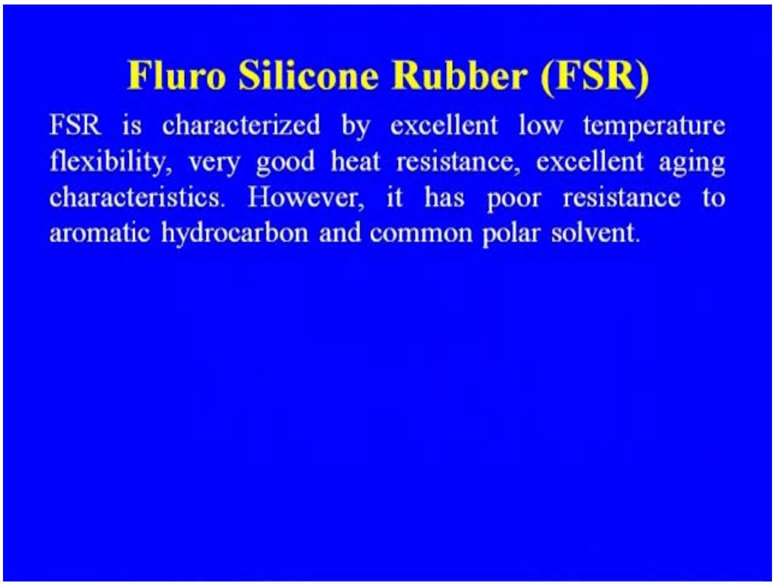

So, this the, so for the silicon rubber is concerned this is used in aerospace appliances electric industry construction industry auto mobile, automotive industry, gaskets, lining spark, plug boots, hose rubber rolls, silicon rubber. This another specialized rubber is characterized by its excellent. Low temperature flexibility very good heat resistance excellent aging characteristic. However, it has poor resistance to aromatic hydrocarbons and common polar solvent. So, this is the another class of the synthetic rubber polyurethane rubber, this is made by reacting.

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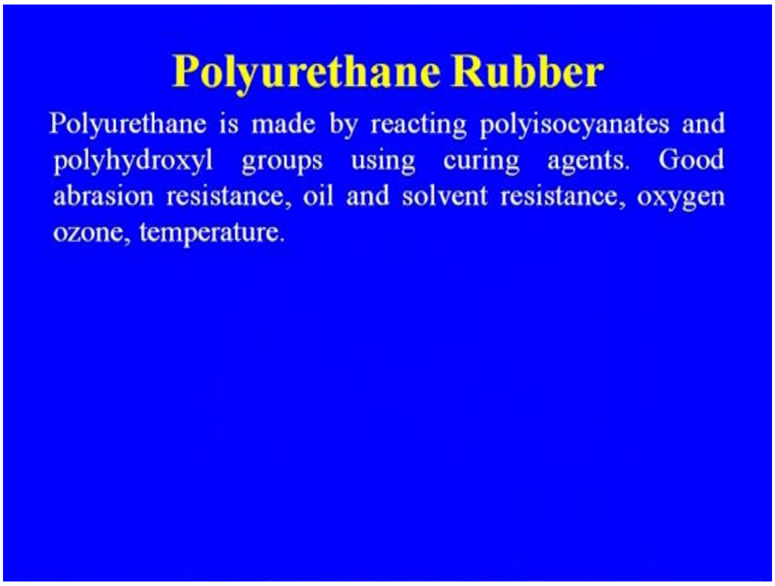

Polyisocyanates and polyhydroxyl group using curing agents, good abrasion resistance oil and solvent resistance oxygen ozone resistance and the temperature resistance. So, this is the actually the some of the characteristics of the polyurethane rubber.

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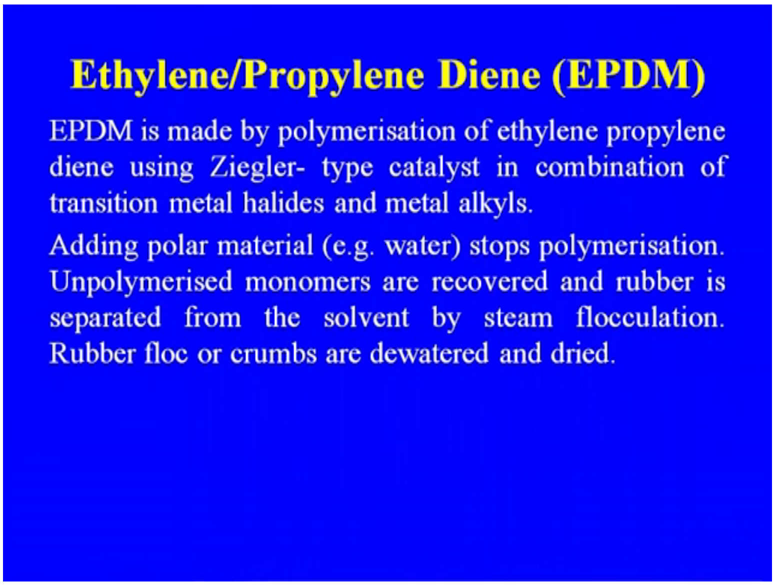

Another very important class of the your specialized elastomer is the ethylene propylene. This is made by the ethylene propylene rubber that is, it is made by polymerization of ethylene propylene diene using Ziegler type the catalyst in combination of the transition metal halides and the metal alkyl. Adding polar material water stops the polymerization.

