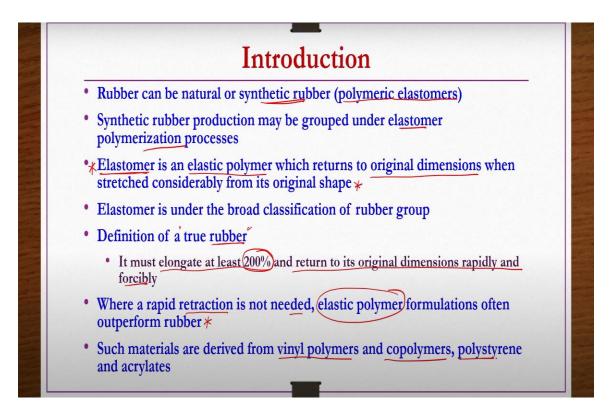
Organic Chemical Technology Prof. Nanda Kishore Department of Chemical Engineering Indian Institute of Technology, Guwahati

Lecture - 34 Rubber Industry

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is Rubber Industry. In this particular chapter, we will be discussing about a few introductory basic concepts of rubber industries and then few important synthetic rubbers that are manufactured industrially that is what we are going to discuss in this particular chapter, okay? Then we are also going to discuss about polymeric oils which are mostly silicon based. So, production of polymeric oils also we are going to discuss in this particular chapter. So, first we have introduction about rubber industry or rubbers.

(Refer Slide Time: 01:10)



Rubber can be natural or synthetic rubber. Synthetic rubbers which are counted under the polymeric elastomers category. If you remember in the previous chapter on polymerization,

polymerization processes when we were discussing processes associated with the plastics where addition and then polycondensation kind of methods we discussed to produced ethnic polymers and then phenyl formaldehyde resins kind of things we have discussed. The second category was rubbers under which most of the elastomer or elastomeric polymerization processes comes into the picture.

Then third one is the polymeric oils and then fourth one is the fibers. So, here what we are doing is that we are discussing about this rubbers, elastomers and then polymeric oils production. The previous lecture or previous chapter we discussed in a mostly polymer processes associated with the plastics production. So, other way what I mean to say that whatever the rubbers especially synthetic rubbers that we are going to discuss and then production of polymeric oils that we are going to discuss, they can be taken as subset of a polymer industry. However, from the applications point of view, these applications are specific towards the rubber or elastomeric materials. That is the reason we are separately discussing the rubbers as a separate chapter. So, these rubbers naturally also available as we know most of the plants when you shred off some of the bark etc., you can see some kind of rubbery material is coming that is natural rubber and then there are specific plants are there which are cultivated and then grown in order to produce natural rubbers. Most of the Indian rubber requirements are fulfilled by the natural rubbers only almost like 70%, 65 to 70% of rubber needs of India are filled by the natural rubbers. That means, natural rubbers are being used mostly in India, almost 70% it is being used and then natural rubber industry of India is indigenous.

However, some of the requirements are also fulfilled by the synthetic rubbers. So, those things associated with the synthetic rubber we are going to discuss in this particular lecture and then coming lecture of the particular chapter. Synthetic rubber production may be grouped under elastomer polymerization process. So, under the polymerization processes, elastomer polymerization process is one of the subcategory or elastomeric polymers may

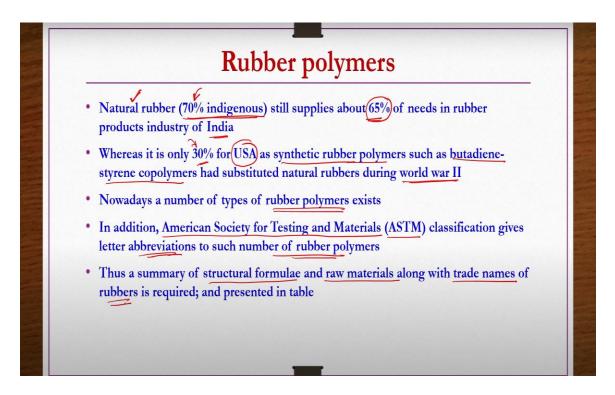
be taken as subtype of one of the polymers. So, polymers whatever the elastomer polymerization processes are there, they are used to produce synthetic rubber.

