

Industrial Inorganic Chemistry
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Lecture – 47
Silicone Rubber

Hello welcome back to this class where we are talking about the Silicones.

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Silicones have been produced industrially since the 1940's.
In 1995 there were thirteen silicone producers in Western industrialized countries.
The largest markets are the USA with a ca. 40% share, followed by the EU and Japan.

Most important silicone products are

- silicone oils and associated products
- silicone rubbers (elastomers)
- silicone resins

The slide also features logos for IIT Kharagpur, Swayam, and the Ministry of Education, India, along with a small video inset of the professor.

So, if we see that this silicon compounds have been produced in industrial scale since 1940. So, if we have if we consider the development during a time span of say 50 years. So, data is available till 1995 when 13 silicon products producers in Western industrialized countries they are engaged in producing these silicon compounds. And the largest markets are in US and they say are of 40 percent and the remaining with EU and Japan. So, why we produce these important silicon products? Because in our country we do not have that much products available till date.

So, most of the time we basically import those compounds. So, in terms of this particular type of inorganic chemistry based on silicon and the silicone as we discussed in our previous class it is very much similar to that of our acetone, but it's not that structural it is completely different. So, first thing what we can see that pure carbon free oil material is your silicon oil because these are large molecular based compounds and they are corrector is basically of that oil type.

So, silicon oils and associated products are one of the important products are there, then if we go further these are the silicon rubbers mostly we know as the elastomers and the silicon resins. So, these are very strong one in terms of the corresponding polymeric analog or the organic oil based a material or the bio organic or the bio, material what we can have is that these silicon oils are completely different when you have the silicon in their backbone.

So, what do you see that how these silicon oils are different in terms of their properties compared to the corresponding mineral oil or the vegetable oil or any other type of oil or the different types of esters what do we know that the esters which is giving you the corresponding wax material or the oil material.

So, the setting point say particular setting point industrially it is well known that is a very wide range of setting 0.4 minus 60 to minus 35 degrees centigrade and with the rise in temperature the corresponding viscosity of that particular oil does not change much. So, little change to viscosity with the rise in temperature that we all know particularly the petroleum industry and the only other oil industry the viscosity also changes and there we add some additive such that we can stop the corresponding change in the viscosity parameter. Then they are also very much stable thermally so they have very good thermal stability.

So, at a very high temperature we can use this particular oil, particularly sometime we can use in some motor or the transformer where the temperature rises there. Then it can have high specific resistance; that means, as resistor these oil in the transformer container or any other place it can be used. It has also low surface tension, lack of smell or taste because it is not contaminating the environment or it is not giving the some order of smell; that means, when the volatility is also not very much.

You can have some smell with these particular material of other type and is also physiologically inert, so if we are able to get something out of this particular oil type when we increase the molecular weight of these theoretical compounds, we can get the corresponding rubbery material or the resin type of materials. So, it is also physiologically compatible one, so that is why it is known as the physiological inert materials, so it will not interfere or it will not give some interaction with the biological system or the physiological system.

As a result what we can have? We have a large number of applications based on the silicon oils. So, while talking in terms of this industrial application of these particular material which is of inorganic origin; that means, this only the silicon origin. So, these particular silicon oil as a an organic version of the oil industry can think of in using these as corresponding heat transfer medium.

So, it can absorb huge amount of heat so if we consider that there will be some heat loss, it can be gone through corresponding silicon oil as the temperature reservoir. It can also be very easily used as a good lubricant and that lubricant is also have a different character compared to the other wax and oil material. It is used is as hydraulic oil, so hydraulic we know the hydraulic pump thing as other hydraulic pressure we use to push something or to pull something.

So, there we have some reservoir as oil, so we can substitute other oils as the hydraulic oils using silicone oils. Then as I told I just know I told you that is it can also be used very much well with as a transformer oil. So, the transformer filled with this oil can have some other advantages. So, there are a large number of advantages that is why because this particular material the silicon oils are pretty costly one also.

Then in the automobile breaks also we can use as the break fluids in a similar fashion like that of your hydraulic or the transformer oils then sometime it can increase the flow as the flow improver. So, when we use in the paint or any other material the corresponding parameter as easily flowing how quickly they are flowing from on a surface or how quickly they are covering a particular type of surface, we can consider these as a flow improving material.

