Industrial Inorganic Chemistry

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Lecture – 41
Barium and its Compounds

Hello. Welcome everybody to the class where we are talking about the Industrial Inorganic Chemistry on calcium.

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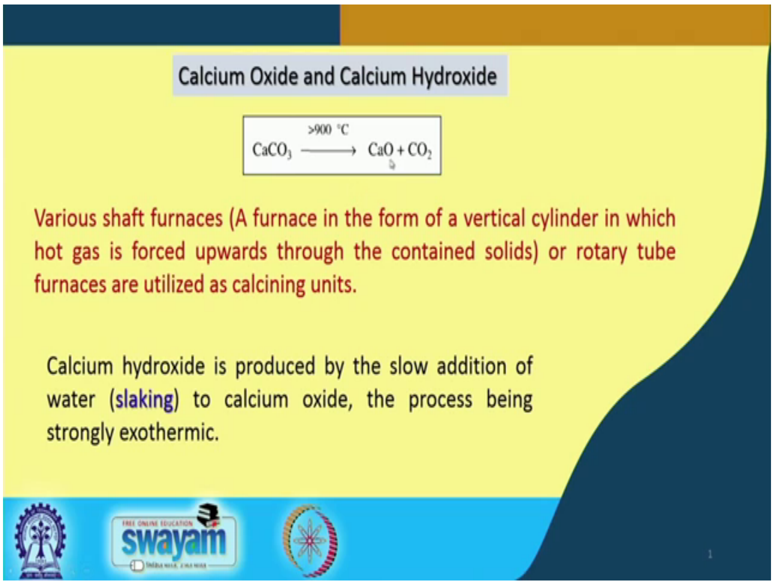

So, we have seen that how we can get from the natural sources, the natural resources the calcium oxide and calcium hydroxide and we have seen how these can be processed for calcium oxide to the select line using different furnaces. So, this we have discussed last time and the reaction, particularly the reaction when we talk in terms of the corresponding industrial inorganic chemistry of the calcium metal ion, how we get that calcium and that calcium can be converted to some useful compounds which will be industrially important.

So, one of the very interesting reaction was therefore, is your slaking thing; that means, the addition of water to the calcium oxide to give you calcium hydroxide and this calcium oxide is very well prepared from burning of calcium carbonate.

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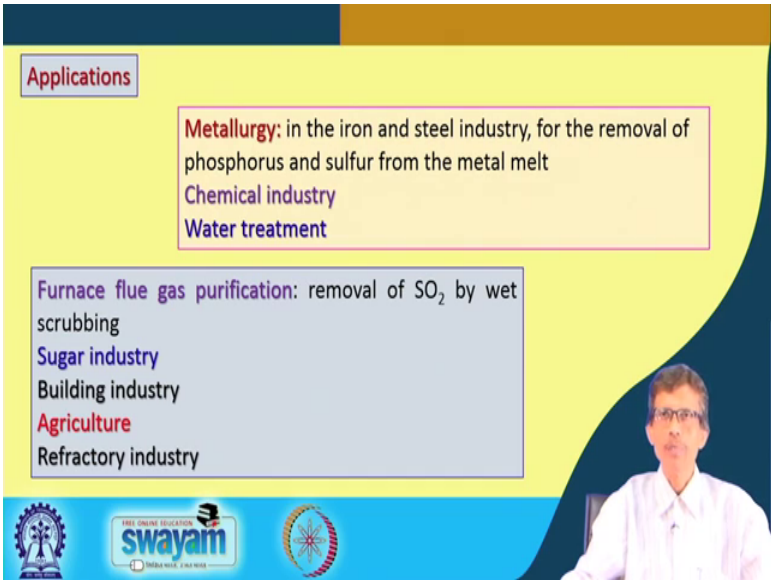

Next, we see that how we can utilize these; that means, the calcium based most important compound is your calcium carbonate what we get naturally also that limestone. So, that limestone as well as the different other compounds has huge application and slowly we are trying to know that if we have some importance of these calcium in our life processes also. So the medical science will be benefited, the life science will be benefited as well as the health science because, the calcium is there everywhere in our body also we go for calcium deposition in bones to teeth to everywhere.

And calcium is also present we know in the typical photo system where we know that the oxidation of water the water oxidation center, you have a manganese cluster belong to four manganese center along with one calcium center and the typical role of that calcium is still unknown, but you see the utilization of calcium is there. So, various utilization and applications will be there we starting from another sector of industry such as that of our metallurgical engineering.