What do you mean by elastomer? By the word elastomer indicate like it is having some kind of elastic property. So, that is elastomer is an elastic polymer which returns to original dimensions when stretched considerably from its original shape. So, that is the definition of elastomer in general, you know elastomer is what mean by when you apply the external force it undergoes some kind of stretching or elongation kind of thing, but when you remove the force that material will get back to its initial position. If it is completely coming back to its initial position or shape then it is known as the perfect elastic material. So likewise, elastic polymers are also defined.

So, elastic polymers are nothing but the materials which returns to original dimensions when stretched considerably from its original shape. So, elastomer is under the broad classification of rubber group as we just seen from these points. Definition of true rubber, so then it is very important to define rubber especially true rubber means what? True rubber means it must elongate at least how much 200% it must elongate and return to its original dimensions rapidly and forcibly then only we can cut that particular material as a true rubber or fully rubber or elastic material. If it is not coming back to its original dimensions rapidly and forcibly then we cannot say that it is a true rubber it is partial rubber it may be counted as a partial rubber but cannot be considered as a true rubber or fully rubbe

outperform the rubbers natural rubbers. Such materials are derived from vinyl polymers and then vinyl copolymers or polystyrenes and then acrylates as well.

(Refer Slide Time: 06:29)

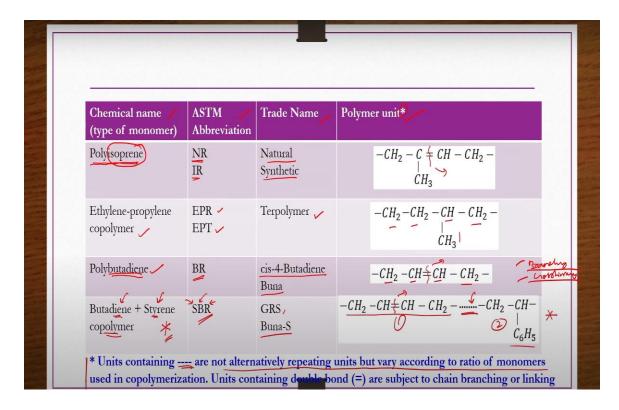


So now we talk about rubber polymers, natural rubber still supplies about 65% of needs in rubber products industry in India out of which 70% is indigenous. Whatever the needs of India are there rubber products need of India whatever is there out of which 65% is fulfilled by natural rubbers and then out of such natural rubbers 70% we are producing indigenous without depending on the outside external foreign resources or technology. So however in the USA the picture is opposite where 30% is only supplied by the natural rubbers in USA whereas the rest everything is by synthetic rubber polymers such as butadiene, styrene copolymers. So the synthetic rubber whatever the SP or butadiene styrene copolymers are there they were developed during World War II and then since then most of the rubber requirements of USA are fulfilled by this synthetic rubber and other kind of a recent developments of the rubbers whereas only 30% is being fulfilled by the natural rubbers.

Nowadays a number of types of rubber polymers exist. So because of such wide number of polymer rubbers are existing American Society for Testing and Materials that is ASTM

classification has been given letter abbreviations to such number of rubber polymers. Thus a summary of structural formulae and raw materials along with the trade names of such rubbers are provided in the table because they are very much essential because technical terminology consumer may not understand. So because of such reasons many of the products are given you know trade names as well. So same is true for the you know rubber products as well. So some of the rubber products along with their ASTM abbreviation trade name and then monomer repeating units whatever is there that structure we are going to discuss in a tabular column now.

(Refer Slide Time: 08:55)



So first column is on chemical name that is type of monomer, second column is the ASTM abbreviation, third column is the trade name whereas the final column is polymer unit. So here what we have let us say first one is polyisoprene. Isoprene production we have already discussed in one of the previous chapter. So if you have the polyisoprene its ASTM abbreviation is NR if it is natural one and then IR if it is synthetic one. Both the abbreviations are given. So trade names are natural as well as synthetic isoprene names are given. Polymer units is given like here like CH2, C, CH3 double bond CH CH2. This is

the repeating unit that is being repeated in isoprene. Another one is the ethylene propylene copolymer.

ASTM abbreviations are EPR, EPT trade name is terpolymer and then repeating units in the polymer this polymer is CH2, CH2, CH, CH3, CH2. Then polybutadiene, butadiene production also we have discussed in one of the previous chapter. So if you do the polymerization of that butadiene whatever the polymer you get that is polybutadiene. So ASTM abbreviation is BR trade name is cis 4 butadiene or buna. It is a repeating unit in the polymer is CH2, CH double bond CH CH2. Then another one is the butadiene styrene copolymer. So since 2 different types of monomers are there so it is a copolymer. It is the one of the most important development of polymer industry or rubber industry. Its ASTM abbreviation is SBR, S stands for styrene, B stands for butadiene R for rubber SBR.