Then gloss improver; that means, the glossy nature of the glossy surface of the material which has been painted with the material or the paint based on the silicon oil can also be improved. Then defoaming agent; that means, to stop somewhere the foaming behavior or the forming characteristic of the material of any type it can be of soap origin it can be used as to stop that particular foaming behavior as a defoaming agent.

Then mold release agent also and the constituent of skin cream and protective policies which is also very important and also from the left hand box where we see that it is physiological inner; that means, it will not have any irritation when we apply on the skin or it can have some other biological application. So, we safely we can use all these

material as the constituent of the skin cream and the different types of protective policies which we come in contact of our hands or contact of our skin.

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Silicone Rubbers

Differ in their crosslinking mechanism and application areas.

Room Temperature Vulcanizable Single Component Silicone Rubbers.

Reaction of a polydimethylsiloxane with hydroxy groups at either end with an excess of a silane.

$$\begin{array}{c}
 \left[\begin{array}{c} \text{CH}_3 \\ | \\ \text{HO}-\text{Si}-\text{O}-\text{H} \\ | \\ \text{CH}_3 \end{array} \right]_n + 2 \text{CH}_3\text{-Si}(\text{-OCCH}_3)_3 \longrightarrow \\
 \\
 \begin{array}{c}
 \text{OC-CH}_3 \quad \text{CH}_3 \quad \text{O-C-CH}_3 \\
 || \quad | \quad || \\
 \text{CH}_3\text{-Si} \text{---} \text{O-Si} \text{---} \text{O-Si-CH}_3 + 2 \text{CH}_3\text{COOH} \\
 || \quad | \quad || \\
 \text{OC-CH}_3 \quad \text{CH}_3 \quad \text{O-C-CH}_3 \\
 || \quad | \quad || \\
 \text{O} \quad \quad \quad \text{O}
 \end{array}
 \end{array}$$



So, what we see then that if we move further from the oil variety to the rubber variety; that means, the nature of the material as we all know what is the difference between the oil and the rubber material? So, rubbery material we get as we move and how we get it. So, the corresponding nature of that cross linking nature the cross linking nature of this particular silicon thing is changed.

So, they differ in their cross linking mechanism and application areas, so we get some different types of material which we consider as our silicon rubbery material. And if we go for a particular type of thing where we use the vulcanization as we all know the vulcanization is a typical process in rubber and the polymer industry using sulfur based compounds, where the mechanism is basically dependent on the typical cross linking.

So, if we are able to do this at room temperature and a single component silicone material or the chain long chain is used, we can get through cross linking the corresponding silicon rubber variety. Then we can do something where the reaction of a polydimethylsiloxane; polydimethylsiloxane with hydroxyl groups at either end with an excess of the silane molecule; that means, Si H 4 molecule.

So, this particular one can give a typical complex structure what we can see simply by looking at it. So, this particular one so we can consider it as the corresponding polydimethylsiloxane material. So, dimethylsiloxane material it can have the methyl substitutions the other variety what we can do is that you can have the corresponding hydroxyl end, so this is also the hydroxyl end at one end and other end is also hydroxy, but what do we do? We use this particular one with the siloxane material the hydroxyl group the one particular silane; so, one particular silane in your hand.

So, this is the polymeric unit where the end having a typical number, if we try to increase that number in end will get some different types of these rubbery material. So, you use this particular silane with that particular material with this particular variety, where you have the corresponding silicon globe attached to the three corresponding acetyl ester groups. So, these are the corresponding acetate groups CH_3CO .

So, 3 CH_3CO group attached to the silicon center and the corresponding methyl group is also already attached to the silicon. So, what we get basically? Because this is then the central part of the material where one H is replaced and one OH is being replaced. So, when we go for the replacement of the O of the OH we get the direct attachment of this particular silicon.

So, this particular silicon center is being attached with the methyl end so with the replacement of one of the acetate group; one of the acetate group is reacting with the corresponding OH group basically this OH groups, so giving rise to that particular reactivity with that proton. So, the proton will go out with removal of the corresponding acetic acid function. So, what happens for the other end, so other end is so one of the group. So, this group is basically on the either end that is why I was telling them either end of with an excess of silanes.

So, you have the silane end we are attaching the same molecule of different type making one silicon oxygen bond and the other end also we are getting this particular attachment of this. So, as a result we get a particularly series symmetrical molecule where we have the silicone at the center which is attached to 2 methyl groups and the repeating unit is with one of the oxygen.

