Lec 35: Rubber Industry – 2.

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is rubber industry part 2.

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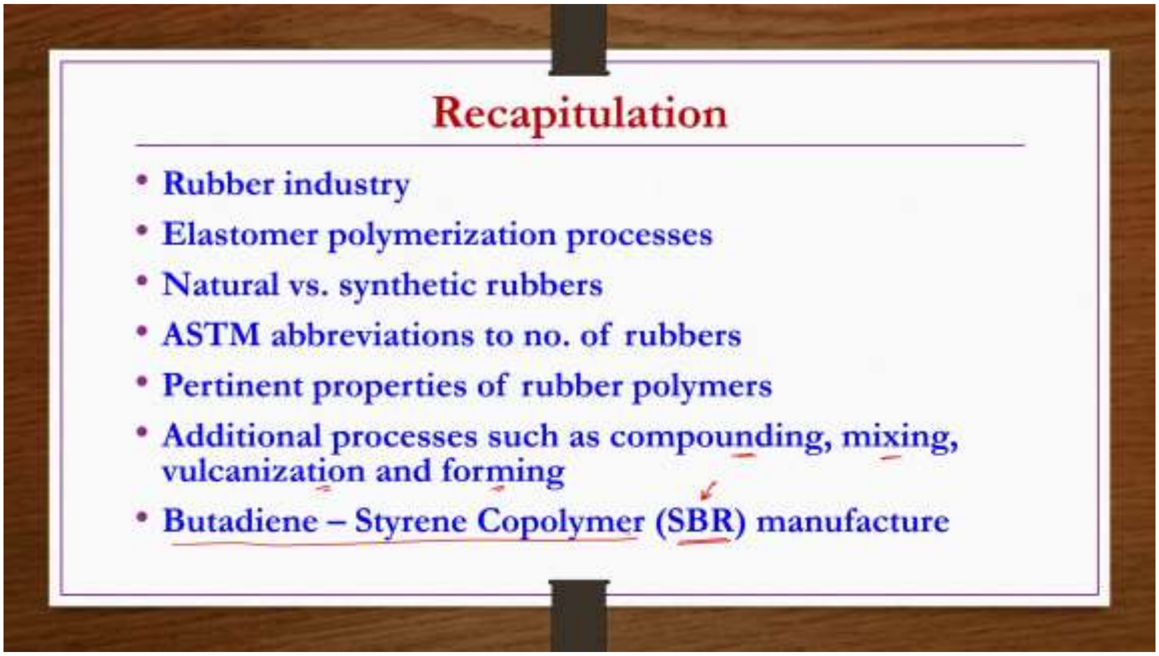

Recapitulation

- Rubber industry
- Elastomer polymerization processes
- Natural vs. synthetic rubbers
- ASTM abbreviations to no. of rubbers
- Pertinent properties of rubber polymers
- Additional processes such as compounding, mixing, vulcanization and forming
- Butadiene – Styrene Copolymer (SBR) manufacture

First, we have a recapitulation of what we have discussed in the previous lecture of this particular chapter on rubber industry. We started discussions on basics of rubber industry where we started contrasting natural versus synthetic rubbers. Synthetic rubbers may be taken as elastomers which are produced by elastomer polymerization processes. Then importance of natural versus synthetic rubbers we have seen and then also production point of view also we have seen.

For example, in Indian conditions or for India most of the rubber needs are being fulfilled by the natural rubbers. In fact, up to 65 to 70 percent of Indian rubber needs are fulfilled by the natural rubbers whereas for the USA it is opposite only 30 percent of their rubber requirements are fulfilled by the natural rubbers whereas the remaining are fulfilled by the synthetic rubber especially after the development of SBR that is butadiene styrene copolymer. Such basics also we have seen from the applications point of view as well as the importance point of view. Then we have discussed ASTM abbreviations provided to different types of rubbers.

Pertinent properties of rubber polymers we have seen rather pertinent properties you know quantitatively discussing we have given a list of properties which one should go through before making a finalization about the applications of a given type of rubber that has been produced or otherwise before producing a rubber what are the properties you need to concentrate in the final product that you can take as a checklist and then appropriately you can decide on the monomers and then polymerization conditions and all that. So, there we have given the list only we did not give the quantitative values of the properties because one rubber to the other rubber is going to be very different. Then additional processes such as compounding while making the final product mixing and vulcanization and final forming of the final product that is obtained by the rubber polymers have also been discussed in the previous lecture. And then we concluded our previous lecture on rubber industry by discussing the manufacturing of SBR that is butadiene styrene copolymer. Now in this lecture we will be discussing about polymeric oils and rubbers based on silicones.

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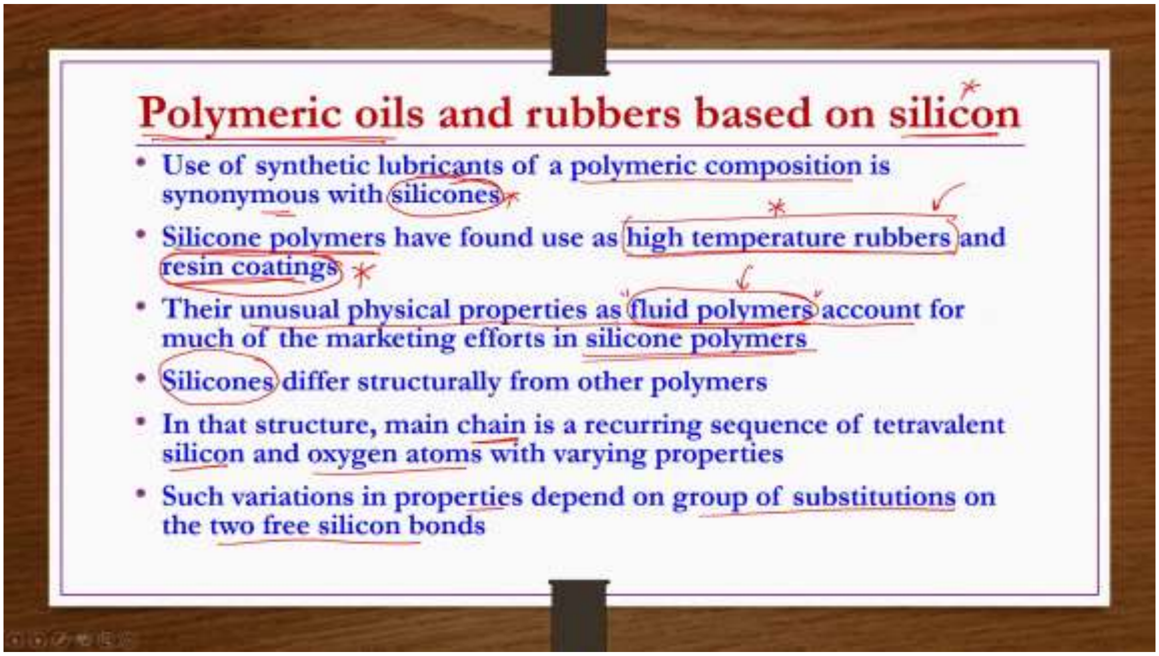

Polymeric oils and rubbers based on silicon

- Use of synthetic lubricants of a polymeric composition is synonymous with silicones
- Silicone polymers have found use as high temperature rubbers and resin coatings
- Their unusual physical properties as fluid polymers account for much of the marketing efforts in silicone polymers
- Silicones differ structurally from other polymers
- In that structure, main chain is a recurring sequence of tetravalent silicon and oxygen atoms with varying properties
- Such variations in properties depend on group of substitutions on the two free silicon bonds

What do you mean by polymeric oils? These are nothing but synthetic lubricants of a polymeric composition. However, the other synonym for such kind of polymeric oils or synthetic lubricants is silicones. These are also known as the silicones. So that is use of synthetic lubricants of a polymeric composition is synonymous with silicones. So, these polymeric oils are nothing but in general we can call them as a synthetic lubricants they are having polymeric compositions and then most of these lubricants are based on the silica.

Silicon polymers have found use as high temperature rubbers and resin coatings in general. So, these silicon polymers are usually in liquid conditions they are considered as fluid polymers. Their unusual physical properties as fluid polymers account for much of the marketing efforts in silicon polymers. So, they are having a lot of applications in high temperature rubbers because these are very stable with respect to the temperature highly stable with respect to temperature. That is the reason the silicon polymers or polymeric oils based on the silicon you know they are very stable with respect to the temperature that is the reason they are used as high temperature rubbers and then resin coatings wherever the applied temperature may be sufficiently high enough.

So, because of these unusual properties as fluid polymers you know much of the marketing efforts in silicon polymers have been diverted towards production of such kind of fluid polymers. Silicones differ structurally from other polymers as well. Now you realize almost by now that is silicones is synonyms to synthetic lubricants of polymeric composition and then those polymers are based on the silicon component. So most of the previous polymers whatever we have discussed in the polymer industry as well as the previous lecture of rubber industry they are based on the carbon. Whereas these polymers you know these are based on the silicon and they are synthetic lubricants having polymeric composition.

So, these silicones differ structurally from other polymers as well. How that we are going to see by structures anyway in that structure main chain is a recurring sequence of tetravalent silicon and in oxygen atoms with varying properties. So, whatever the free silicones that are available how they are being connected to the other monomers or the other similar monomer if not the different one accordingly the properties of the final material is going to change. Such variations in the properties depend on group of substitutions on two free silicon bonds.