Trade name are GRS and buna-S. Repeating units 2 units are there because 2 monomers are there it is a copolymer. So one unit is CH2, CH double bond CH CH2 like butadiene. Another one is the CH2, CH C6H5 that is for the styrene. Now here dotted things are there. So now here these dotted things does not mean that these one monomer and then this is another monomer are occurring you know alternatively or it does not mean that you know so many of these butadiene monomers are being coupling together and then after that this styrene is joining the polymer chain it is not like that. It is depends on the you know weight ratio or it depends on the you know ratio of the butadiene and styrene that has been taken in the polymer and such things are true for any other copolymers as well. Then another thing is that whatever these double bonds are there whichever polymer it is. So these double bonds are you know are kind of you know sources to form the branching or you know cross linking or both as we have discussed in the previous chapter on polymerization. We have seen branched polymers cross linked polymers and then mostly this branching or cross linking is occurring at double or triple bonds. So the same information is given here the star indicates here for the ones which are having these dotted lines like this. They are not alternatively repeating units but vary according to ratio of monomers used in copolymerization because more than one monomer is there it is a copolymer and then units containing double bonds are subject to chain branching or linking in general.

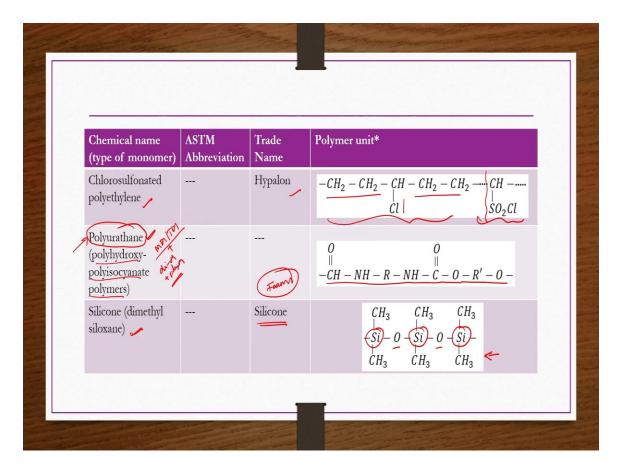
Chemical name	ASTM	Trade Name	Polymer unit*
(type of monomer)	Abbreviation	Trade Marine	1 olymer unit.
Butadiene + acrylonitrile	NBR	Nitrile rubber Buna-N	$-CH_2 - CH \neq CH - CH_2 - CH_2 - CH_1$
Polychloroprene	Č.	Neoprene 🧹	$\frac{-CH_2 - C}{Cl} \neq \frac{-CH - CH_2}{Cl} - CH = \frac{-CH_2}{Cl} - CH = \frac{-CH_2}{CH} - CH = $
Isobutylene-isoprene copolymer /	IR * 2400 *	Butyl	$-CH_2 - CH_3 - CH_2 -$
Polysulfide 🏑		Thiokols 🧹	$-CH_2 - CH_2 - S - S - \checkmark$

(Refer Slide Time: 12:57)

Some other polymers details are provided here. Let us say butadiene acrylonitrile copolymer if you have ASTM abbreviation is NBR trade name is nitrile rubber or Buna - N repeating unit of this particular polymer is given here that is CH2CH double bond CH CH2 CH2 CH CN. So another one is the polychloroprene ASTM abbreviation is CR trade name is neoprene its structure is CH2CCL double bond CH CH2 isobutylene isoprene copolymer is the other one its ASTM abbreviation is IIR trade name is butyl rubber.

Here isobutylene and isoprene two monomers are there. So here dotted dots are indicating you know these monomers are you know joining together to form you know copolymer. So now we have polysulfide its trade name is thiokols it is CH2CH2SS structure it is having. Now this here IIR is another important one that is used in the tires and tubes usually either SBR alone or in combination with IIR polymers are used for the production of most of the you know tires and tubes that are being used for you know automobiles in general. Even if they are using in combination contribution of SBR is more compared to the contribution of IIR. Here also this dotted does not mean that they are joining repeatedly alternatively repeated units are being joined it does not mean like that it depends on the ratio of monomers that has been taken to form the copolymer and also these double bonds are subject to cross linking right or possibility of branching and cross linking may take place at these double bonds.