So, these repeating unit along with the other part where you have the oxygen and the other group with a silicone methyl and the 2 acetate on the other end also you have the

silicone methyl and the 2 acetate groups attached to it. So, we get some complex type of that particular reactivity or we get something some replacement of these molecules will give you some type of those silicone rubber material.

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Inorganic Solids

Silicate Products

Glass Structure

Are inorganic melt products, which solidify without crystallization. Three dimensional networks are built up without regular, periodic arrangement of atoms.

Glass Composition

Glass formation being probable with higher bonding enthalpies and low system melting points.

The oxides, which form the network necessary for glass formation, are known as **network-formers**

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Then we can move now to getting that particular area where we consider them as the typical in organic solid. So, whatever type of material in terms of its material characteristics we can use typical in organic samples as the solids and some of these solids will have tremendous applications. So, we are still with that silicon element from the periodic table. So, how we get the different varieties of silicate products? As we all know that we get the corresponding silicon dioxide; silicon dioxide is the quad variety or the sand variety. So, that particular silicon dioxide is a polymeric structure.

So, that silicate from there how we get the silicate entity coming from that of the simple silicic acid. So, one of these particular variety is your glass variety. So, that glass variety what we get is that particular type of silicate product and it has different structure and sometimes the structures are pretty complex and we get different types of all these glasses.

So, what are these basically by definition these are the inorganic melt products. So, through the melting process with a different constituents basically we get something which ultimately solidifies to get something and after crystallization we get that glassy material. So, they are basically therefore, the inorganic melt products which solidify

sometimes without crystallization. So, if we go for crystallization we get something, but if we get something as a solidified product without crystallization.

So, we get that glass and sometimes we get certain temperature, so temperature will play some important role because you can have some glass transition temperature T_g for this particular purpose that when we get from the amorphous material to the crystalline material. So, we get basically the glasses are basically a three dimensional network and three dimensional networks having the building block of these silicate unit; that means, the Si O 4 tetrahedron.

So, when we have the silicon center and that particular silicon center is surrounded by 4 oxygen centers which are very much similar to that of our phosphate arsenate all these type or even perchlorate. Where we know that the central element is present and which is surrounded by 4 oxygen centers in a tetrahedral geometry. Similarly the silicon center when surrounded by 4 oxygen centers in a tetrahedral structure, we get something which is the basic building block of all these silicate products and the glass products.

But what we see now that you can have a three dimensional structure that is already we have discussed earlier in terms of your silicon oil or the silicone rubber formation, but also the different types of silicate formation. That if we are able to get silicon oxygen, silicon network and which continues from one end to the other we get a linear chain which is made up of one end from oxygen silicon; oxygen silicon; oxygen silicon in this way, so we get something like a network and is build up without regular periodic arrangement of atom.

So, it's basically a mixture, we do not have a very regular; that means, what we get in crystals because the crystals have some definite positions, so the crystal positions are very definite in terms of your a x y and z values of a particular coordinate of the corresponding atom silicon or the oxygen. But when we do not get that regular structure or a periodic arrangement or the repeating arrangement, what do we get in the crystalline structure? We get a glassy material or a glassy product.

So, how we get basically a particular type of glass because there are a different varieties. So, varieties of glasses what do we use at the home utensil, glass material to that of our glass window in different types of sophisticated instruments or the sophisticated spectro photo meters where you use these glasses as they are basic component or the basic part.

So, glass formation is dependent on a particular type of mixture and when it is forming is being probable with higher bonding enthalpies and low system melting points. So, we basically get a melt and that is why we are telling these as that in organic melt product we are getting and we which are ultimately solidifying. So, because of these higher bonding enthalpies and low system melting points we get something and which is getting solidified as a glass.

And if we consider these as a oxide, so we can have these oxides which form the network necessary for glass formation and some of these oxides which we can classify as a type of oxides, they are known as network formers. So, how it is different from that of that particular quartz or the other type of glass variety that only SiO_2 , but what we get that that we should add something such that we can establish some network, where we can have the corresponding chain or the corresponding street light or the three dimensional structures. So, basically we are relying on some of these oxides and those oxides are basically nothing, but your network formers.

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The ions, which through lower connectivity degrade or change the network are known as **network-modifying ions**.

Quartz glass, consists of SiO_2 , is the only industrially utilized single component glass.

