# Industrial Inorganic Chemistry Prof. Debashis Ray Department of Chemistry Indian Institute of Technology, Kharagpur

# Lecture - 54 Ferrites and Porcelain Enamel

Hello and welcome back to the class, once again where we are talking about the different titanates particularly one example I have given is your barium titanate.

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Ferrites	Two ty	Two types			
	Cubic ferrites (soft ferrites) M <sup>2+</sup> Fe <sub>2</sub> <sup>3+</sup> O <sub>4</sub> Used in recording and erasing heads for tape recorders, ferrite antenna.		Hexagonal ferrites (hard ferrites) M <sup>2+</sup> Fe <sub>12</sub> <sup>3+</sup> O <sub>19</sub> Used in DC-motors, alternators, magneto-igniter, magnetic couplings etc.		
Refractory Ceramics Exhibit a cone-fusion point of minimum SK17 in					
Alumina-R	Rich Products	the Seger cone test			
Aluminum silicates, bauxite, bauxite+kaolin, corundum used. Mechanical pressing of mixtures of granular raw materials and binders and then firing.					
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So, like that of your titanate if we go for the ferrite material, because we all know that the ferrite materials are also very much useful as the solid state material inorganic solid state product. But under the category of ceramic, we can have that particular application of these ferrite material.

So, application of these ferrite materials can have in our hand and we basically make types of these ferrite materials. And, these two types of ferrite materials two are industrially very important and definitely these are all iron based materials.

So, these iron based materials when we get, one particular variety is known as your cubic ferrites. So, the structure is having a solid state cubic structure, it has and these are depending upon it is utilization, it is known as soft ferrites. So, soft ferrites is basically is

iron oxide based material we know that iron it can you have with that the corresponding ferric oxide, or ferrouso ferric oxide like that of your F e 3 O 4 or Fe 2 O 3.

But, if we can have something which are having some kind of spinal type of arrangement; that means, it is not typically Fe 3 O 4, but it is Fe 2 O 4 type of thing along with some amount of M as the bivalent metal ions present in it.

So, the formula of that particular material with a bivalent material like, your barium like, your calcium like, your magnesium, which will be your barium Fe 2 O 4. Like your chromite we have seen earlier that the chromium getting material chromium based material your, typical material which is naturally available also the erode material is your chromite. Chromite is your chromium based oxide material having some amount of iron. So, similarly any other divalent is M 2 plus can be present over there with the basic unit is there Fe 2 O 4, it is neither F e or F e 2 O 3 nor F e 3 O 4 it is something else like your chromite which was your that is here 2 O 4.

So, it is F e 2 O 4. So, this F e 2 O 4 and both the ferric centers present in this molecular formula or the solid state formula or the chemical composition of the material is in the trivalent state; no ferrous state is present. So, you have the ferric state present, which is 2 unit and the charge balancing for the 8 negative charges from the 4 oxygen center will be balanced by one single bivalent ion as M 2 plus.

So, this M 2 plus is therefore, giving us M F e 2 O 4 material as the soft ferrite material which is cubic M 1, and is used in recording and erasing of heads for tape recorder. So, tape recorder we know the tape is moving and we know that the corresponding recording item is there. So, corresponding head is there. So, recorder head and sometimes it can also be utilized for the erasing purpose, and also for the use of this particular material as your ferrite antenna.

So, for your electronic application or some sound application for their corresponding tape recorders, we use these as the very useful ferrite material and from the iron sources basically iron oxide sources, we get these ferrets as a typical ceramic material. So, is a specialty ceramic material under the category of the ferrites. So, following cubic you have now the another variety since I told you that you have two types, one type is your cubic type and another type is your hexagonal type.

So, hexagonal type is of different type and is known as the hard ferrites; hard ferrites having a different formula, basically you know the large number of iron is there in the unit formula, which is F e 12 now. F e 12, but less oxygen, because earlier you have F e 2 O 4 the double amount of oxygen now is not the double is less than that amount. So, 19 oxygen you can have instead of 24 and only a single bivalent M 2 plus is one again once again it is there. But this ferrite material as the core substance when we coil for the different types of DC motors.

If, you have seen that some DC-fan motors, because nowadays what we use that the AC fans, but the DC-fan motors how we use how we get the corresponding coil for the entire motor and how we go for the corresponding armature and all this. So, use they are basically used as the ferrite material.