Unpolymerised monomers are recovered and rubber is separated from the solvent by steam rubber flocs or because it is the flocculation that we are carrying the rubber flocs or crumbs are dewatered and dried. So, this is about the ethylene E P D M is has outstanding resistance to heat ozone oxidation weathering and aging due to the saturated backbone. Low brittle point glass transition temperature low density except the aliphatic.

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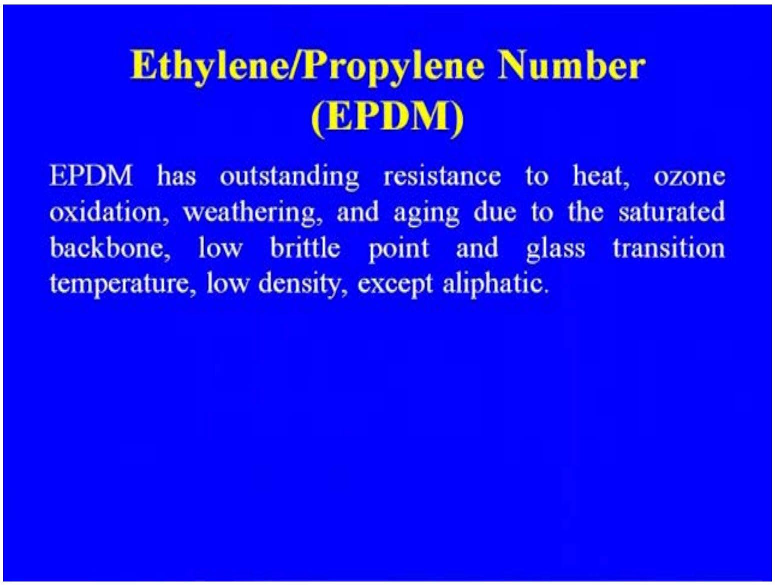

Another class of the synthetic rubber is the hypalon are the chlorosulphonated polyethylene and are made by free radical catalysed reaction of the chlorinated S O 2 with polyethylene.

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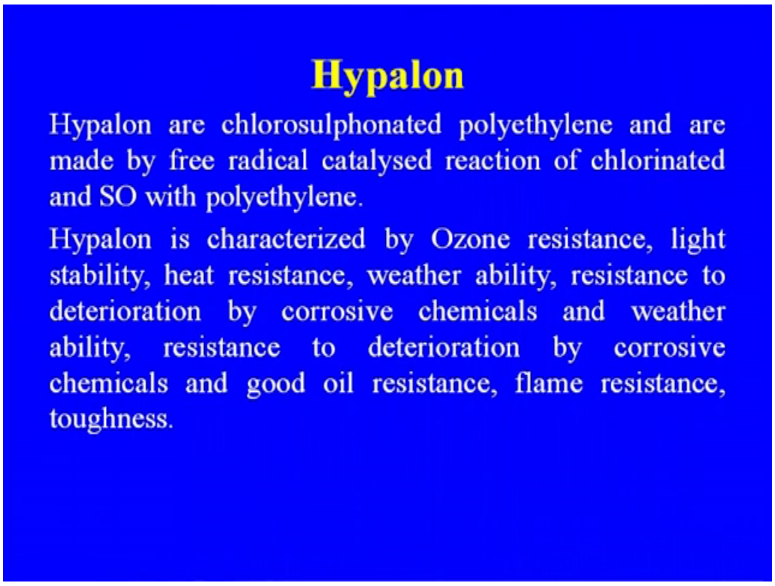

So, hypalon is characterized by ozone resistance, light stability, heat resistance, weather ability, resistance to deterioration by corrosive chemicals weather ability resistance to the deterioration of the corrosive chemicals and good oil resistance, flame resistance and the toughness. So, these are the some of the important characteristics of the hypalon. These are the some of the in case of the hypalon automotive car liner coatings spark plug, boots primary and ignition wire tarpaulins.

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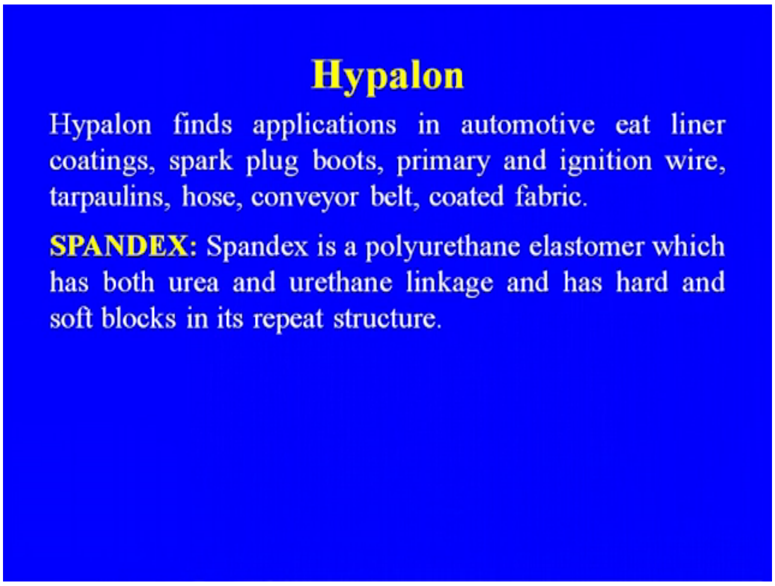