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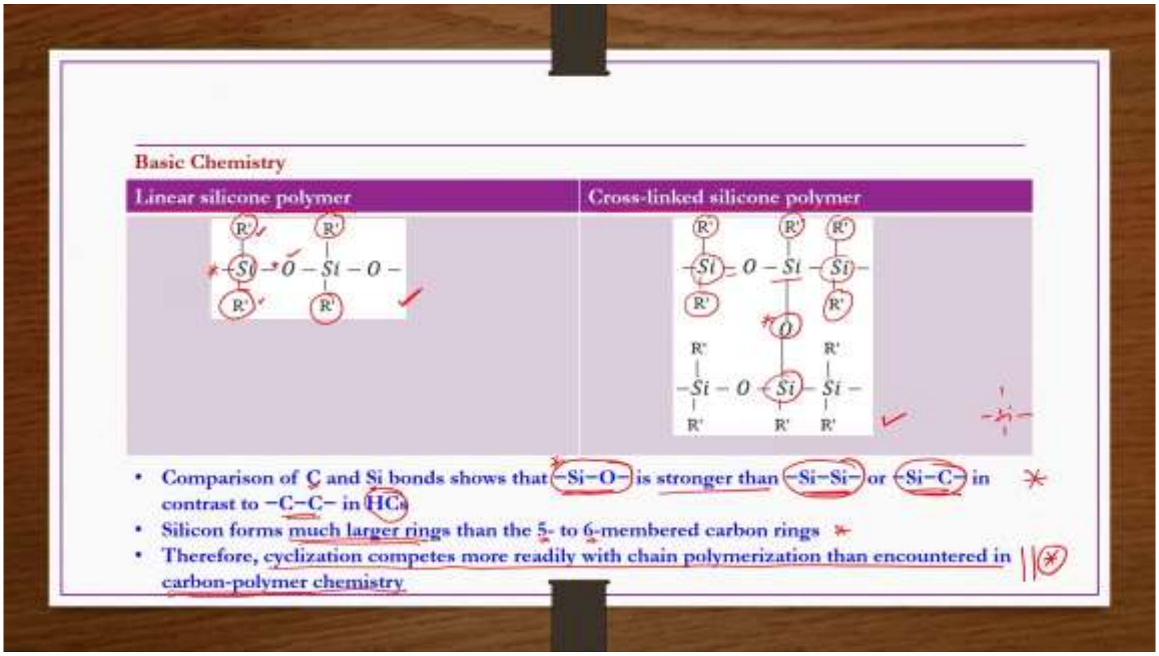

Basic Chemistry

Linear silicone polymer	Cross-linked silicone polymer

- Comparison of C and Si bonds shows that $-Si-O-$ is stronger than $-Si-Si-$ or $-Si-C-$ in contrast to $-C-C-$ in HCs
- Silicon forms much larger rings than the 5- to 6-membered carbon rings
- Therefore, cyclization competes more readily with chain polymerization than encountered in carbon-polymer chemistry

So, the same thing we see by structure wise also if you see the basic chemistry of this material if you produce this linear silicon polymers or linear silicones here this Si actually you know connected with some kind of alkyl or aryl groups in general like this.

So, Si is also having 4 bonds so these bonds now they are you know occupied by the alkyl groups aryl groups along with the oxygen atoms. So, these 2 bonds of each Si atom are free how are they going to be connected with the oxygen atom or other substitutions based on that one the properties are going to vary. So, if you have this linear silicones then this is the structure that you get but if you try to produce cross linked silicon polymer or cross linked silicones then the same structure this Si connected with R prime R prime and then O so that is connected with other Si R prime and then O. So, this now this Si is connected to another Si R prime and then R prime. So now this in between that O is whatever is there how it is connected to the other one other monomer based on that one you can get either branched or fully cross-linked silicon.

So now here this O is connected to the Si and then like this you can have a cross linked silicon polymer. So, this is the important thing actually you know tetravalent silicon out of which you know 2 bonds are usually occupied by the oxygen and then alkyl or aryl group. So, the remaining one how are being substituted with the other monomers or other functional so accordingly the structure would be developed. So theoretically that is what pictorially that you understand but doing experimentally you know one has to be very sure about the temperature, pressure and then time of the operations to get the desired properties in the final silicones. The comparison of carbon and silicon bonds have been found or shows that silicon oxygen bond is much stronger than silicon-silicon or silicon-carbon bonds in contrast to C-C bonds in hydrocarbons.

In hydrocarbons whatever C-C bonds are there in contrast to that one if you come make a comparison Si-O bonds are much stronger than Si-Si bonds or Si-C bonds. So, this information how it is going to be useful if you wanted to make a particular bond breaking and then add other substitutions so then this information is going to be very useful. Accordingly, you can target certain bonds which can be cleaved easily and then do the required substitutions. Silicon forms much larger rings than 5 to 6 membered carbon rings. So much larger rings are formed by the silicones.

Therefore, cyclization competes more readily with chain polymerization than encountered in carbon polymer chemistry. So, we are going to see the chemistry also subsequently in the subsequent slides. You know where whatever the intermediates that are produced in a monomer intermediates are produced they are highly active. They are highly active that they immediately undergo polymerization to form silicones. Whereas that is not that much easy such kind of polymerization is not that much easy in the case of carbon polymer formations or polymers based on the carbon whatever we have seen that is not that much easy in case of carbon polymers.

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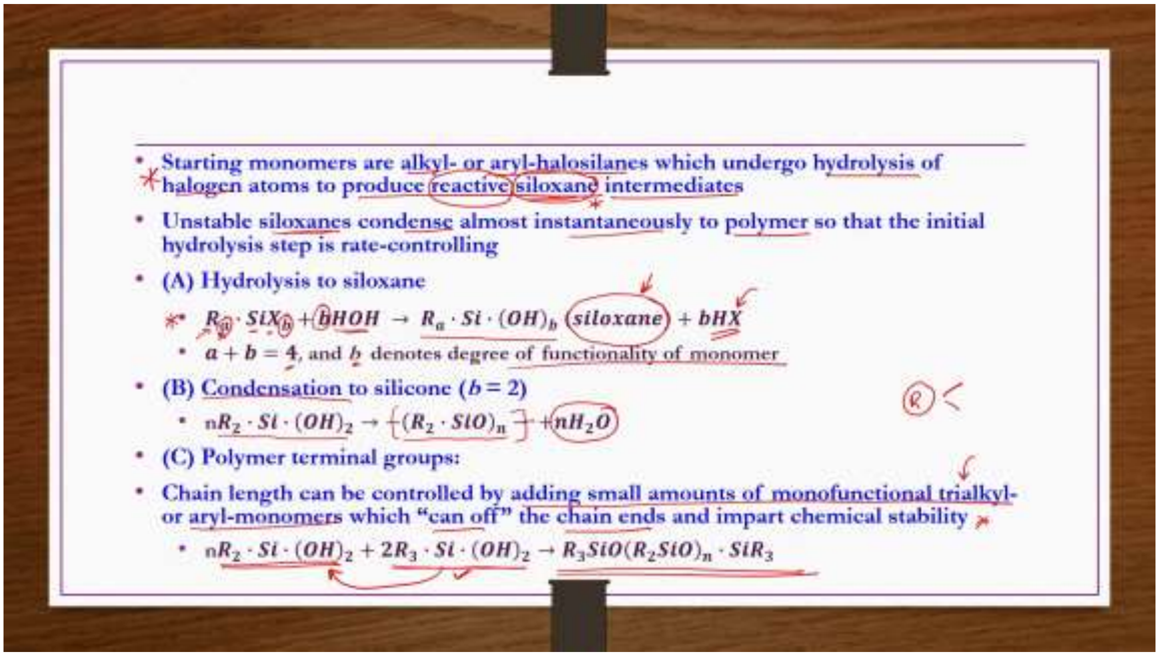

- Starting monomers are alkyl- or aryl-halosilanes which undergo hydrolysis of halogen atoms to produce reactive siloxane intermediates
- Unstable siloxanes condense almost instantaneously to polymer so that the initial hydrolysis step is rate-controlling
- (A) Hydrolysis to siloxane
  - $R_a \cdot SiX_b + bHOH \rightarrow R_a \cdot Si \cdot (OH)_b$ (siloxane) $+ bHX$
  - $a + b = 4$, and b denotes degree of functionality of monomer
- (B) Condensation to silicone ($b = 2$)
  - $nR_2 \cdot Si \cdot (OH)_2 \rightarrow (R_2 \cdot SiO)_n + nH_2O$
- (C) Polymer terminal groups:
- Chain length can be controlled by adding small amounts of monofunctional trialkyl- or aryl-monomers which "can off" the chain ends and impart chemical stability
  - $nR_2 \cdot Si \cdot (OH)_2 + 2R_3 \cdot Si \cdot (OH)_2 \rightarrow R_3SiO(R_2SiO)_n \cdot SiR_3$

Starting monomers are usually alkyl or aryl halosilanes which undergo hydrolysis of halogen atoms to produce reactive siloxane intermediates. These siloxane intermediates are very reactive highly reactive. So, what happens immediately they undergo you know polymerization. So, whatever the intermediate siloxanes are formed they are very active very highly active. So immediately they undergo polymerization and then they form silicones.

They form silicones. So, we are going to see with the reactions also but when we discuss polymerization or other types of rubbers without silicon where the carbon is the main material or main atom to undergoing the polymerization. So, carbon-based polymerization does not take place so much easily whereas silicon-based polymerization takes place easily immediately because the intermediate monomers are very very reactive. Unstable siloxanes condense almost instantaneously to polymer that is they will undergo condensation polymer immediately to produce polymer. So that initial hydrolysis step whatever is there this first step where hydrolysis is taking place to produce siloxane that is the rate controlling step because that is you know slow process whereas the production of silicones from the unstable siloxanes is instantaneous. So that cannot be rate controlling step.