So, people who are talking about the metallurgical things and the metallurgy which will be dependent on the use of calcium. So, the materials which we get from the metallurgy of the calcium sources is that, we use that in iron and steel industry because this particular calcium can be utilized for removal of phosphorus and sulfur from the metal melt.

If we try to get a very pure quality of your calcium melt and the calcium cast afterwards and the calcium bar afterwards, so we have to remove the impurities like sulphur and phosphorus. Then, it has huge application in chemical industry and how we get the different compounds from this particular starting material as the different useful compounds such as your calcium hydride.

Earlier, we have seen that how we can use the different useful reducing agent like borohydride and aluminum hydride such as that you get sodium borohydride or lithium aluminum hydride for different chemical reactions as well as in chemical industry. So, these calcium hydride is also useful if you can make that calcium hydride from calcium oxide or calcium carbonate. That calcium hydride can be useful for the purification of the organic solvent such as your dichloromethane or any other useful solvent where we can remove the impurity which can be removed through reduction using calcium hydride.

Then, for water treatment also, we use calcium carbonate and calcium hydroxides and one most important application regarding the furnaces where we use huge furnaces in the industry. So, the furnace flue gas purification. So, flue gas is coming out say we burn something where the sulfur dioxide is formed and that burning of that particular process we get huge amount of sulfur dioxide from that particular furnace.

So, how we remove that particular sulfur dioxide because removal of the particular sulfur dioxide can be useful. If we are able to convert that sulfur dioxide to sulfur trioxide because as we have seen earlier that particular sulfur trioxide if we make it from sulfur dioxide, can be useful and we can use it for making of sulfuric acid; that means, sulfur trioxide plus water will give you sulfuric acid.

So, this particular technique which is known as wet scrubbing also that wet scrubbing; that means, you get in presence of the water; that means, in presence of water, you take out that sulfur dioxide and if you go for a base treatment of that sulfur dioxide, so you get the different sulfide salts as well as the sulfate salts from that particular recovery.

So, this particular recovery process from the different furnaces because huge amount of those things are coming out and it is also a very important area of understanding as well as research that you cannot leave all the gases to the environment because the environmental restrictions will be there. So, you have to convert that particular gas and if the gas is saturated with sulfur dioxide, you have to trap that particular sulfur dioxide and use it or convert in regular either in solution or in the solid state that the converted form of sulfur dioxide.

Then, it is used in sugar industry, the building industry like the building material for cement making also, in agriculture also, and in refractory industry. Because, in agriculture and some other cases, we get or give the corresponding line the limestone powder or sometimes the slack line to adjust the pH of that particular soil medium. So, control of pH in the soil medium can also be achieved through the use of different calcium base salts.

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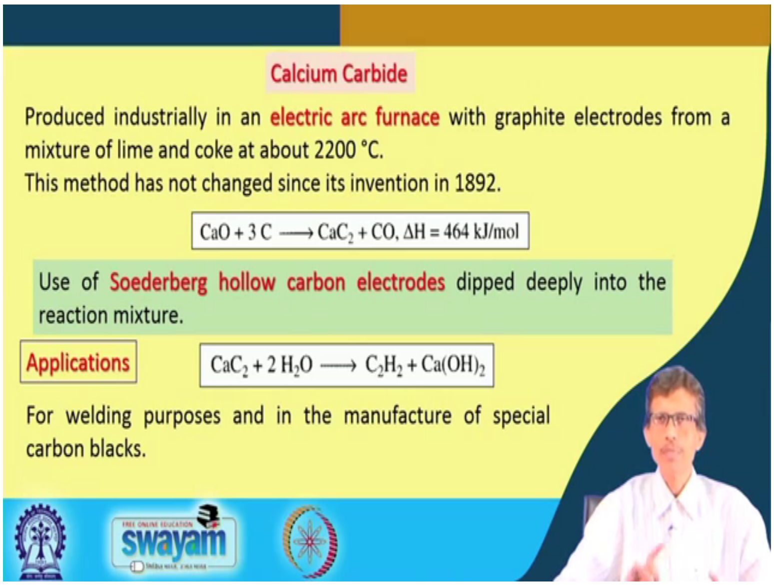

Then, one most important compound will now proceed for studying is that how we get that because we have already seen that you have calcium carbonate in your hand from your limestone, you burn it you get calcium oxide and when you go for slacking of that calcium oxide, you get calcium hydroxide. Now, we directly move to very useful compound and it is the only compound which can be obtained as its corresponding calcium salt only.