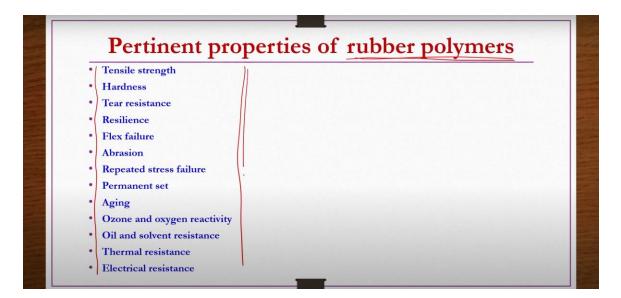
(Refer Slide Time: 15:14)



If you see some more rubber polymers we have a chlorosulfonated polyethylene trade name is hypalon and then its polymer unit is CH2CH2CHClCH2CH2 and then another one is the CHSO2Cl it is also having 2 monomers this is one monomer this is another monomer. So here there are no double bonds but you know these monomers are also not necessarily be alternatively joining and that depends on the ratio of monomers that have been taken. And then polyurethane this we have seen in the previous lecture it is produced by the reaction between MDI or TDI and then diols alcohols or polyols. So polyhydroxy polyisocyanate polymers are nothing but these things right. So these polyurethanes are nothing but the foams that are obtained by the reaction between MDI TDI or both of them and then reacting with some kind of alcohols diols or polyols are used.

So whatever the product name is there commercially chemical name is the polyhydroxy polyisocyanate polymers okay they are in general known as the polyurethane okay. So trade name specifically it is not there but mostly they are referred as foams okay. The repeating structure is given here CH double bond O NH R NH C double bond O O R prime O like this okay. Then silicon or dimethylsiloxane which we are going to discuss production in the next lecture its trade name is silicon it is a oil high temperature resistance oil it is having so many applications. So it is repeating units one of them is shown here.So like Si CH3 CH3 O Si CH3 CH3 O Si CH3 CH3. So now this Si how it is being connected to the other monomers or other molecules depending on that one the final properties of this silicon oils would be changing okay.

(Refer Slide Time: 17:43)



Now we see pertinent properties of rubber polymers actually quantitatively having some values about pertinent properties of rubbers is very difficult because the rubber polymers

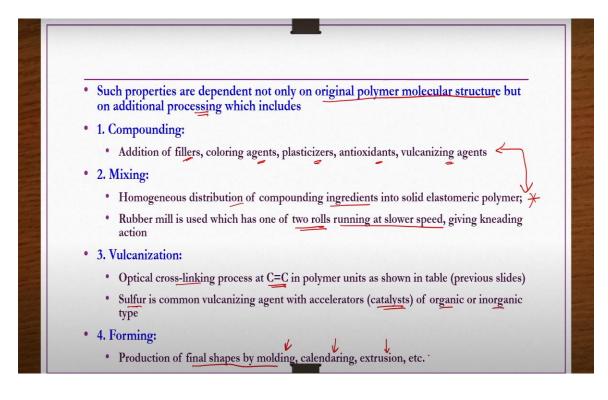
we have seen so many types of rubber polymers are there. So many different types of monomers are there polymers are there copolymers are there different types of co monomers are there and then their weight ratio or the ratio of the monomers how much they have been taken based on that one the final property is going to change. Let us say SBR if you take how many moles of butadiene how many moles of styrene you have taken accordingly final SBR polymer that you are going to get the properties would change.

So definitely the properties of SBR are going to be very different from IIR or any Buna or any Guna S kind of polymers that we have discussed. So having quantitative values about the properties of rubber polymers is not possible. However we are going to list the you know important properties that are to be taken care or consider while selecting the polymers based on your applications.

So what are those properties we are going to list now here. First one is the tensile strength second one is the hardness like that tear resistance resilience flex failure abrasion repeated stress failure permanent set aging ozone and oxygen reactivity oil and solvent resistance thermal resistance chemical resistance electrical resistance all of them are very essential.

In fact you know a few may be missing from the list. So all of these properties you have to estimate for the rubber that has been produced and then accordingly you have to choose the application or you have based on your application you have to select certain kind of monomers and then comonomers if required their mole ratios etc. and then working conditions all those things you have to see so that to get you know desired properties in your final rubber.

(Refer Slide Time: 19:52)



Such properties are dependent not only on original polymer molecular structure but on additional processing as well. So those properties are also dependent on the processing not the polymer reaction polymerization processes but you know subsequent compounding vulcanization shaping or form formation etc steps are there they are also playing vital role on such properties.