So, first step is hydrolysis to siloxane so that reaction we see generalized reactions we are going to see this R can be alkyl or aryl group or a stands for some kind of number and then Si silicon X stands for halogens b some kind of number that is like functionality it gives about the functionality if it is 2 it is a bi-functional plus bHOH that is hydrolysis it is undergoing. So, then what you get you get R_a·Si· $(OH)_b$ which is nothing but siloxane intermediate and then which is unstable highly reactive which undergoes polymerization immediately and then it also releases HX let us say X is Cl then HCl you will be getting here. Now the a and b also there is a relation the functionality the a and then b whatever are there so there is a relation the summation of these 2 is 4 the reaction this reaction is a generalized one. So, in the generalized reaction we have a and b like this so but wherever you take if a is 1 then b has to be 3 if b is 2 then a should also be 2 like that. So, a plus b is equals to 4 and then b denotes the degree of functionality of the monomer whether it is mono functional or bi-functional or tri-functional as we have seen in the polymers industry chapter.

Let us say if b is 2 then a is also 2 then what it would be $R_2 \cdot Si \cdot (OH)_2$ siloxane that should be undergoing condensation reaction immediately that is n moles of $R_2 \cdot Si \cdot (OH)_2$ undergoing polymerization to give $(R_2 \cdot Si \cdot O)_n$ polymer this is silicon actually. So, and then also releasing n moles of H_2O because it is a condensation reaction condensation polymer is taking place immediately. So, but now you have to have a provision to stop the reaction also how to stop? So, there are different provisions are possible one of the important provision is that chain length can be controlled by adding small amounts of mono functional tri-alkyl or aryl monomers which can off the chain ends and impart chemical stability by adding such kind of monomers also you can do you can stop the polymer continuation reaction. It has to be stopped somewhere as per the requirement. So, if you add mono functional tri-alkyl or tri-aryl monomer so this is what this one this is that particular component.

Now this is being added to the siloxane so this is the generalized representation of the siloxane. So, to this siloxane you add this monomer so then reaction would stop and then you will get this particular structure. So here R whatever is there that can be alkyl or aryl group.

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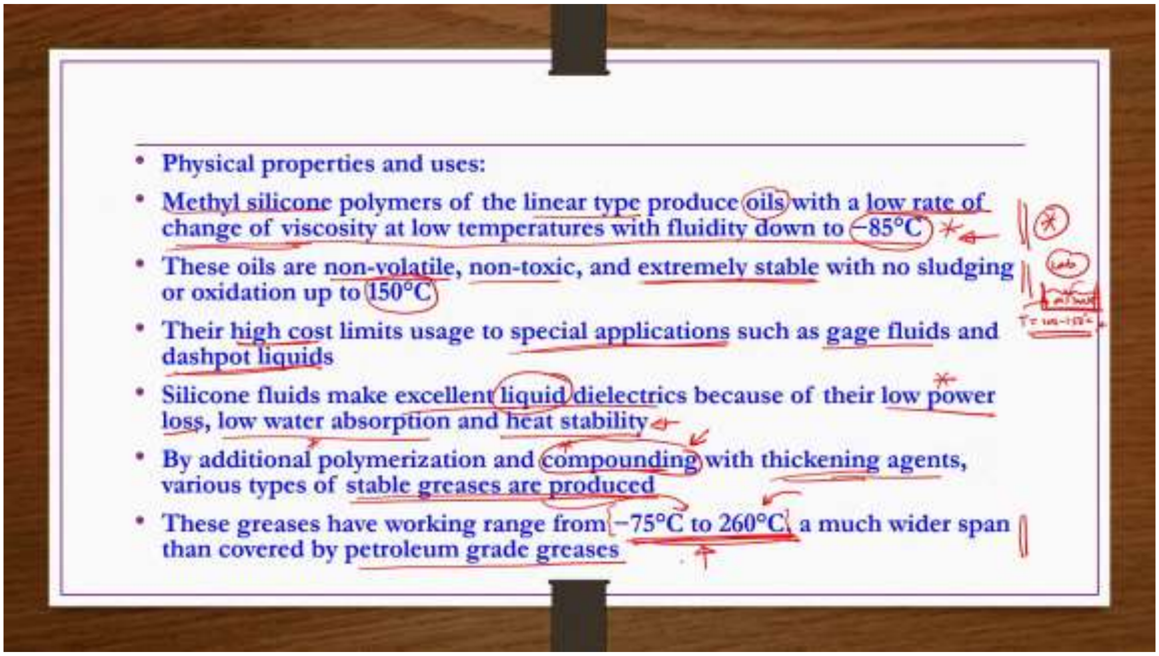

- Physical properties and uses:
- Methyl silicone polymers of the linear type produce oils with a low rate of change of viscosity at low temperatures with fluidity down to −85°C
- These oils are non-volatile, non-toxic, and extremely stable with no sludging or oxidation up to 150°C
- Their high cost limits usage to special applications such as gage fluids and dashpot liquids
- Silicone fluids make excellent liquid dielectrics because of their low power loss, low water absorption and heat stability
- By additional polymerization and compounding with thickening agents, various types of stable greases are produced
- These greases have working range from −75°C to 260°C, a much wider span than covered by petroleum grade greases

Physical properties and uses of silicones if you see methyl silicon polymers of the linear type produce oils with a low rate of change of viscosity at low temperatures with fluidity down to minus 85 degrees centigrade. You can see even at minus 85 degrees centigrade it is having low rate of change of viscosity there is no much change in the viscosity almost negligible change in the viscosity whatever is there at the room temperature.

So almost that much viscosity is there it is not changing much even if you change the temperature of the storing or flowing conditions of the temperature if you change it to minus 85 degrees centigrade. So, such are the stable silicon oils that is the reason and they have very good market. So, we talk about only methyl silicon about this specific example but almost it is true that is thermostability is very high for almost all silicon polymers. These oils are in general non-volatile obviously if they are so much stable with respect to temperature that means they are non-volatile in addition to that one they are also non-toxic and an extremely stable with no sludging or oxidation even up to 150 degrees centigrade. So, because of such reasons most of the laboratory experiments especially where you need to conduct the reaction at 100 to 150 degrees centigrade.

So, what you use, you use the oil baths in general use and then you heat this oil bath to certain temperature whatever 100 to 150 degrees centigrade temperature you wanted to do and then in this oil bath you keep your beaker or conical flux in which you are doing the reaction. The reason is that even at this such high temperature the sludging of silicon oils does not takes place or oxidation of silicon oils does not takes place it is stable. It is not going to be lost it is non-volatile. So, because of that reason in most of the chemical engineering laboratories or chemistry laboratories wherever these kind of heating requirements are there silicon oil baths are used. However, there is a disadvantage with this one that is the high cost because of this high cost the application of silicon oils to special applications only it is restricted.

So, their high cost limits uses to special applications such as gauge fluids and dash pot liquids as for such kind of important applications only these are used because they are highly costly that is the one disadvantage. Silicon fluids make excellent liquid dielectric because of their low power loss, low water absorption and then heat stability as already mentioned because of these 3 important characteristics that is low power loss, low water absorption and then high heat stability. The silicon oils or silicon fluids are used as a liquid dielectrics in general. By additional polymerization and compounding with thickening agents various types of stable greases are also produced. So many greases are also produced from the silicon oils but however you have to add appropriate compounding fillers, activators, plasticizers, etc. these are the compounding agents. So, they should be added so that to make the silicon oils thick enough and then once they become thicker they can be used as stable greases. Whereas these greases have high working range see minus 75 to 260 degrees centigrade they are stable these greases whatever that you produce. So, because of such high thermal stability these greases are often used. Now this temperature range is much wider compared to the greases that are produced from the petroleum grid. So that means indirectly compared to the petroleum grid greases obtained by the thickening of silicon fluids or silicon oils are better ones because they are stable to a very wider range of temperatures minus 75 to plus 260 degrees centigrade.