So, it is the interesting area of understanding industrially which is also important that you make those as calcium salts. So, calcium can be provided from calcium carbonate or calcium oxide, but whatever other part the anionic part will be doing by using that particular calcium because the other salt you can have sodium, you can have potassium or you can have ammonium as well, but those salts are not so stable, not so rugged also and industrially it is not also cheap.

So, the first of that category is your calcium carbide, CaC 2. How we make that particular calcium carbide is very simple reaction that if you have that calcium any source of calcium and reacting that with the carbon. So, carbon will be the direct source and calcium is not in it is elemental form, but most cheaply available form of calcium oxide, calcium hydroxide or calcium carbonate.

So, basically, we prepare at a very high temperature reaction of 2200 degree centigrade in electric arc furnace and in that particular electric arc furnace using graphite electrodes from a mixture of lime and coke. So, this is a very simple reaction you take lime. Lime is very cheaply available and coke is also very cheaply available. But you do that particular reaction; obviously, at a very high temperature and that particular high temperature reaction can give you something which is pretty costlier one. Because at one time, it was having a very high demand in the industry because we are using so many other compounds from calcium carbide.

But it was invented long back around 100 and 20 or 30 years back in around 1890 or 92, people first discovered this particular process when nothing was known very well and they got it and they characterize it as the corresponding form as a CaC 2 molecule. So, you react calcium oxide with three carbon giving you calcium carbide CaC 2 plus removal of carbon monoxide. And that removal of carbon monoxide can be useful what do we get that we have to remove that particular carbon monoxide such that we can recover this calcium carbide.

So, we what we use for this high temperature reaction, we use a particular type of electrode and which is also known as hollow carbon electrodes and those hollow carbon electrodes were first invented by Soederberg and its named that is why, Soederberg hollow carbon electrodes. So, that means, is a not a solid carbon electrode but is the hollow carbon electrode, but we will dip it in the into the reaction mixture.

So, the reaction mixture is a basically a solid mixture of calcium oxide and carbon and the coke or sometime you can use also charcoal. So, the coke and the lime when it is mixed and you put the hollow carbon electrode and that hollow carbon electrode is going inside and within the hollow space, your material also can enter.

So, once we make this calcium carbide, now the question comes that how we can use that particular calcium carbide for some other very useful purposes. So, do not forget it that where from we have start it started our journey. That with limestone, we have started our journey; so from limestone, we moved to different calcium fragments, then that calcium fragments; that means, the calcium salts like calcium oxide or hydroxide has been converted to calcium carbide.

So, how we directly use that particular calcium carbide? Why calcium carbide is so useful is the very interesting reaction, we all know because we study this from our school days that reaction of calcium carbide with the addition of water molecules giving you acetylene gas and it is the basic principle for getting your the corresponding acetylene flame or acetylene lamp earlier we used to light our domestic places or domestic houses.

So, you very cheaply and very useful way, you can generate acetylene because these acetylene can be useful also for high temperature flame generation as we all know that the oxy acetylene flames. So, if we try to go beyond 2200 or beyond 2600. So, we use a oxy acetylene flame for welding purpose or for arc welding and all these things. So, this can be some process where you can in situ generate acetylene gas because it has huge application in chemical industry as well as in chemical laboratories, particularly the different R and D laboratories.

So, this particular acetylene, we use CH; CH you have acetylene molecule. You all know that is CH triple bonded CH and that acetylene it can also be utilized for modification of different pharmaceutical or other important organic molecules. But for industrial purpose, it is very much used for welding in the manufacture of also in the manufacture of special type of carbon blacks because it is a useful source of carbon also.

So, when we burn it, high temperature cracking can give you carbon back from the acetylene gas is a gas which make it from coke. So, coke has been converted earlier to carbide and that carbide to acetylene and that acetylene further can be cracked down to give you a carbon variety which is different from your coke. So, specialty type of because the nowadays we know that the different types of carbon particles, the nano carbons the carbon tubes and all these are very useful.

So, special type of carbon blacks which are catalytically important also because the carbon blacks we all know, it gives you a huge surface. So, it is as a corresponding catalytic effect also. Then, we know that it is very useful reducing agent is the palladium charcoal. So, a special type of carbon black or charcoal can be prepared by simply burning your acetylene gas which we may not get from burning of methane or ethane.