So what are those processes that we are going to see these are the additional processes to get the final product. So one most important thing that may be there for almost all polymers is the compounding another one is the mixing another one is the vulcanization and then forming or shape formation. So what do you mean by compounding maybe sometimes the pure polymer whatever you produce is of no use or maybe less use then what you do you add some kind of fillers and then additives etc to make the polymer more suitable for a given application. So adding such kind of foreign materials is known as the compounding.

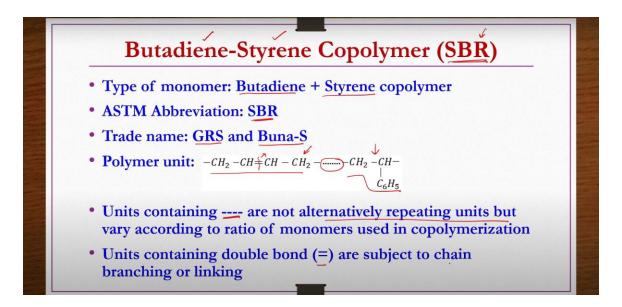
So addition of fillers, coloring agents, plasticizers, antioxidants, vulcanizing agents etc whatever is there that process is known as the compounding.

Some of them are maybe used in some polymers some of them are not at all required some of the polymers all of them may be required that depends on the applications to application and then quantity how much it of these fillers agents etc required that also depends on application to application and then one polymer to another polymer it will definitely change because no two polymers may be very similar to each other. Then what do you mean by mixing? So these fillers, coloring agents, plasticizers etc that you are adding to the polymer so that to make you know suitable to have a better applications as per the required. So that addition should be done homogeneously properly it has to be done. So for that purpose this mixing is done. So mixing is homogeneous distribution of compounding ingredients into solid elastomeric polymers.

This is very much essential otherwise adding these you know here is not going to solve the purpose they should be added such a way that homogeneous distribution of compounding ingredients into solid elastomeric polymers should be taking place. For that purpose this mixing is done and then it is done using roll mills using roll mills whatever are there or rubber mills are being used which are having two rolls same like you know roll mills but you know they are made up of the rubbers. So one of the two rolls running at the slowest speed so that giving kneading action and then when this kneading action is you know supplied or you know transmitted to the components that are being mixed so then homogenization takes place. Then vulcanization is something like cross linking kind of thing or stabilization kind of thing is referred to the vulcanization. So optical cross linking processes that occurs at double bonds in polymer units is known as the vulcanization.

Often sulfur is common vulcanizing agent with some accelerators or catalyst those catalyst may be organic or inorganic in the nature. So that are being added sometimes even some monomers are also different monomers are also added for this purpose. Now finally forming is nothing but production of final shapes by processes like molding, calendaring and then extrusion etc. So many other processes may also be there depending on the final shape of the product that you are going to get. So that is all basic about the rubber industries, rubbers and then chemical structures, properties etc. those things we have seen and then additional processes required to get the final rubber as per the consumer application those things we have seen.

(Refer Slide Time: 24:07)

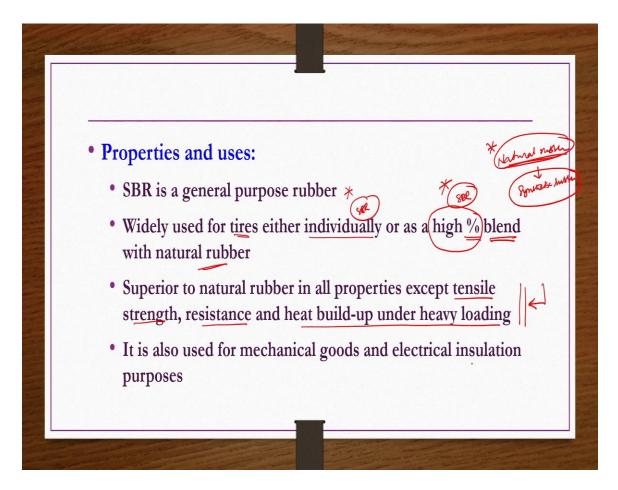


Now what we do we discuss production of SBR polymer or SBR rubber. What do you mean by SBR? It is nothing but butadiene styrene copolymer. Individually butadiene production we have seen individually styrene production we have seen in the previous chapter. Now we take them together and try to do the copolymerization to get the so called rubber polymer which is having trade name SBR.