Excellent dielectric properties
 High chemical resistance
 Very low thermal expansion co-eff.
 High temp. stability
 Very high transparency to UV-light

Network formers	Network-modifiers	Amphoteric cations
SiO_2	Li_2O	NaO
GeO_2	Na_2O	Ga_2O_3
B_2O_3	K_2O	In_2O_3
P_2O_5	Rb_2O	Sc_2O_3
As_2O_3	Cs_2O	Y_2O_3
Sb_2O_3	MgO	La_2O_3
V_2O_5	CaO	SnO_2
	SrO	PbO_2
		ThO_2

So, these network formers as well as one other variety will be calling as network modifying ions what are those ions? The ions which through lower connectivity degrade or change the network; that means, silicon can have a particular connectivity which equals to 4; that means, can have 4 oxygen surrounding that particular silicon. But if we go to use that particular other methods the other ions based on boron or aluminum, what

do you get the boron and the aluminum is happy or can satisfy its corresponding bonding by forming 3 boron oxygen or 3 aluminum oxygen bonds.

So, basically it can have lower connectivity that is why it degrades or changes the network structure, whatever we have the original network structure that will be degraded due to the addition of these network modifying ions. So, we can have categorically a large list basically, but do not worry about all these things to memorize all these things, but the basic idea of what we gave that some of these basically if we start from silicon dioxide SiO_2 to up to vanadium pentoxide.

So, SiO_2 silicon dioxide, germanium dioxide, boron oxide phosphorus pentoxide, arsenic oxide, antimony oxide and the vanadium pentoxide. So, all these are basically being classified as the corresponding network formers, but if we add not that boron, not that aluminium, if we add to that some of them like that of your aluminum, lead, titanium dioxide, zirconium and the thorium dioxide.

So, a mixture of these two oxides can give rise to a one particular type of product, but those are empathetic cations, but the network modifies which can modify the network is basically the first example what we will consider over here is your sodium oxide. So, if we add sodium oxide Na_2O plus SiO_2 what you expect we basically Na_2SiO_3 we get which is nothing, but your sodium silicate. When it gets hydrolyzed in presence of water it can be water soluble also, so we call it as a water glass.

So, the sodium silicate and this thing is very easily obtained from the reaction of SiO_2 with that of your sodium oxide or Na_2O . So, you see like that that sodium oxide you can have lithium oxide to lead dioxide. So, all these are under the category of network modifier, so we can have a large number of or the large varieties of these glass materials through the introduction of these different types of oxides only, as we all know the inorganic chemists are always happy to have a huge periodic table to handle.

So, we will have large number of oxides the basic oxides sometimes the empathetic oxides and acidic oxides. So, if we can balance all these things and if we get something which is a composite of all these oxides and high temperature firing of that will give you a glassy material. So, we can change or we can enhance property wise of all these glassy material or the glass.

So, the first type we consider as the quartz this can also be very useful for making the windows of the spectro photometers, then the quartz cell also to take the corresponding sample within the cavities of those cells the corresponding simply visible spectro photometers what we can have? We can have the corresponding quartz cells, the quartz cells are utilized because you are recording the spectrum from the visible range to the ultra violet range.

So, when you go to the ultra violet range we must have this particular quartz cell or the quartz glasses. So, which consist of SiO_2 and is the only industrially utilize single component glass. So, it does not have any other oxide it will have only SiO_2 . So, a particular variety of only SiO_2 is your quartz variety. So, why do we use all these things? Because they have excellent dielectric properties.

So, the dielectric properties are very well so glass can also function as a very good insulator, glass material starting from your window pane to any other glassy environment or the glasses for the automobiles or any other places, it can have high chemical resistance which is a very important thing. So, it can have good acid resistance, it can have good basic resistance also. So, any other material even your working top table top in laboratories can be made of glass.

So, these glass even if you go to your kitchen it can be of your glass and what sort of glass because it should be affordable, it should be pretty cheap such that we can use the corresponding thick of the glass thickness of the glass what do we use in our office tables also. So, it should have a good chemical resistivity such that it should not be attacked by acid or it should not be degraded by the acid that is why the glass containers what do we use in the laboratory common glass containers the, the beakers, the borates the (Refer Time: 22:54) and many other down bottom flasks and all, we know the standard material what we use is the boro silicate glasses.

And those boro silicate glasses are also acid resistant also are base resistant and sometimes only one particular type of thing; that means, it is the hydrophloric acid which can only attack that particular type of glassy material, otherwise it has very good chemical resistance. Then it can have low thermal expansion coefficient such that with the change in the temperature, there should not be good very good expansions such that there will be a crack.