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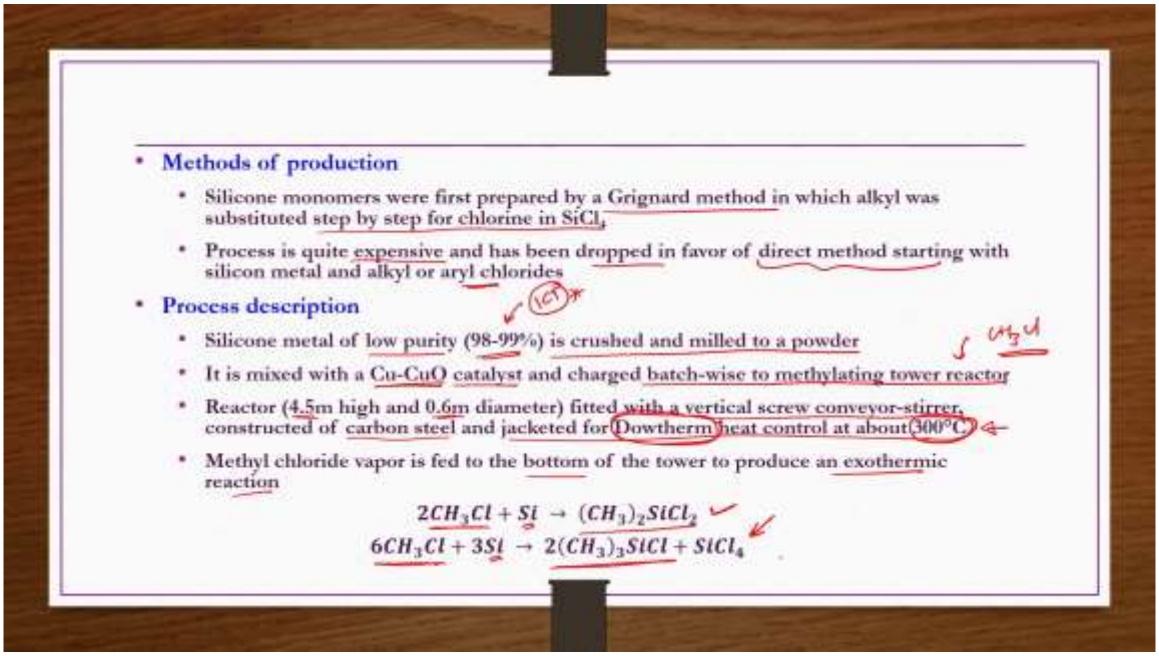

- **Methods of production**
  - Silicone monomers were first prepared by a Grignard method in which alkyl was substituted step by step for chlorine in $SiCl_4$
  - Process is quite expensive and has been dropped in favor of direct method starting with silicon metal and alkyl or aryl chlorides
- **Process description**
  - Silicone metal of low purity (98-99%) is crushed and milled to a powder
  - It is mixed with a Cu-CuO catalyst and charged batch-wise to methylating tower reactor
  - Reactor (4.5m high and 0.6m diameter) fitted with a vertical screw conveyor-stirrer, constructed of carbon steel and jacketed for Dowtherm heat control at about 300°C
  - Methyl chloride vapor is fed to the bottom of the tower to produce an exothermic reaction

$$2CH_3Cl + Si \rightarrow (CH_3)_2SiCl_2$$

$$6CH_3Cl + 3Si \rightarrow 2(CH_3)_3SiCl + SiCl_4$$

Now coming to the methods of production the conventional process was silicon monomers were first prepared by a Grignard method in which alkyl was substituted step by step for chlorine in $SiCl_4$ that is you have a $SiCl_4$ like this. Now you react with some kind of alkyls so that this one of this Cl is being replaced by let us say for example alkyl or CH_3 this is done at once. Now to replace the other one say the next again alkylation reaction you have to do to replace the other Cl with the second CH_3 group. So, like that stepwise reaction is taking place and then because of the stepwise reaction the cost of production of silicon monomers increases because of such reasons this kind of method is not used nowadays. Because of such kind of stepwise reaction this process is quite expensive and has been dropped in favor of direct method starting with silicon metal and alkyl or aryl chlorides that is what we are going to discuss by flowchart as well.

So, process description silicon metal of low purity having 98 to 99 percent see in the case of silicon you can produce up to 99.99 percent purity as well that we have seen in the our previous course inorganic chemical technology. So, but you know if you have 98 percent silicon metal then also it is considered as a low purity. So, low purity silicon metal like 98 to 99 percent purity is crushed and milled to a powder. This powder is then mixed with Cu copper, copper oxide catalyst and charged batch wise to methylating tower reactor to this methylating tower reactor you are supplying methyl chloride actually.

So, that methylation of silicon metal takes place and then you get the monomers okay those monomers you purify and then do the polymerization to get the silicon oils that is the you know in the nutshell the process to get the silicon oils but we see all the details with flowchart as well. Usually this methylating tower reactors are 4.5 meters high and 0.6 meters diameter fitted with a vertical screw conveyor stirrer constructed of carbon steel and jacketed for dowtherm heat control at about 300 degrees centigrade. So, you wanted to control the temperature at around 300 degrees centigrade within the methylating tower reactor.

So, the reactor is provided with the jackets for dowtherm heat control as well. So, dowtherm are you know some kind of heat transfer fluids when you circulate them. So, the temperature would be controlled. Methyl chloride vapor is fed to the bottom of the tower to produce an exothermic reaction that reaction is like methyl chloride 2 moles of methyl chloride is reacting with the silicon to give dimethyl chloro or dimethyl dichlorosilane okay. Otherwise 6 moles of methyl chloride reacting with silicon to give trimethyl chlorosilane okay plus this silicon tetrachloride is also formed okay.

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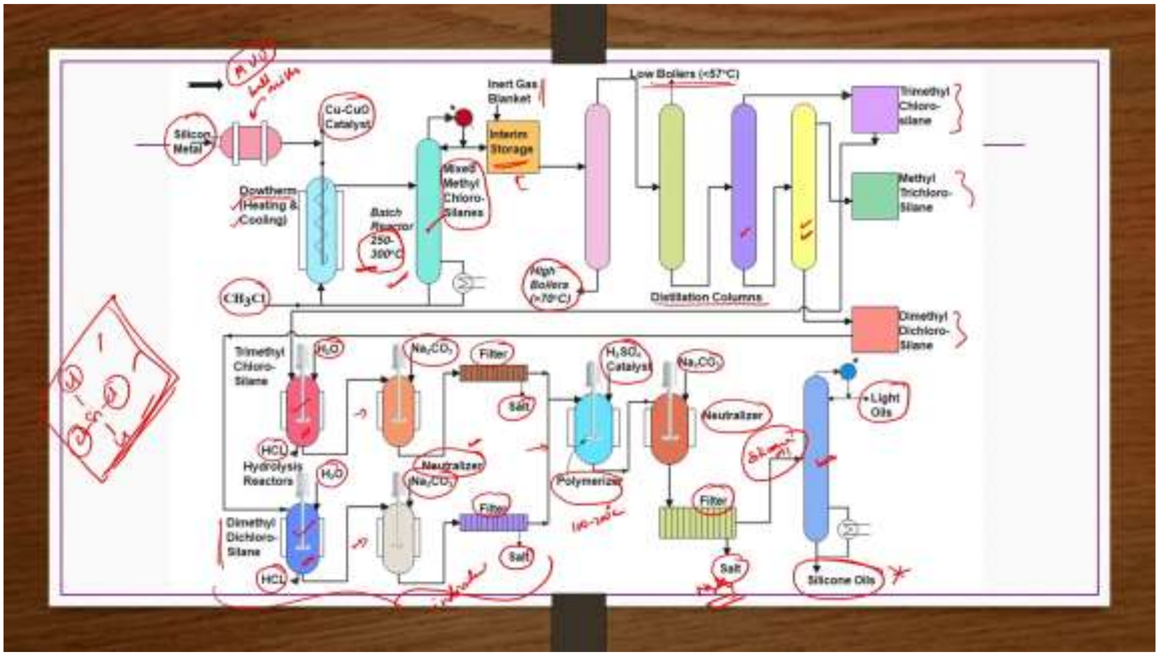

Now flowchart we see here same process the remaining description of the process we discuss after discussing the same through the flowchart okay. So, here what we are doing the silicon metals or whatever are there we are taking to some kind of ball mills which you might have studied in mechanical unit operations course otherwise this course is also available online in the MOOCs course that I have done under the title of mechanical unit operations. So, here you can crush the silicon metal to the desired size of the smaller size and then you mix them with the copper and copper oxide catalyst and then take it to the methylating tower this is the reactor which is known as the methylating tower reactor right. So, this reactor is approximately operating at 250 to 300 degrees centigrade right. So, now to this reactor there is a jacket is also provided because this reaction is exothermic reaction right.

So, through this jacket you can send the dowtherm heat transfer fluid both for purpose it is done for the cooling as well as for the heating is okay. So, when this metal along with the catalyst interacts with the methyl chloride vapor that is coming from the bottom. So, then what you get you get mixed methyl chlorosilanes you get okay. So, those mixed methyl chlorosilanes along with the unreacted silicon or you know metal chloride etc. maybe there of course that you can take to a fractionating column right.

So, where you know you can remove the impurities, vent gases, etc. and then almost like pure mixed metal chlorosilanes you can take to the storage with inert gas blanket as well right. Now then what you do this mixture of methyl chlorosilanes mixture in the sense whatever this Si Cl Cl like these 4 bonds are there some of them are you know chloro and then some of them are alkyl or aryl right. So, now here it is methyl actually. So, if it is like you know 2 or chloro so then it is dimethyl dichlorosilane if it is 3 methyl and 1 chloro then trimethyl chlorosilane if it is 1 methyl and then 3 chloro then it is methyl trichlorosilane.

So, in all 3 are there so that mixture is there. So, all of them would be forming in fact you cannot control the reaction conditions contact time exactly in the industry as per the theory so that you can produce only desired product you will also getting the other products also and then this is we have already seen this replacement of Cl with the methyl groups or any other alkyl groups is a series reaction step by step series reaction. So, all of them would be forming. So, that mixture of methyl chlorosilanes would be taken to series of distillation columns. In the first distillation column from the bottom high boiling components which are having boiling points more than 70 degrees centigrade are taken as the residues whereas the low boiling components having you know less than 70 degrees centigrade are taken to you know second distillation column where you know low boiling components which are having less than 57 degrees centigrades of boiling point are taken as the top product and then remaining mixture is taken to the subsequent distillation column. From the third column you get the tri methyl chlorosilane as the top product from the bottom what you have you have the dimethyl dichloro as well as the methyl trichlorosilane mixture that you take to the fourth column.