Type of monomers used in the SBR obviously by the name they are nothing but butadiene and styrene copolymers or comonomers. It is ASTM abbreviation is SBR trade name is GRS and Buna-S. If you see the polymer unit what you have? You have the butadiene unit and then styrene unit they are being joined coupled together to form copolymer. So, these dots does not mean that they are occurring alternatively like you know when all butadiene monomers are polymerized then the styrene is being added it is not like that. It is depends on the ratio of this butadiene and styrene at what mole ratio have been taken.

That ratio again depends on the properties of the final rubber that you are producing. And then also this double bond is you know is a source to do the required branching and cross linking so that the high molecular weight SBR can be formed easily. So, here the units whatever the dots containing are not alternatively repeating units but vary according to ratio of monomers used in copolymerization. Units containing double bond are subject to chain branching or linking.

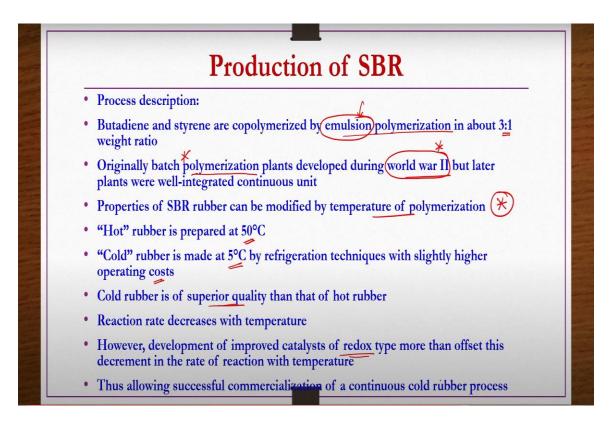
(Refer Slide Time: 25:54)



Properties and uses if you see for the SBR. SBR is a general purpose rubber very often it is used for the tubes and tires manufacturing. It is widely used for tires either individually or as a high percentage blend with natural rubber. Actually natural rubber is the best one for most of the cases. Different types of natural rubbers you take and then you compare with the similar synthetic rubbers. So then obviously the properties of natural rubbers are superior in general in most of the cases.

But SBR is one kind of synthetic rubber that its properties are superior to the natural rubber except the 3 properties those 3 are nothing but the tensile strength resistance and then heat build up under heavy loading except these 3 properties if you compare all other properties SBR is better than the natural rubber. However, when you make tires either you use individually SBR or you do blending with the natural rubber. Even when you do the blending with natural rubber SBR percentage that you are going to take is very high. Such superior is this SBR in comparison with the natural rubbers. It is also used for mechanical goods and electrical insulation purposes.

(Refer Slide Time: 27:27)



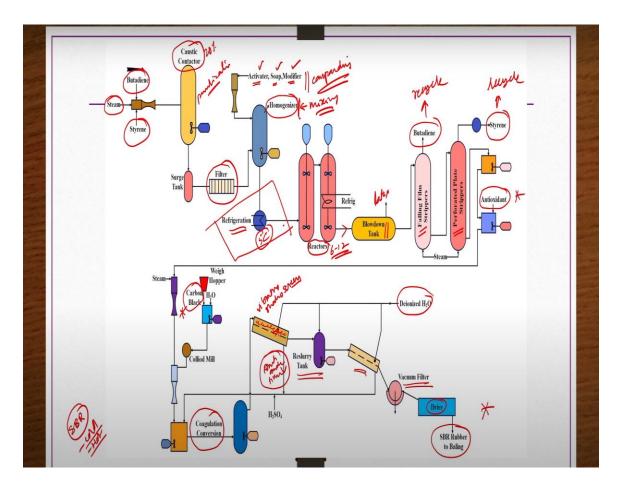
Now we see the production of SBR. First we see few steps of process description then we see the flowchart and then we see the remaining steps of the flowchart in the description form. Butadiene and styrene are copolymerized by emulsion polymerization in about 3 to 1 weight ratios. So emulsion polymerization is taking place. Originally batch

polymerization plants developed during World War II, but later plants were well integrated continuous units were also developed usually what happened emulsion polymerization whatever the monomers you take and then you take catalyst if at all required and then you take some kind of solvents if at all required and then take it to a batch or continuous reactor provide the required temperature of polymerization and then duration of the polymerization so that the polymerization takes place. So then whatever the polymer mixture is there that you take to the separation unit so separate out the monomers and then take them for the recycle and then this wet polymers whatever would be there drying shaping kind of things are you know done that is what in general done.