The DC motors we have, then alternators we can make out of this particular hexagonal ferrite material, then magneto igniter and magneto couplings. So, the electromagnetic application of all these ferrite materials, we can have and we can produce as then typical industrial in organic chemist we can supply, the all this material as the raw material for these out of the sources. Only thing that you have to know that how this material can be converted as a corresponding, ceramic finished product. So, that ceramic finished products can be utilized for different engineering areas that starting from your electrical engineering to your magneto electrical applications.

Then, we now see that the different types of other variety that your refractory material we know that refractory bricks, because the bricks are also a kind of ceramic material. So, what are those refractory ceramics? That means, having high withstand of temperature. So, it can be made basically from a typical cone fusion point. So, it basically when we go for making the refractory ceramic material, it exhibit a cone fusion point of minimum SK17 is the scaling basically is the particular type of scaling in Seger cone test.

So, is the technicality is that you have a seger cone test and when it crosses the minimum level of SK 17 which is seger cone value, during that particular cone fusion point we qualify those material as your typical refractory ceramic product. So, what are those refractive ceramic products?

It chemically or the chemical composition why is basically alumina rich; that means, more amount of al 2 O 3 you can have in these particular materials such that you can, have high temperature withstand for that particular material, only the introduction of more amount of alumina. That means, the ratio of alumina should be more while you make the refractory ceramic material.

So, what are those raw materials, what you can use for this purpose is that your aluminum silicates in your hand. Then bauxite, or a mixture of bauxite and kaolin, corundum you can use, then for the different mechanical pressing basically. The mechanical pressing once you make those material for making the alumina rich refractory material or alumina rich refractory ceramics.

We go for mechanical pressing of those mixtures to get certain variety of granules and those granular raw materials are then mixed with the binders and then the whole mixture basically once you add the binder, because you have the solid state. And, if you do not have the typical amount of other flux material, the fusion material, you can add some amount of binding.

So, this is the particular variation in making this particular material is that you now add the binder. So, after addition of this binder to the granular raw material, you go for the firing process. That means, you choose the temperature, and you choose the furnace for the firing, and at that particular temperature you go for the firing to get this sort of alumina rich ceramic product.

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Then, we see the example because so far we are talking about we are considering all these things as your typically the metal iron oxide based material. So, obviously, we will find that whether you have a titanate material or a corresponding ferrite material. Since the metal oxides are typically a hard material, then if we consider that some other purposes we can have some non-oxide; that means, these are not oxide material, but the metal ions are still there.

So, you can have other nonmetallic part also, but if you can have the non-oxide materials so, what do you get there, that now you can have the aluminum nitride. So, far we are talking about aluminum oxide or Al 2 O 3 or alumina.

So, the variety so, if we just consider which are non-oxide ceramics. So, non-oxide ceramics are either carbide or the nitride. So, carbides are containing silicon or the boron. So, you have the boron carbide and the corresponding molecular composition or the composition in the solid state will be different for the different types or different varieties. So, in one case you can have the silicon carbide, which we all know that is the only one is to one composition of the silicon and the carbide in it, then we can have the S i 3 N 4, when the nitrogen content is different compared to your silicon content. So, it is 3 is to 4, then boron carbide or the boron nitride or aluminum nitrate. So, carbide and nitrate making you the corresponding formation of this non oxide ceramic.

The first category is your silicon carbide. So, how you make that particular silicon carbide is basically the Acheson process. The Acheson process is basically a typically electrochemical reaction; will be utilizing electrochemical reaction of pure sand. So, S i O 2 we know that is a very stable material so, but if we go for the electrochemical processing with that with carbon in an electric resistance furnace or S i O 2 mixed with carbon. In a particular electrochemical reaction is giving you because the carbon, what is present as simply carbon is 0.

So, the corresponding oxidation state or oxidation number of carbon is 0 as the elemental carbon in it so, this carbon. When you go for is mixing up with the silicon you know that the silicon is giving you the corresponding silicon carbide. So, it is typically electron transfer reaction can take place; carbon can take up electrons making this particular species as the carbide species.

So, after accepting those electrons it is forming from typical carbon elemental carbon to a carbide form and when it is attached to the silicon will be in the corresponding oxidized form now, and that oxidized form of silicon it is in the corresponding plus 2 or plus 4 stage. So, if you have a corresponding plus 4 state of S i carbon is the 4 minus state. So, you get the corresponding alpha form of silicon carbide, with the elimination of some amount of that carbon as the carbon monoxide because oxygen what was present with silicon dioxide can be taken out.