So, from the top of the fourth column you get a methyl trichlorosilane whereas from the bottom you get dimethyl dichlorosilane. So, now until now what you have done you have done you prepared only monomers that is tri methyl chlorosilane and then dimethyl dichlorosilane monomers you prepared of course you also got methyl trichlorosilane which is not required for the polymerization. So, these tri methyl chlorosilane and dimethyl dichlorosilanes are taken to hydrolysis reactors this is one hydrolysis reactor this is another hydrolysis reactor separately these are taken to hydrolysis reactor where they are interacting with the water. So, that hydrolysis takes place and then you get the HCl from the bottom of the both reactors individually they have been done. Let us say hydrolysis of dimethyl dichlorosilane is done in the bottom reactor bottom hydrolysis reactor whereas the hydrolysis of tri methyl chlorosilane has been done in the top hydrolysis reactor.

So, from both the reactors HCl you get it as a bottom product after removing that HCl the material whatever is there you know obviously HCl you are separating out that means in the monomer there would also be some HCl present. So, neutralization is done so the products of these hydrolysis reactors are individually or separately neutralized into neutralizers where Na_2CO_3 is being added from the top to contact with the monomers so that they would be neutralized if at all any traces of HCl were present along with them. So, after neutralization with Na_2CO_3 in both of these neutralizers individually their mixtures are taken to the filters where if at all some solid salts are there they would be separated out and then neutralized monomers are taken to polymerization reactor which is a continuous stir tank reactor to which H_2SO_4 catalyst is supplied from the top. So, that depolymerization takes place here the temperature of polymerization is usually 100 to 200 degrees centigrade and then 3 to 4 atmospheric gauge pressure. So, after the polymerization the mixture is taken to another neutralizer where again Na_2CO_3 is supplied.

So, until this step whatever purification and the neutralization filtering were there individual so that you get the pure monomers those pure monomers are mixed in a polymerization reactor and then polymerization is taken place after that neutralization is only single there is nothing like a individual one. So, here also neutralization is done with Na_2CO_3 to separate out if at all any traces of H_2SO_4 were there along with the silicon oils. So, those H_2SO_4 traces would be separated out when they interact with Na_2CO_3 in the form of Na_2SO_4 salts that is done in filtration in the filtration Na_2SO_4 salts are separated and then silicon oil silicon liquids whatever are there or polymers are there they will be taken to a final fractionating column to separate out if at all any light oils are there. Because this oil silicon oils since they are non-volatile and then highly stable with against temperature obviously they would be heavier products and in such heavier products are collected from the bottom as silicon oils.

So, this is the flow chart. So, in this flow chart we have seen all the details of the process about the description up to this part of you know methylating tower to get the mixed methyl chlorosilanes we have discussed remaining steps we are discussing now here in the text form.

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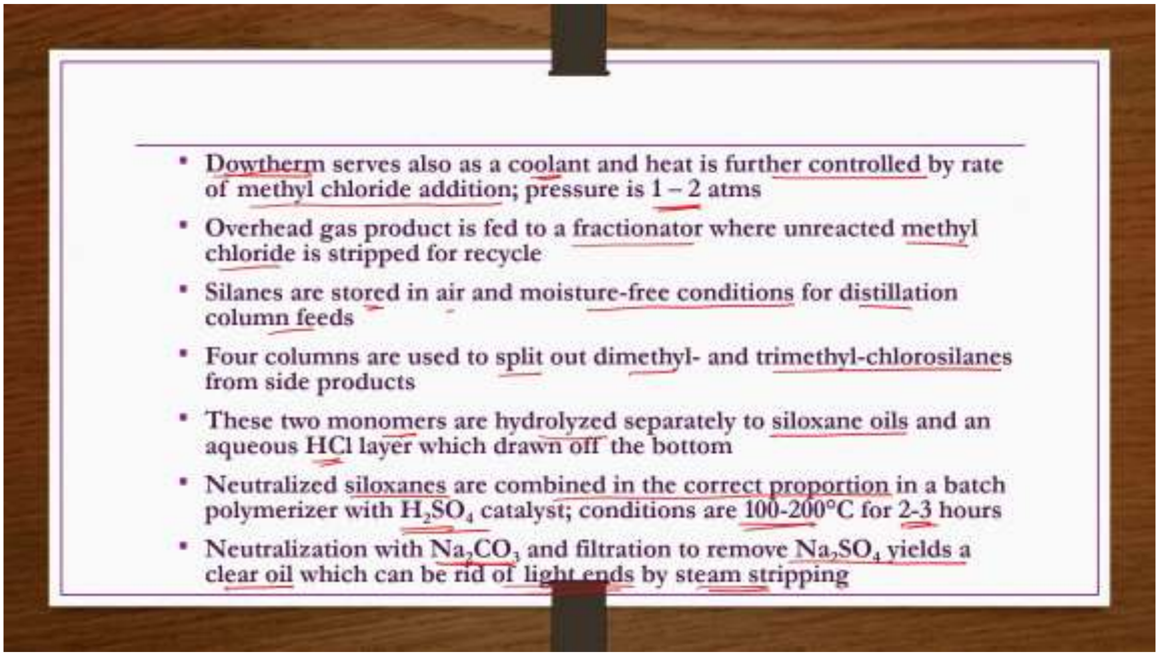

- Dowtherm serves also as a coolant and heat is further controlled by rate of methyl chloride addition; pressure is 1 – 2 atms
- Overhead gas product is fed to a fractionator where unreacted methyl chloride is stripped for recycle
- Silanes are stored in air and moisture-free conditions for distillation column feeds
- Four columns are used to split out dimethyl- and trimethyl-chlorosilanes from side products
- These two monomers are hydrolyzed separately to siloxane oils and an aqueous HCl layer which drawn off the bottom
- Neutralized siloxanes are combined in the correct proportion in a batch polymerizer with H_2SO_4 catalyst; conditions are 100-200°C for 2-3 hours
- Neutralization with Na_2CO_3 and filtration to remove Na_2SO_4 yields a clear oil which can be rid of light ends by steam stripping

Though the same thing we have discussed in the flow chart. The dowtherm also serves as a coolant not only for the heat transfer fluid it is also used as a coolant that is the good thing about such kind of fluids and heat is further controlled by rate of methyl chloride addition and then pressure is usually 1 to 2 atmosphere in the methylating tower reactor. Overhead gas product is fed to a fractionator where unreacted methyl chloride is stripped off for a recycle though it is not shown in the flow chart but that is in general followed. Then silanes are stored in air and moisture free conditions for distillation column feeds.

Four columns are used to split out dimethyl and trimethyl chlorosilanes from side products. These two monomers are hydrolyzed separately to siloxane oils and an aqueous HCl layer which drawn off the bottom. Neutralized siloxanes are combined in the correct proportions in a batch polymerizer with H_2SO_4 as the catalyst conditions temperature usually 100 to 200 degrees centigrade for 2 to 3 hours and then neutralization with Na_2CO_3 and filtration to remove Na_2SO_4 yields a clear oil which can be rid off light ends by steam stripping as we have seen in the flow chart.

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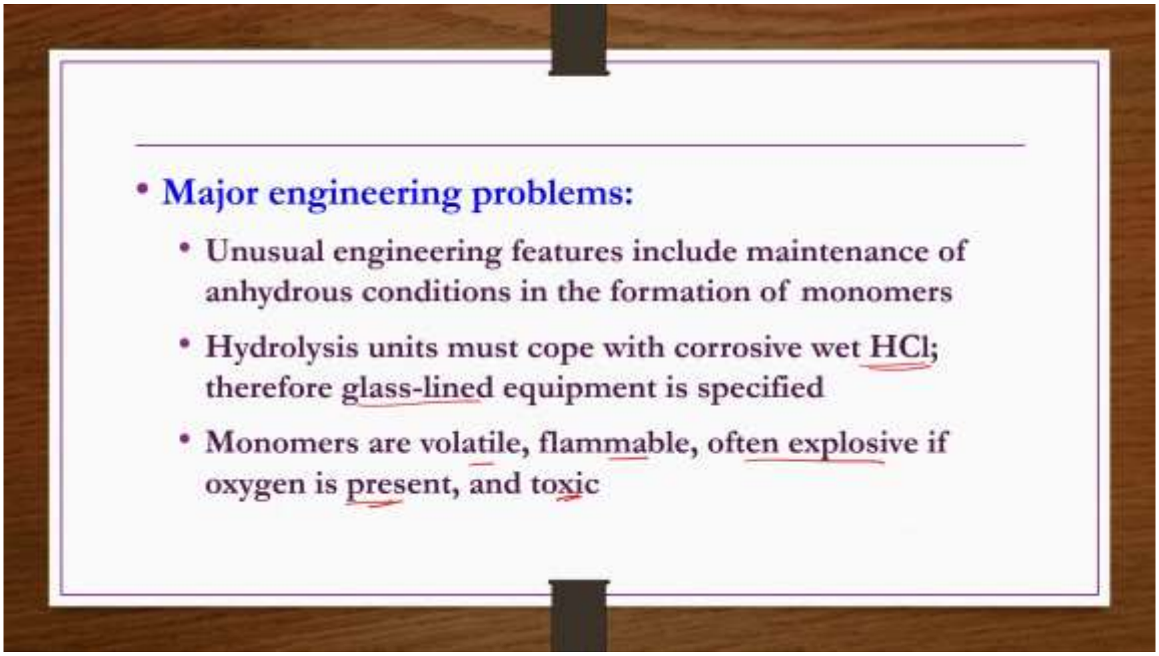

- **Major engineering problems:**
  - Unusual engineering features include maintenance of anhydrous conditions in the formation of monomers
  - Hydrolysis units must cope with corrosive wet HCl; therefore glass-lined equipment is specified
  - Monomers are volatile, flammable, often explosive if oxygen is present, and toxic

Major engineering problems of this process. Unusual engineering features include maintenance of anhydrous conditions in the formation of monomer that is one important thing.