Same is true here also almost all we see from the flowchart point of view. So mostly the initial original process whatever developed for this SBR you know I told this is developed during the World War II and then any material that has been developed during the World Wars is having so much significance because those materials have been developed based you know because of the dire requirements very high requirements at that particular critical times. So pencilin is also one of the such kind of you know product that has been developed as we have discussed in one of the previous chapter. SBR is also one of the such kind of product which is developed during the World War when it was developed basically it was developed in a batch process however now continuous processes are also there. Properties of SBR rubber can be modified by temperature of polymerization.

So what does it mean by so then temperature is having a very good effect so or maybe you know different temperatures you operate different SBR material of different properties you may be getting okay. So you have hot rubber that can be prepared at 50 degrees centigrade and then cold rubber that can be prepared at 5 degrees centigrade by refrigeration techniques. However the operating cost are slightly higher for the cold rubber but the properties wise are the final product wise if you see the cold rubber is superior in quality than that of hot rubber okay. So however in this case reaction rate decreases with temperature but development of improved catalyst for redox type are more than offset this

decrement in the rate of reaction with the temperature thus allowing successful commercialization of cold rubber process in the continuous mode okay.



(Refer Slide Time: 30:38)

So this is the flowchart if you see here this is the flowchart for production of SBR both cold and hot processes may be taken or discussed here without any difficulty. So whatever the monomers butadiene and then styrene are there they are mixed and then along with the steam they are taken to a caustic contactor or this mixture is contacted with the caustic 20% NaOH solution.

What is the purpose? The purpose of this one is the purification for the purification of the monomer because sometimes impurities if at all they are present in the monomers so then final polymerization may not take place or you know polymerization may be stopped in between. So you know having very pure monomer is very much essential from the

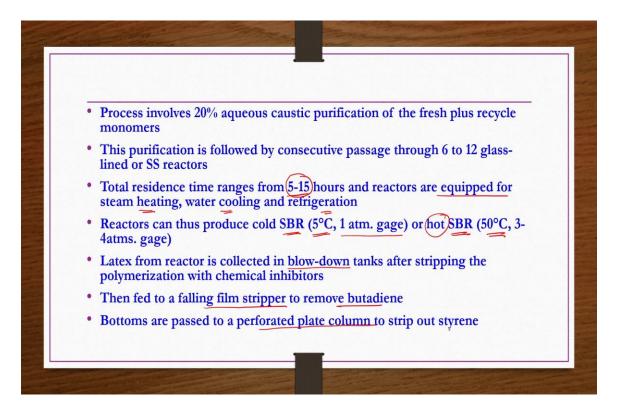
polymerization or continuation of polymerization point of view okay. So then after purification these are sent to the search tank and then to the filter to separate out whatever the caustic solution etc if at all they are and then after removing these caustic solutions etc the mixture is taken to the homogenizer to which activator, soap, modifier are added. These are nothing but compounding agents or compounding processes that we discussed for that purpose these are being added and then they are taken to homogenizer where mixing operation is taking place as we have seen few slides before.

So the monomers and then these compounding agents whatever are there activators, modifier, detergent soaps etc they would be homogenized in the homogenizer by mixing. Then they will be passed through a refrigeration unit to reduce the temperature to 5 degrees centigrade or so if you are doing the cold process otherwise it is not required right. So since we are discussing cold process so here we have the refrigeration where the temperature of the mixture reduced to 5 degrees centigrade and then it passed through series of reactors 6 to 12 reactors are there in series in which the required conversion of the monomers will take place to get the copolymer SPR. Then the after passing through all the reactors whatever the reaction mixture is there that is passed through blowdown tank to separate out latex if at all it is there right. So then after separating the latex the mixture is taken to a falling film stripper where butadiene is separated out from the top of the falling film stripper and then that is taken for the recycle.

After removing the butadiene the mixture is taken to perforated plate stripper where unreacted styrene is separated from the top and then taken to recycle. Then whatever the emulsion polymer whatever is there that is taken to mixing chamber where antioxidants etcetera are added if they required and then there are also carbon blocks etcetera would also be added as per the requirement. So these antioxidants carbon blocks etcetera are depending on the requirement they will be added and then the material is sent to the coagulation conversion to separate out the so called latex etcetera. And then the mixture is taken to a vibrating shaker shaking screen where crumbs of the polymer whatever are there they would be floating on the top of the screens and then collected further for the further processing whereas the materials like you know antioxidants or you know fillers etcetera or whatever the soluble materials etcetera are there they would be washed out from the crumbs by using deionized water spray to this mixture. So when you use the deionized water onto the vibrating shaking screens so soluble materials would be separated out and then treated with H2SO4 as per the requirement.