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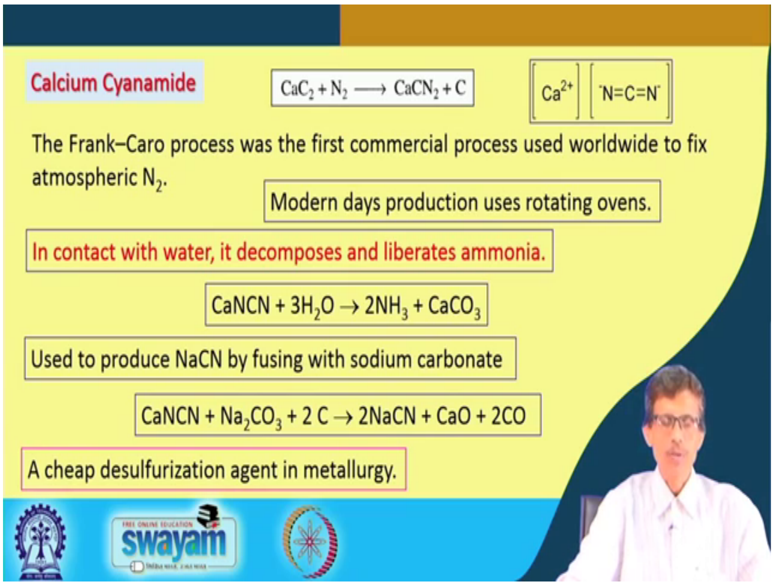

Then, proceeding further, we go from calcium carbide to calcium cyanamide. So, cyanamide, so you have some amide function and we have also the corresponding cyanide; that means, the C N function. Already, what we have seen that in case of your calcium carbide though we write it as CaCN 2, but when we write that is a calcium cyanide, calcium cyanide is CaCN whole 2. You have a bracket and over that, you write that 2 but it is we write some time by writing two nitrogen together, we write CaC 2. But most appropriate one of way of writing is your Ca N C N.

Because the species the anionic part itself is N carbon N; N double bonded carbon again double bonded nitrogen, so, that we get like this. So, you have the cationic part as calcium 2 plus and anionic part is N C N part. So, best way of writing this molecule as Ca N C N and that N C N is your corresponding cyanamide we get. So, that cyanamide we are getting from carbide. So, definitely, what earlier we had in case of your carbide which is producing your acetylene.

So, acetylene has the corresponding carbon carbon triple bond and on the both the two ends, you have the hydrogen atom or hydrogen centers attached to it. So, in carbide, what you are making by making that carbide from coke, you are fusing two carbon centers together making a carbon carbon triple bonded species which is a very strong one and one and which is very robust one. And from that basically you have a carbon carbon triple bonded situation that you now break it through the introduction of nitrogen and you are making something where carbon is at the center and on the two sides, you have the nitrogen.

So, a complete change in the corresponding positioning of the atoms in the species, the anionic species from carbide to corresponding cyanamide, so you should know very well that how this particular species and the structure is known to you. What is the structure of the anionic part Ca C 2, 2 minus and what is the corresponding anionic part which is C N 2, 2 minus. It is the process known as the Frank Caro process and is the first commercial process worldwide people were utilizing to fix atmospheric nitrogen.

Because fixing of carbon is not a challenge, we can fix it in some important compound through coke or charcoal with the help of calcium. So, get calcium carbide. Now, that calcium carbide can take up huge amount of nitrogen from atmosphere. So, it is a particular process of fixing nitrogen as we have seen earlier that we can fix nitrogen by making that nitrogen to ammonia and that nitrogen can be converted to your urea.

So, this particular process basically, what we use in modern days is the production by using rotating ovens. So, ovens are there with time is it can rotate. So, the whole thing can be have a slowed motion and you get the corresponding stirring procedure for that particular preparation. So, when you make it; that means, you prepare Ca N C N molecules through the absorption of nitrogen and it presents of water what is forming? Earlier, we have seen that calcium carbide when it is reacting with water molecule, it is producing you giving you acetylene gas.

Now, in contact with that water, cyanamide also decomposes very easily giving you ammonia. So, our goal is fulfilled that through some procedure, we try to absorb nitrogen, the atmospheric nitrogen is being fixed which is a very difficult task. Biologically, it is available the plants, the leguminous plants, they basically fix the rhizobium, can fix the nitrogen directly from the atmosphere to your nitrates and nitrites only.