Then hydrolysis units must cope with corrosive wet HCl because that is being produced and that has to be separated out. Therefore, glass lined equipment are used for this hydrolysis purpose. Monomers are volatile, flammable and often explosive if oxygen is present and toxic. So, you have to make sure that oxygen free atmosphere that is the reason you know these mixed methyl monomers or mixed methyl silanes are you know stored in the presence of inert gas blankets as shown in the flow chart. So that is all about silicones or silicon oil or silicon polymers production process.

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Indian rubber industry

- Indian rubber industry may be broadly divided into three categories
- Well-organized auto tire units:
  - Accounting for ≈ 50% elastomer consumption
- Medium scale units:
  - Accounting for another 25% of polymer consumption
- Small units and tiny sector:
  - Accounting for balance 25% consumption
  - Backbone of Indian rubber industry
  - Consisting of > 5000 manufacturing units spread all over country

So now before concluding the lecture we have a few basics about Indian rubber industry. Indian rubber industry may be broadly divided into 3 categories. First one is well organized auto tire units. Second one is medium scale units.

Third one is small units and tiny sector. Under the well-organized auto tire units mostly whatever elastomers are there 50% are being consumed for this well-organized auto tire units. Then 25% of elastomer is being consumed for medium scale units. Whereas the small units and tiny sectors accounting for balanced 25% consumption of elastomer polymers or rubbers. So however, though these units are small units and consuming only 25% they are the backbone of Indian rubber industry because there are about more than 5000 manufacturing units are there and they are spread all over the India.

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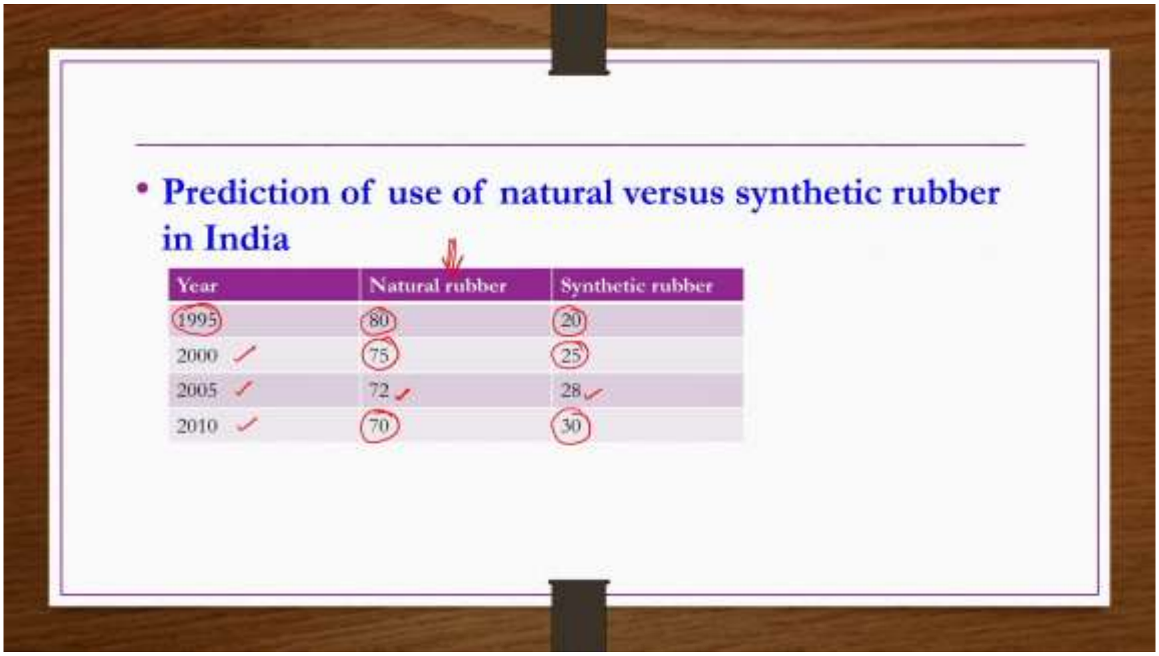

- **Prediction of use of natural versus synthetic rubber in India**

Year	Natural rubber	Synthetic rubber
1995	80	20
2000 ✓	75	25
2005 ✓	72 ✓	28 ✓
2010 ✓	70	30

Prediction of use of natural versus synthetic rubber in India if you see in 1995 whatever the rubber needs of India were there 80% of them were fulfilled by the natural rubbers whereas remaining 20% only by synthetic rubber.

By 2000 natural rubber contribution decreased to 75% whereas synthetic rubber contribution to fulfill the Indian rubber needs increased to 25%. 2005 these numbers changed to 72% and 28% respectively for natural rubber and synthetic rubber. And by 2010 almost 70% of Indian rubber needs were fulfilled by the natural rubbers whereas the 30% are being fulfilled by the synthetic rubbers. Even the recent years also these numbers have not changed much significantly that indicates that still for Indian rubber needs natural rubber is a primary source.

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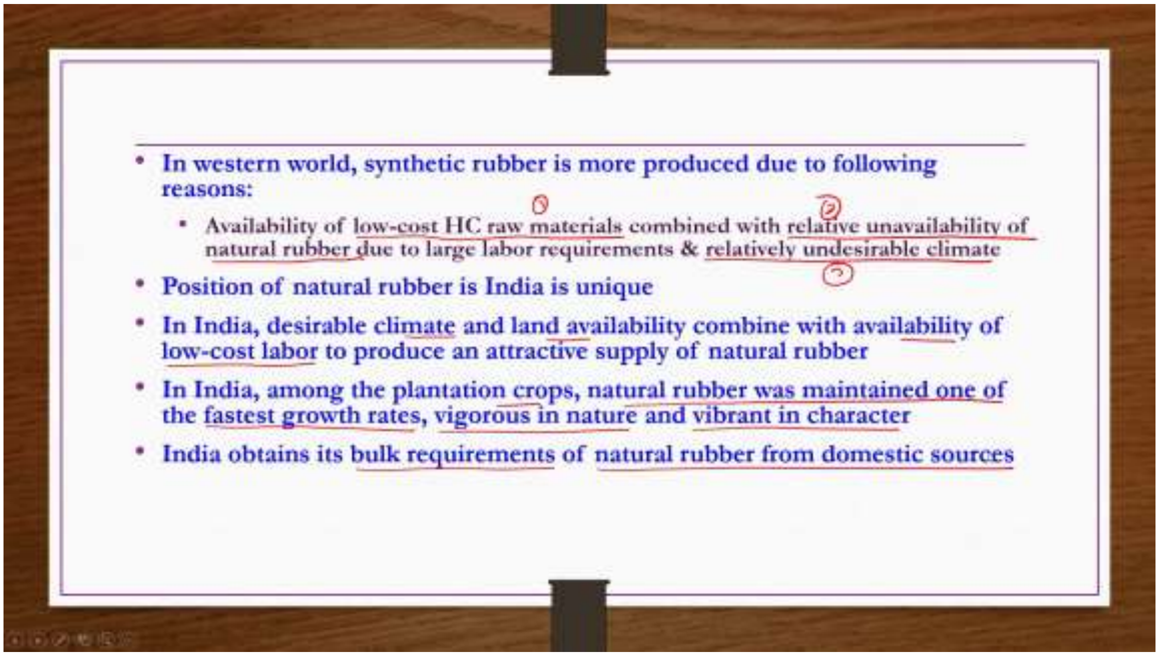

- In western world, synthetic rubber is more produced due to following reasons:
  - Availability of low-cost HC ① raw materials combined with ② relative unavailability of natural rubber due to large labor requirements & relatively undesirable climate ③
- Position of natural rubber is India is unique
- In India, desirable climate and land availability combine with availability of low-cost labor to produce an attractive supply of natural rubber
- In India, among the plantation crops, natural rubber was maintained one of the fastest growth rates, vigorous in nature and vibrant in character
- India obtains its bulk requirements of natural rubber from domestic sources

In western world synthetic rubber is more produced due to the following reasons that is availability of low-cost hydrocarbon raw materials and it is combined with relative unavailability of natural rubber due to large labor requirements and relative undesirable climate because of these 3 reasons that is availability of low-cost hydrocarbon raw materials and then relative unavailability of natural rubber and then relative undesirable climate conditions of foreign conditions.

Natural rubber contribution is not much there whereas the synthetic rubber contribution is more to fulfill their rubber needs. Position of natural rubber in India is unique. In India desirable climate and in land availability combined with availability of low-cost labor to produce an attractive supply of natural rubber. In India among the plantation crops natural rubber was maintained one of the fastest growth rates vigorous in nature and vibrant in character as well. India obtained its bulk requirements of natural rubber from domestic sources.