We called for the lining that sometimes. We are using earlier, it was very common use of the tarpaulins was there hose, conveyor, belt coated fabrics. Another class of the synthetic rubber that is spandex is a polyurethane elastomer which has both urea and urethane linkage and has hard and soft blocks in its repeat structure.

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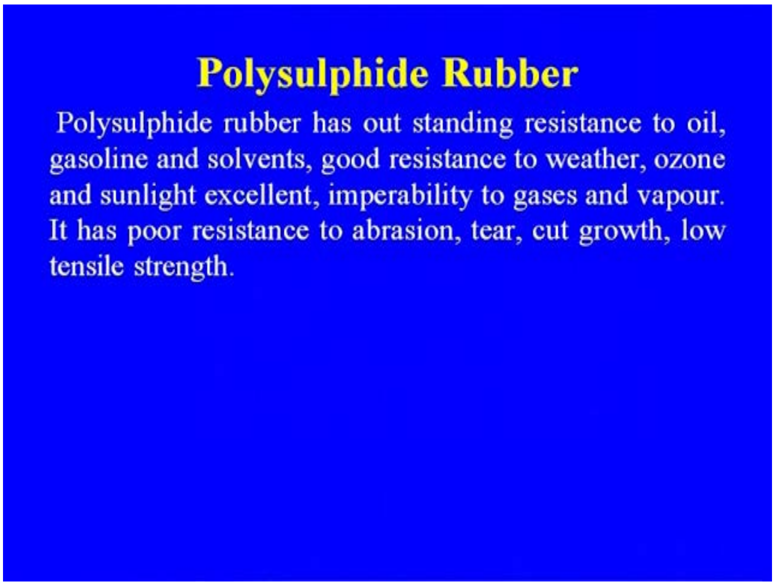

Polysulphide rubber, polysulphide rubber has outstanding resistance to oil, gasoline and solvent, good resistance to weather, ozone and sunlight excellent imperability to gases and vapor. It has poor resistance to abrasion tear cut growth and the low tensile strength. Ethylene vinyl acetate rubber E V A this is very commonly known as E V A has the excellent resistance to because this was the with the availability of the vinyl acetate.

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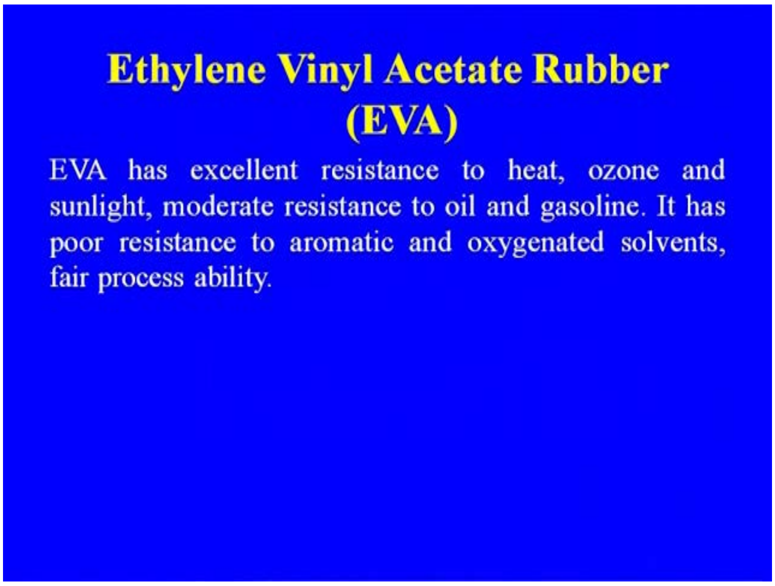

E V A has excellent resistance to heat, ozone and sunlight moderate resistance to oil and gasoline it has poor resistance to aromatic and oxygenated solvent fair process ability. So, these are the some of the advantages in the and the E VA that is the also one of the facility, so this was all about the elastomer the various type of the some of the elastomer. I could not discuss in detail, but in the next lecture will be now on the 2-3 lectures of this module that will be on the synthetic fiber industry where we will be discussing about the first page, about the caprolactam nylons, nylon 6 nylon 66.

Then, it will be on the terra ethylic acid purified terra ethylic, then polyester. Another lecture that will be on the acrylic fiber and the last lecture that will be on the viscous rayon, acetate rayon and the (( )). Because that is also one of the very importance sector of the synthetic fiber. So, introduction of the synthetic fiber raw material and other aspect that will be discussing in detail in the next lecture.