But here, if we want to get the nitrogen from air to ammonia, it is the process through which we go basically. So, you always keep in mind that we can go for the fixation of atmospheric nitrogen through a calcium salt or a calcium compound which is nothing but your calcium carbide, then calcium carbide to calcium cyanamide and that calcium cyanamide is getting hydrolyzed producing ammonia.

So, the reaction is typically a very simple reaction but very useful reaction. You can try to understand it, you can try to remember it very well because it is producing ammonia. So, you have two nitrogen atoms present in your calcium cyanamide and both the two nitrogen's are getting converted to your ammonia. So that means, it is getting hydrogen from water molecules like that of your getting hydrogen from water molecule by your carbide anion, similarly your cyanamide anionic part is also getting hydrogen from water molecule. So, that is also a very useful procedural that you get nitrogen originally from atmosphere and now you get hydrogen from water molecules.

So, these are the very well known cheap sources to us such that we get a value added compound which is your ammonia molecule. So, this can be apart from your Haber process or ammonia formation process. This can also give you a very good idea that how you can have a alternative procedure where you can make ammonia through some calcium process where calcium salts are utilized where both nitrogen is coming from air and water is giving you the hydrogen for your ammonia formation and the cationic part of calcium in presence of your calcium cyanamide salt, it is being converted to calcium carbonate.

So, carbon present in cyanamide is getting converted to carbonate. So, you see that carbon was there which is bound to two nitrogen; one in the left and another on the right is getting converted to a species where carbon is at the center. And you have now three oxygen attached to that particular carbon center because carbonate we know that is a trigonal planar molecule. So, you convert again back the calcium carbonate which is our limestone.

So, we are getting back indirectly that calcium carbonate back. So, if you are use that particular calcium carbonate, what has been your by product now. So, that calcium carbonate again can be utilized. So, you can get a regular cycling process where you start with calcium carbonate, you produce ammonia and then again you recycle back the calcium carbonate what has been produced so far. So, this is a very useful reaction and industrially also very useful and you can understand in that way that how we can utilize calcium carbonate for the preparation of ammonia.

It is used to produce calcium cyanide also. So, calcium cyanamide to calcium cyanide by simple fusion with sodium carbonate, so now, you use something which is your sodium carbonate and that sodium carbonate is doing some other type of reaction compared to the previous one which is a very simple reaction. So, the reaction of calcium cyanamide, so you get some understanding that, the reactivity of calcium cyanamide which is pretty good also because it can react with water as well as it can react with sodium carbonate in presence of some charcoal.

So, you apply not only the carbon source as sodium carbonate, but you add some extra carbon as the charcoal powder to react or convert the entire amount of N C N the entire amount of N C N can be converted to your C N molecules. So, the whole amount of N C N because what you need, because the atom balance wise if you consider that N C N has one carbon and two nitrogen. So, you have to put one more carbon making it to C N or C N twice like your cyanogen gas. That you can cut it by through this two carbon if you consider, that you have carbon thing also there.

So, in terms of that, you can consider that you get that particular species; that means, C N minus the cyanide species and that particular cyanide species can be achieved in your hand if you add that particular reaction through the addition of extra carbon. So, that extra carbon introduction into the system will convert your cyanamide to cyanide only and your calcium thing what was present will be converted to calcium oxide and the carbon of carbonate will be reduced to carbon monoxide.

So, it is basically a reaction where your carbonate is converting to both oxide as well as corresponding oxide ion giving you calcium oxide as well as your carbon monoxide. So, is this particular process is also utilized for desulfurization process because you can take out the sulfur present in the metallurgical processes. So, it is a basically a very useful desulfurization agent in metallurgy.

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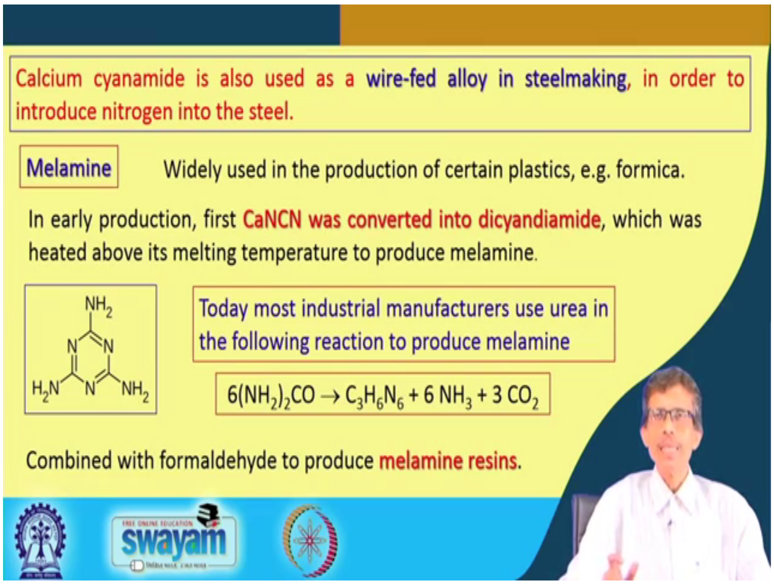