High temperature stability such that with the rise in temperature it will not break and very high transparency to the UV light what I just know I told you, that if you are handling the ultra violet ray for recording your spectrum in invisible spectro photometer you should take care of the thing that says that you are ultra violet light or ultra violet rays are passing through those material which is made up of SiO_2 .

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Flat glass and hollow glass are soda-lime glass with the approximate composition.

Lead glass suitable for fine glass articles (crystal glass), optical glasses and television tubes.

Glass ceramics largely consisting of fine crystalline phases formed upon heating at the nucleation temperature and then at a nuclei growth temperature.

Glass Manufacture

Glass Raw Materials

Sand, lime, dolomite, sodium carbonate, feldspars and other aluminium silicates, boric acid and boron minerals, cullet (broken glass) from the plant itself.

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Then what we go there, that another variety of glass which is known as the flat glass the other varieties also known as the hollow glasses are basically soda lime glass. So, when you introduce sodium oxide we know that it get the corresponding sodium silicate so we know the soda glass we know now. Now we are putting lime is nothing, but your calcium based compounds; that means, calcium oxide or calcium carbonate or calcium hydroxide. So, when both of them together the nature of the glass is changing. So, we can have both sodium as well as calcium in your soda lime glasses with some rough or approximate composition of the material.

Then we can have the lead oxide; that means, the lead glass, if we have the lead glass just now what we have seen that the lead oxide, the lead dioxide we have considered as the corresponding material for the glass. So, it's suitable for fine glass articles; that means, that crystal glass the flower vases what we buy in the market and what do we use for decorating our home.

So, the crystal glass material the flower vase or any other glass cutting for the your different types of containers that crystal glass what we can have that particular crystal glass can be obtained from your lead variety; that means, addition of lead oxide or lead dioxide can giving you those glasses. Then optical glasses another variety of useful glasses we can make and also the television tubes what we can have.

Then glass ceramics another particular type of thing is known as glass ceramics will be considering when we separately considered the ceramic material or the ceramics, but right now what we see that a particular type of composite material if we consider that the glass serum is largely consisting of fine crystalline phases formed upon heating at the nucleus and temperature.

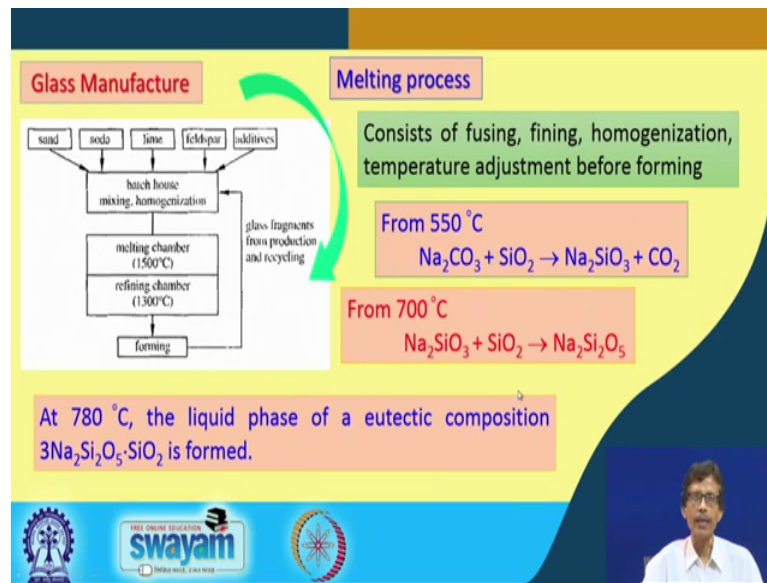
So, there will be some known nucleus and temperature and then at a nuclei growth temperature. So, the adjustment of the temperature or heating of that particular material at two different temperature can give rise to a particular type of variety which is known as your corresponding glass ceramics.

Then how we use those as your typical glass manufacturing process and those glass manufacturing process are very difficult to know and we have must select those glass raw material and what are those raw material just now what we have seen, that you can have the soda, you can have the lime for the soda lime glasses. So, stepwise you now see that we can have sand already we know that sand is SiO_2 . So, then we can have the lime we can have therefore, the calcium carbonate or calcium oxide then we can have the dolomite the corresponding varieties of sulfates.

Then sodium carbonate, then feldspars and other aluminum silicates boric acid boron minerals and sometimes the cullet the cullet is nothing, but your broken glass the glass material from the broken material or the corresponding throw away material what we can reuse; that means, the glass making of the glass is typically a well known recyclable process from the plant itself.