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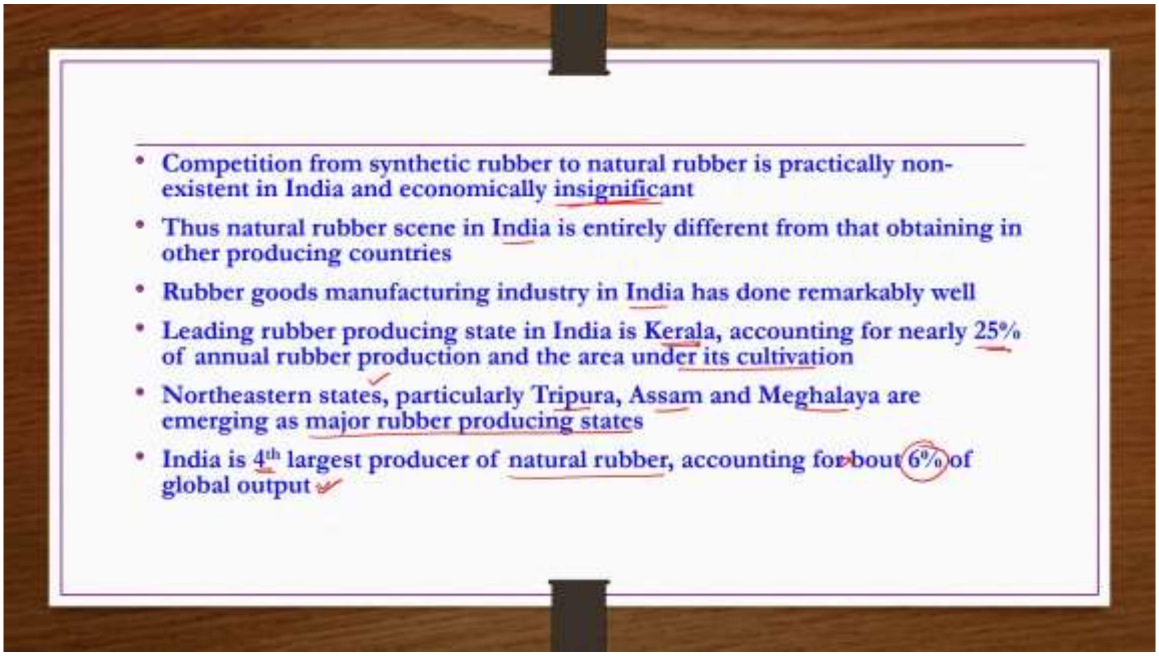

- Competition from synthetic rubber to natural rubber is practically non-existent in India and economically insignificant
- Thus natural rubber scene in India is entirely different from that obtaining in other producing countries
- Rubber goods manufacturing industry in India has done remarkably well
- Leading rubber producing state in India is Kerala, accounting for nearly 25% of annual rubber production and the area under its cultivation
- Northeastern states, particularly Tripura, Assam and Meghalaya are emerging as major rubber producing states
- India is 4th largest producer of natural rubber, accounting for about 6% of global output

Competition from synthetic rubber to natural rubber is practically non-existent in India and economically also insignificant. Thus, natural rubber seen in India is entirely different from that obtaining in other producing countries. Rubber goods manufacturing industry in India has done remarkably well leading rubber producing state in India is Kerala according for nearly 25% of annual rubber production and the area under its cultivation. Northeastern states particularly Tripura, Assam and Meghalaya are emerging as major rubber producing states for India. India is the fourth largest producer of natural rubber accounting for about 6% of global output.

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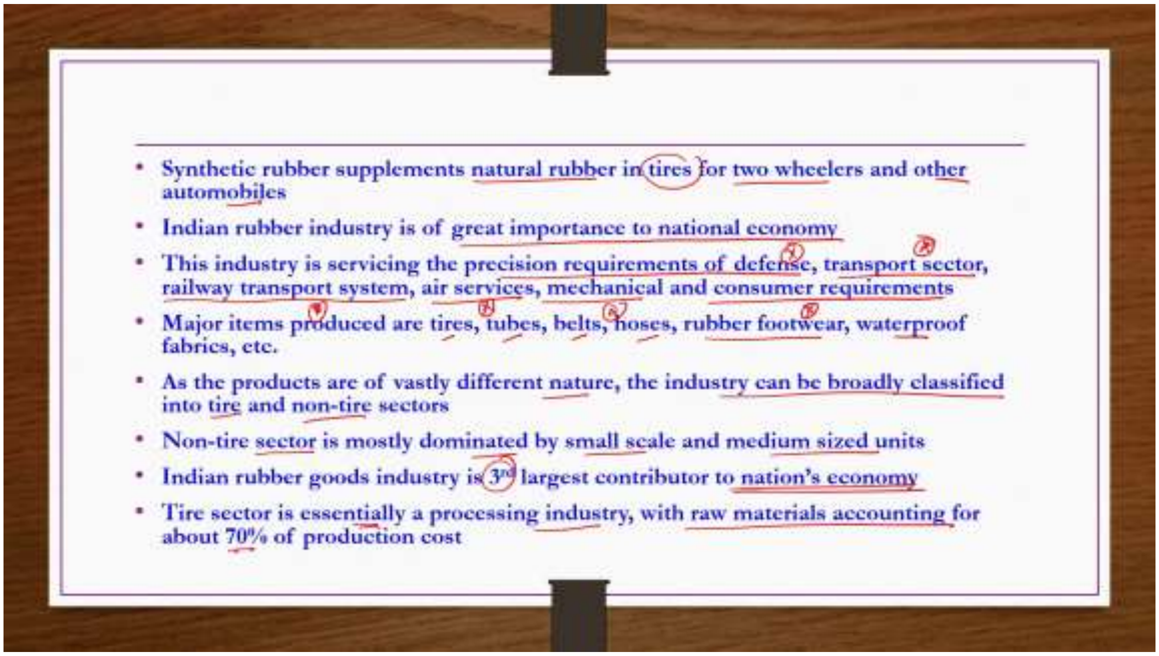

- Synthetic rubber supplements natural rubber in tires for two wheelers and other automobiles
- Indian rubber industry is of great importance to national economy
- This industry is servicing the precision requirements of defense, transport sector, railway transport system, air services, mechanical and consumer requirements
- Major items produced are tires, tubes, belts, hoses, rubber footwear, waterproof fabrics, etc.
- As the products are of vastly different nature, the industry can be broadly classified into tire and non-tire sectors
- Non-tire sector is mostly dominated by small scale and medium sized units
- Indian rubber goods industry is 3rd largest contributor to nation's economy
- Tire sector is essentially a processing industry, with raw materials accounting for about 70% of production cost

Synthetic rubber supplements natural rubber in tires for two wheelers and other automobiles only. Indian rubber industry is of great importance to national economy because of such reasons because most of the rubber requirements are fulfilled by the natural rubbers. This industry is servicing the precision requirements of defense, transportation sector, railway transport systems, air services, mechanical requirements and then consumer requirements. So almost all sectors whatever the rubber requirements are there that are being fulfilled by the you know natural rubber produced by the Indian rubber industry. Major items produced are tires, tubes, belts, horses, rubber footwear, waterproof fabrics, etc.

As the products are of vastly different nature the industry can be broadly classified into tire and non-tire sectors. Non-tire sector is mostly dominated by small scale and medium sized units. Indian rubber goods industry is the third largest contributor to nation's economy that is the reason we were discussing about the rubber industry separately as a separate chapter. Tire sector is essentially a processing industry with raw materials accounting for about 70% of production cost.

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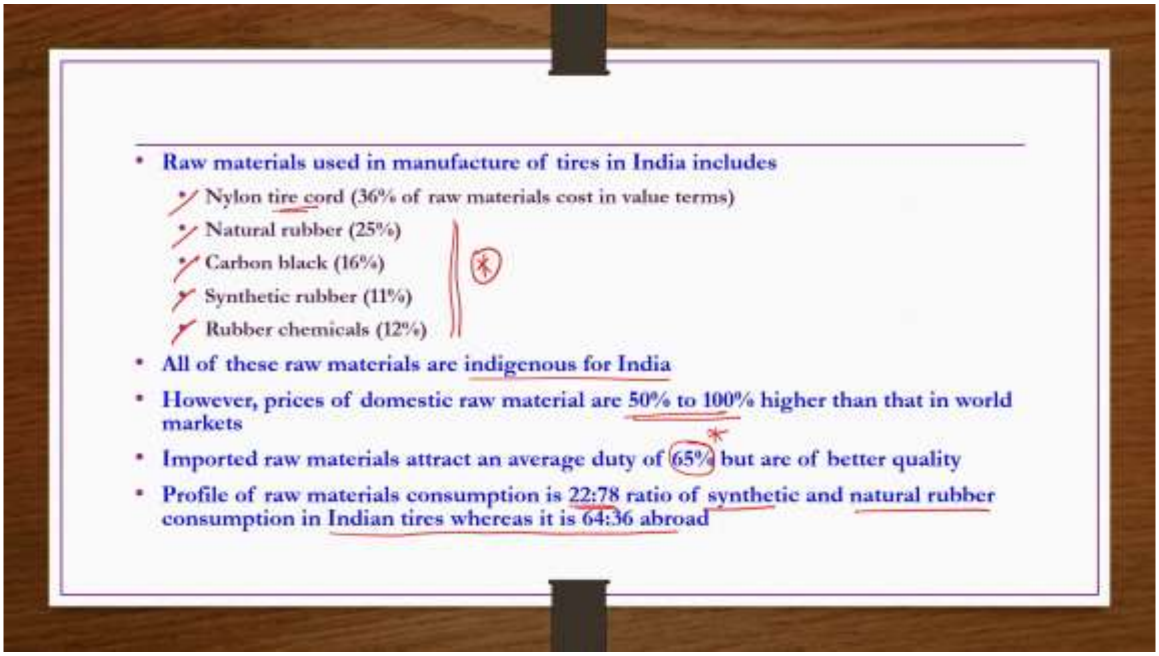

- **Raw materials used in manufacture of tires in India includes**
  - Nylon tire cord (36% of raw materials cost in value terms)
  - Natural rubber (25%)
  - Carbon black (16%)
  - Synthetic rubber (11%)
  - Rubber chemicals (12%)
- **All of these raw materials are indigenous for India**
- **However, prices of domestic raw material are 50% to 100% higher than that in world markets**
- **Imported raw materials attract an average duty of 65% but are of better quality**
- **Profile of raw materials consumption is 22:78 ratio of synthetic and natural rubber consumption in Indian tires whereas it is 64:36 abroad**

Raw materials used in manufacture of tires in India includes different types of raw materials are used other than the natural rubber.