This calcium cyanamide is also used very well for wire fed alloy in steelmaking. So, while we make this particular steelmaking and wire fed wire fed alloy, a particular type of alloy if we make by the introduction of elemental nitrogen into the steel. So, nitrogen cannot go through any other nitrogen salt or nitrogen from the air but it can grow via calcium cyanamide.

Then, one most important molecule we will talk about because it has a huge demand in the industry and it is also a good news in the production sector where the China is producing huge amount of melamine is a white powder and the contamination of the baby food and the baby powder, milk powder is this news in this end time.

So, what is that melamine? So, melamine is nothing but a certain kind of plastic and which is widely used for making of a plastic type of seat, the mica type of seats, Sunmica we usually called when we the table surface or any other surface we put, we know that we always say that we are putting Sunmica. Sunmica is a brand basically sun brand Sunmica type of thing, but is basically a Formica.

So, that kind of plastic can be made out of that melamine and its polymerization process. So, in the early days, calcium cyanamide was first converted to dicyandiamide basically. So, you have N C N type of things. So, you can put another carbon nitrogen attached to 2 C N unit. So, center you have nitrogen and attached to 2 C N unit; one left and another right. So, you are getting more branching like that of your carbon at the center you have

2 nitrogen. Now, you have nitrogen at the center and 2 cyanide groups there, that is known as your dicyandiamide.

So, dicyano groups are there attach to your amide function. Amide function we know that is attached to your nitrogen, attached to hydrogen, we call it is N H 2 minus which is your amide. So, that amide when two hydrogens are substituted by your cyanide ions, it is known as dicyandiamide. When it is heated above its melting temperature, we produced melamine.

So, I gave the clue reaction wise that what is your cyanamide, how we get that cyanamide from carbide, now we move to dicyandiamide and we heat it now. So, can we expect at that this particular point that what is the molecular formula of melamine because the process is given to you. So, you should have some idea you should be able to think because your thinking process is also very important to know that what molecular transformation is taking place though we have huge number of avenues; one is very difficult to achieve is the industrial processes which we cannot replicate in the laboratory and the reverse is also true whatever we make in the laboratory cannot be going to the industry next day.

So, this is the typical balance because we have to think something as for our R and D sector; that means, Research and Development, we study some of the reactions, some of the products, some of the metal ions and there compounds and at the same time how we can produce that in large scale. If we are able to prepare some compounds in the milligrams sale scale say 50 to 100 milligram in the laboratory, we cannot think that the next day we will be able to make that compound in a 50 gram or 50 kilogram scale in industry.

So, the molecular processes and we always consider at lower concentration; that means, the laboratory scale, R and D laboratory or any other teaching laboratory, any other laboratory you get that particular one. So, when we heat it, what is that molecule? That molecule is a very beautiful one is a organic molecule. Now, you go for a cyclization process. So, already you have a linear carbide, then against cyanamide is also a linear one, nitrogen and two ends you have carbon.

But when you go for the amide; amide is typically a angular one. So, nitrogen 2 C N unit left and right, so that particular angular molecule is getting fused. So, getting fused, fusion of this particular unit by a backbone of only carbon and nitrogen and hydrogen since like a making of borazine type of molecule, so we know that borazine as the inorganic benzene. So, this particular one is also some kind of aniline type of derivative.

So, we know that meta phenylenediamine or is a triethylenetetramine. So, it is basically a phenoline triamine type of thing and that particular one having 3 nitrogen's in the ring also. So, what we get there is the most industrial manufacturing processes, they do not go through the process where we use that dicyanamide for the preparation of melamine but it was the discovery we should know how people can go for that and industrially when we use a large amount, because urea is also a costly one we cannot go through this particular one. But if you go for urea which is the cheaper variety, you can make urea very easily.