So, if we have some discarded material or the discarded or the broken glass material already in our hand, we can reuse it with the addition of the other materials stoichiometrically to get these particular mixture of all these raw material for making of this glass.

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So, this glass manufacture that way is a very important one where we can have the corresponding sand, soda, lime, feldspar and the different types of additive. So, we can have a batch house where we mix all together and all of them is getting when you have a typical homogenized mixture. So, homogenization process we can call, then we put simply put at a very high temperature reactor.

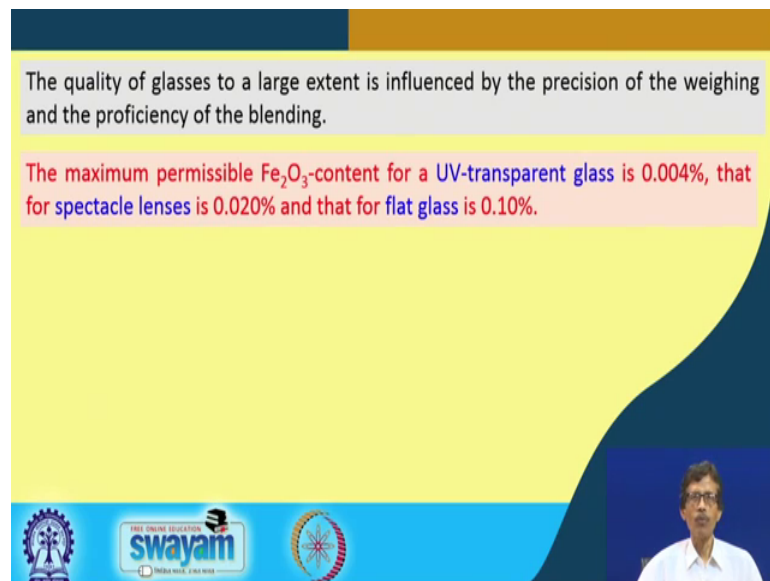
So, the melting temperature where the all the ingredients will be in the molten condition or the molten state, then at that particular temperature when everything is mixed nicely at a very high temperature not very high it is only 1500 degrees indicate which we can make any time in a chamber or in a furnace. Then we can have slowly we cool down that particular one such that we can have a refining chamber; that means, the corresponding one can start solidifying at a lower temperature which is 1300 degree centigrade, then the glass forming temperature can be reached over there.

And we can cycle back the glass fragments from the production and the recycling process; that means, the forming process then we put in the batch house, mixing homogenization and again it can undergo with that corresponding temperature annealing. So, we can have the typical melting process and what are those process, what is happening there during the melting process? The melting process basically consists of the fusion, fining homogenization and temperature adjustment before forming.

So, at the last step what we get as the forming process and the reaction wise what we find because it started reacting at 550 degrees centigrade with sodium carbonate what we can have as the corresponding material, what we already added with that of your sand. So, sodium carbonate will be reacting we also seen that you can see consider it as the reaction in sodium oxide, giving you sodium silicate at 550 degrees centigrade, then after that we can have at 700 degrees centigrade further SiO_2 can react with Na_2SiO_3 given Na_2SiO_5 .

And at 780 degree temperature the liquid phase at it eutectic composition of this which is $3\text{Na}_2\text{Si}_2\text{O}_5 \cdot \text{SiO}_2$, which is like that of your SiO_2 which can be formed as a corresponding formula, but which is not in the typical component of the whole material which is form. So, a particular eutectic composition is formed and formed that basically we get the corresponding glass as the corresponding solid material.

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The quality of glasses to a large extent is influenced by the precision of the weighing and the proficiency of the blending.

The maximum permissible Fe_2O_3 -content for a UV-transparent glass is 0.004%, that for spectacle lenses is 0.020% and that for flat glass is 0.10%.

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And during that particular process the quality of the glasses to a large extent is influenced by the precision of the weighing and the proficiency of the blending, what type of blending we go and what are the corresponding ratios basically will be using for that particular blending process. So, is basically nothing, but a mixture at a high temperature mixing and blending will give you this particular glass material.

And we continue this to our next class where will again consider these as the correspond level of other material what we can have starting from your Fe_2O_3 or any other things.

So, component wise if we add one after another we can improve the quality of those glass material ok.

Thank you very much.