Whereas the crumbs whatever are there they would be taken to a re-slurry tank and then another vibrating a shaking screen to remove if at all some many more you know soluble compounds are there after separating soluble compounds the polymer crumbs whatever are there they would be passed through vacuum filter to separate out the undesired liquid etcetera then send dried in a continuous rotary dryer to get the SBR rubber to welling operations. So this is the process to produce the SBR by cold process but if you wanted to do the hot process the same flowchart process may be followed but without needing of this refrigerator.

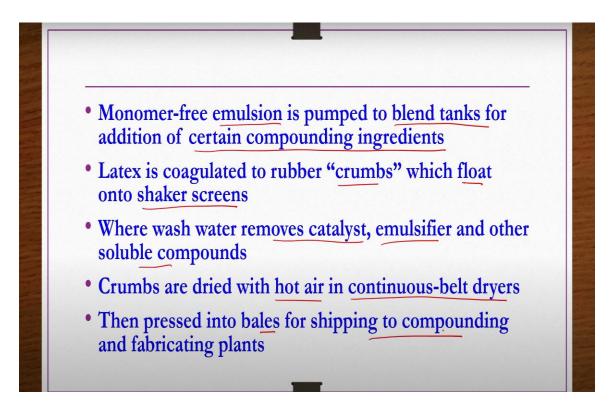
(Refer Slide Time: 35:58)



Now we describe the remaining steps of the process. Process involves 20% aqueous caustic purification of the fresh plus recycled monomers. This purification is followed by

consecutive passes through 6 to 12 glass lined reactors or stainless steel reactors. Total residence time ranges from 5 to 15 hours most of the polymerization processes are time consuming process that is the reason many people prefer to produce them in a batch mode if the low tonnage production is there. But however SBR is a high tonnage production because of its market so then the reactors are in general continuous though the process time is very high. And reactors are equipped with steam heating water cooling and refrigeration provisions. Reactors can thus produce cold SBR at 5 degree centigrade and then 1 atmosphere gauge pressure or hot SBR at 50 degree centigrade and 3 to 4 atmospheric gauge pressures. Latex from reactor is collected in blowdown tanks after stripping the polymerization with chemical inhibitors. Then fed to a falling film stripper to remove butadiene and recycle it. Bottoms are passed to perforated plate column to strip out the styrene and then recycle it.

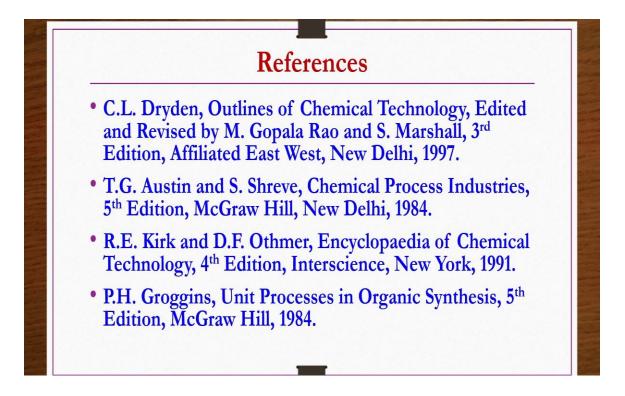
(Refer Slide Time: 37:23)



Monomer free emulsion is pumped to blend tanks for addition of certain compounding ingredients like antioxidants, carbon blacks etc. as we have shown others may also be added as per the requirement. Latex is coagulated to rubber crumbs which float onto shaker

screens where wash water removes catalyst, emulsifier other soluble compounds. Crumbs are dried with hot air in a continuous belt dryer then pressed into bales for shipping to compounding and fabricating plants.

(Refer Slide Time: 38:05)



References for today's lecture are presented here. Outlines of chemical technology by Dryden edited and revised by Gopala rao and Marshall in 3rd edition. Chemical process industries by Austin and Shreve 5th edition. Encyclopedia of chemical technology by Kirk and Othmer 4th edition. Unit processes in organic synthesis by Groggins 5th edition. However, most of the lecture notes that is prepared and presented in today's lecture is prepared from this particular reference book that is outlines of chemical technology by Dryden. Thank you.