So, that urea can be converted to melamine, but previously if we get that through dicyanamide that time dicyanamide is the only proceed process where from we get the melamine. Now, urea is cheaper one compared to your dicyanamide and use of dicyanamide was also not there because the urea we use as agriculture. So, large amount of urea we produce industrially also.

So, the industrial scale of production of urea is basically tempted asked to prepare melamine through that particular process where we use urea. So, again, this is the basically a solid state burning process and that particular solid state burning process what we get is simply the burning at a high temperature burning process. So, urea you have and urea is also like that of your dicyanamide or your cyanamide having carbon nitrogen hydrogen bearing compounds. So, urea is also one extra thing is that you have also oxygen in urea.

So, that oxygen has to be removed from there and when you go for this burning process, you basically get back some amount of ammonia as well as carbon monoxide from that particular reaction. So, during melamine preparation, we also get back some amount of ammonia. So, if we use industrially the particular reaction, so, industrial scale of production of melamine can also produce 6 molecules of NH 3.

So, that huge amount of ammonia what we make over there, so that huge amount of ammonia once we get, that ammonia can again be utilized, so, this is a by-product. So, the utilization of by-product can also be very useful process where urea can again be trapped for making sorry ammonia can be trapped for making urea and that urea can again be utilized for your melamine preparation.

So, when it is combined with formaldehyde, because we all know that formaldehyde can give some time the polymeric species that urea formaldehyde we know get, get some resins a Bakelite we know. So, you formaldehyde always we have formaldehyde is CH 2 O. So, when this particular species that CH 2 O is reacting very fast with some nitrogen bearing compound is basically can link between two nitrogen giving you a methylene bridge; that means, C H 2 is coming as the methylene bridge. So, you get a methylene bridge polymeric structure which is also true for Bakelite. So, you get here as the melamine resins.

So, you have the eminents and that eminents is reacting with your NH 2, sorry CH 2 N of the formaldehyde and that CH 2 N basically linking that particular species.

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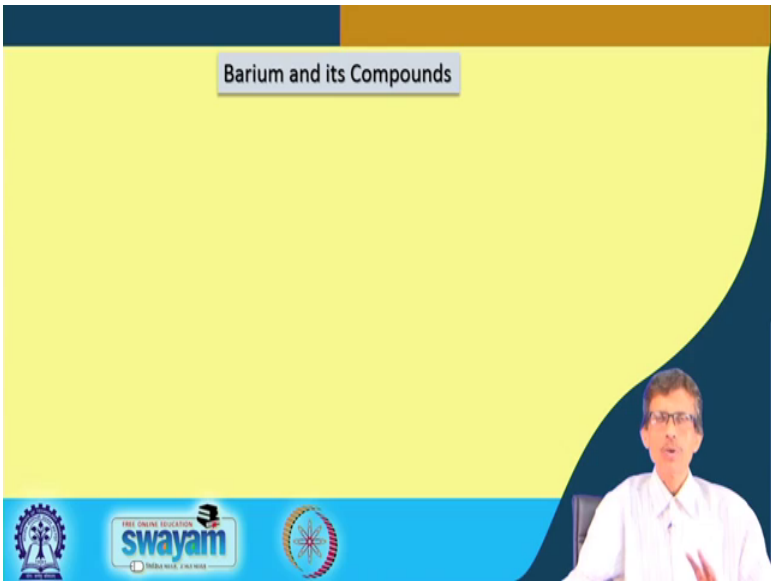

So, this is all about your nitrogen and the calcium and some useful nitrogen compound based on calcium. So, we will proceed for after calcium to the barium compound, but before we finish here, we will just 1 or 2 minutes we will just take for saying these thing that when we get these that you get the melamine itself is a material. We know that nowadays that household cook wires, the plates, the dining plates, all we get for the melamine material.

So, with formaldehyde we can improve the resin material. So, this particular one use of melamine, use of formaldehyde giving you an another area where you make new types of resins. So, we can add some other compound to it such that you can get a basically a composite material and that composite material based on melamine can have some other useful property and that useful property can also be industrially very important for making some application; that means, the sealing agent or some covering agent, we can use with all those resins.

So, resin industry can also be benefited if we go for the melamine. But, we have moved from calcium to the preparation of melamine, but we will be with that calcium because in the next class, we will be talking about the next element which is your barium.

Thank you very much.