They include nylon tire cord 36% of raw materials cost in value terms. The natural rubber 25%, carbon black 16%, synthetic rubber 11%, rubber chemicals 12%. All of these raw materials are indigenous for India. However, you know their cost is almost 50 to 100% higher than that available from the world markets. So, whatever we get from the world markets their purity is better. But however, importing such raw materials attract an average duty of 65% you know that is quite high that is the reason we depend on our own indigenous raw materials listed above here.

Profile of raw material consumption is 22 to 78 ratio of synthetic and natural rubbers. Consumption in Indian tires whereas it is 64 to 36 abroad. So, you can see almost reverse. So, in Indian rubber industry for the tires especially you know most of the natural rubber is supplying the demand whereas in the foreign synthetic rubber is supplying the demand of you know their rubbers.

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- This difference in use of natural and synthetic rubbers in India and abroad are due to
  - Larger production of truck tires in India
  - And natural rubber is preferred choice for truck tires by virtue of being cheaper and more rugged
- All raw materials required for automobile tires and tubes are indigenous as already mentioned
- However, for manufacture of radial tires, the unit may also have to import special steel cord fabric from abroad

This difference in use of natural and synthetic rubbers in India and abroad are due to larger production of truck tires in India and natural rubber is preferred choice for truck tires by virtue of being cheaper and more rugged.

All raw materials required for automobile tires and tubes are indigenous as already mentioned. However, for manufacture of radial tires the unit may also have to import special steel cord fabric from abroad.

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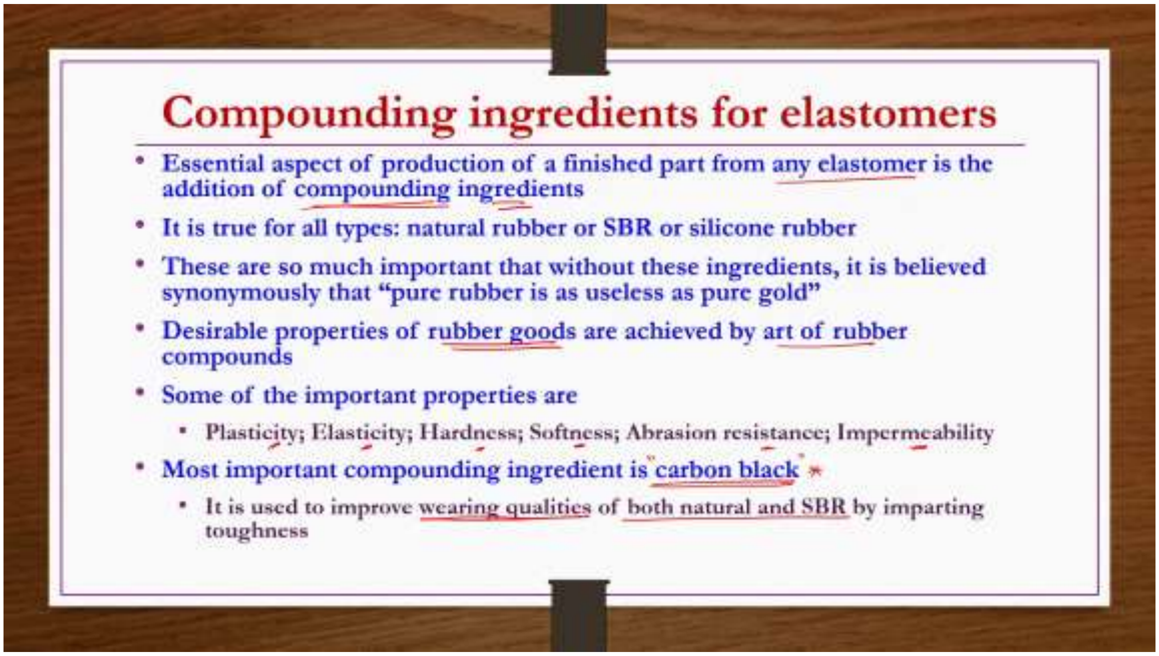

Compounding ingredients for elastomers

- Essential aspect of production of a finished part from any elastomer is the addition of compounding ingredients
- It is true for all types: natural rubber or SBR or silicone rubber
- These are so much important that without these ingredients, it is believed synonymously that "pure rubber is as useless as pure gold"
- Desirable properties of rubber goods are achieved by art of rubber compounds
- Some of the important properties are
    - Plasticity; Elasticity; Hardness; Softness; Abrasion resistance; Impermeability
- Most important compounding ingredient is carbon black *
    - It is used to improve wearing qualities of both natural and SBR by imparting toughness

Finally, compounding ingredients for the elastomers would be discussed before concluding the lecture. Essential aspect of production of finished part from any elastomer is the addition of compounding ingredients that is what we have seen additives, fillers, plasticizers, antioxidants, etc. are being added to the basic elastomers then only final products would be in the usable conditions otherwise you know pure elastomer is as useless as pure gold.

Pure gold is useless because until and unless you dilute with the other metal like copper it cannot gain the strength to make ornaments, etc. Likewise, elastomers also if you are not using compounding ingredients it is as useless as pure gold. It is true for all types of natural rubber or SBR or silicon rubbers. These are so much important that without these ingredients it is believed synonymously that pure rubber is as useless as pure gold.

Desirable properties of rubber goods are achieved by art of rubber compounds. Some of the important properties of rubber goods which are you know achieved by art of rubber compounding by ingredients or after adding ingredients necessary ingredients whatever the rubber goods that you get their properties if you see they include plasticity, elasticity, hardness, softness, abrasion resistance, impermeability as well. Most important compounding ingredient is carbon black. In almost all tires and tubes manufacturing this carbon black is used. It is used to improve wearing qualities of both natural and in synthetic SBR by imparting toughness. For that purpose, this carbon black carbon black compounding ingredient is used.

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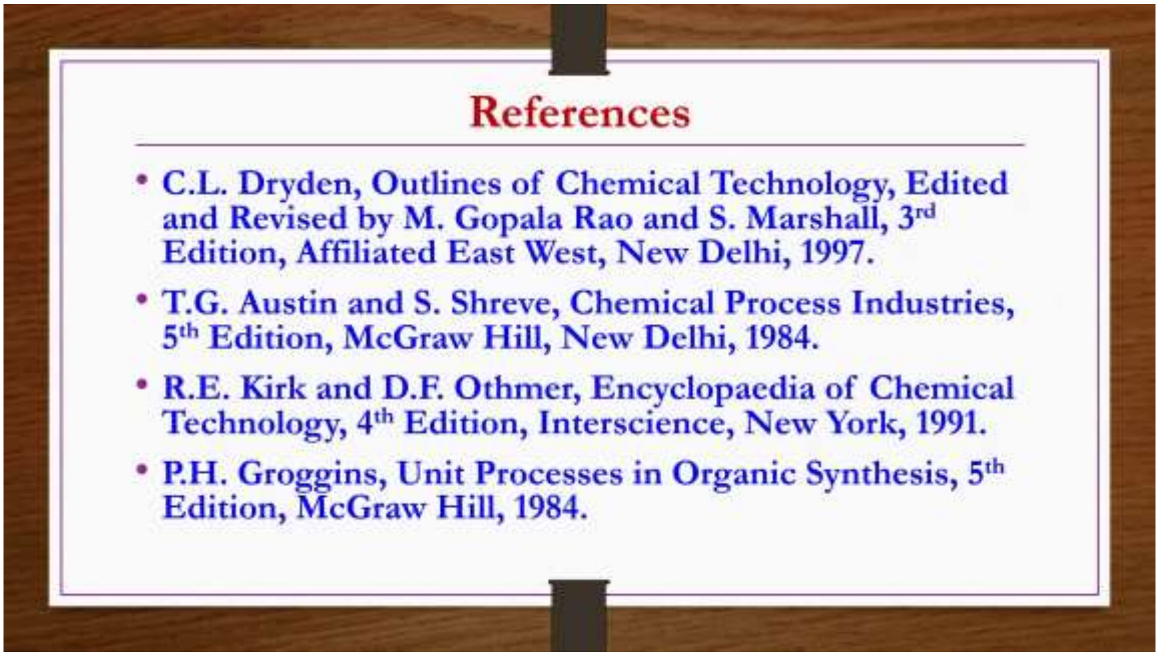

References

- C.L. Dryden, Outlines of Chemical Technology, Edited and Revised by M. Gopala Rao and S. Marshall, 3rd Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, Chemical Process Industries, 5th Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

References for today's lecture are provided here. Outlines of Chemical Technology by Dryden edited and revised by Gopal Rao and Marshall third edition. Then Chemical Process Industries by Austin and Shreve. Then Encyclopedia of Chemical Technology by Kirk and Othmer fourth edition and Unit Processes in Organic Synthesis by Groggins fifth edition.

Thank you. With this we complete our organic chemical technology MOOCs course. I hope you must have enjoyed it a lot. Thank you so much for your attention and all the best. Thank you.