So, that oxygen will be removed as the carbon monoxide and we get the silicon carbide. So, this silicon carbide apart from your Acheson process, you can have the CVD process; that means the chemical vapour deposition process. And, in that particular process we now get the other variety; that means the beta silicon carbide. The beta silicon carbide has the cubic structure and now instead of your electrochemical reaction process we go for the thermal decomposition of other silicon sources.

One of the source is your silicon dioxide or the quartz variety for your source, but if we take the corresponding unstable species at high temperature the different silanes basically. So, we can take the alkyl silane or the alkyl dichlorosilanes for this purpose. So, these are very pure in nature and they are sometime can we can consider them their volatility is also very high, and at high temperature we can break them.

So, if we go for in the plasma or the flow reactor. So, two types of reactors we can use either a plasma reactor or a flow reactor can be utilized to get a temperature which is not very high which is not 2000 or 3000 is only 1000 degree centigrade. So, temperature in the range of 1000 degree centigrade is suitable for making this chemical vapour deposition of your beta form of silicon carbide from say Methyl silane. So, mono methyl silane is CH 3 S i C 1 3.

So, the mono methyl or methyl silane is in your hand and you basically heat it at 1000 degree centigrade in a particular variety of those reactors. So, what is happening therefore, that already when we get this silane material earlier we have seen I have studied in detail all these thing how we get the silane molecules. So, these are basically the corresponding inorganic rubbery material. So, the inorganic polymer material we know that the corresponding silanes. So, this particular already you have the corresponding silicon carbon bond.

So, that silicon carbon bond basically we will retain that in it in the solid state material of your silicon carbide formation. So, you can have only one material within your hand is your alkyl silane or the methyl silane. So, methyl silane is basically degraded at high temperature, which is 1000 degree centigrade, which is giving you a silicon carbide.

So, is basically a very useful inorganic reaction what you can consider it as that the formation of silicon carbide from your silane material. So, if you have some material which can be available from your silicon industry silicon rubber industry that this can also be a very good starting material we know for making the silicon rubber silicon polymer.

So, this starting material for the silicon polymer industry can be utilized for making another compound which is your silicon carbide and with the elimination of 3 HCl molecules.

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	n Nitride 1) $3Si + 2N_2 \rightarrow Si_3N_4$ 2) $3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$			
Manufactured by Hot pressing Pressure less sintering	3) $3SiCl_4 + 16NH_3 \rightarrow Si_3N_4 + 12NH_4Cl$ 4) $3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$			
Reaction sintering	Incorporation of $AI_2O_3$ or BeO in $Si_3N_4$ produces new ceramic materials such as SiAION and SiBeON.			
Boron Carbide Coarse particulate B <sub>4</sub> C	$2B_2O_3 + 7C \rightarrow B_4C + 6CO$			
$4H_3BO_3 + 7C \rightarrow B_4C + 6CO + 6H_2O$ Fine particulate $B_4C \implies 2B_2O_3 + 6Mg + C \rightarrow B_4C + 6MgO$				

Then, we go for the corresponding one as the silicon nitride. So, after a carbide you consider as the corresponding silicon nitride, how we get those nitrites. So, what are the starting material for that only so, you can think of these things in a such a way that industrially how we can think of which is cheaply available to you for, your silicon source as well as the corresponding nitride source. This can be combined these two can be combined together to get the corresponding compound.

So, the element wise reaction the direct element wise reaction from the silicon to nitrogen; that means, the nitrogen gas only. So, the gas phase burning of pure silicon, the elemental silicon the silicon rods we know, the high purity silicon rods we have prepared earlier we know that the zone refining is useful, for making the silicon rods in your hand.

So, the solid silicon rods basically when it is burnt in nitrogen atmosphere at a high temperature it gives you S i 3 N 4. Then another reaction if you consider, because we always be very much interested with the inorganic chemist when we consider in terms of your making the material industrially also, because what should be the starting material for those reactions, what are the products of those reactions, how we manipulate a simple chemical reactions, what we have learned in our early days the school days?

So, these reactions basically we have learnt in your school days only thing that we do not know, what are the difficulties in making these reactions and when we go for the industrial application. The making of this through the pilot plant or the application in the

industry is much more difficult. Because, you have to handle a huge amount making 1 gram or making 0.5 gram is always easy you can go to any laboratory and make all these things in the laboratory.

So, laboratory scale preparation to the industry scale preparation is always a difficult talks all in your type of these reactions. So, always we consider in that way only, we are talking in terms of the corresponding industrial chemical reactions or industrial inorganic chemical reactions.

So, now you go back to take silica as S i O 2. So, we know that that silicon can be directly combined with nitrogen to give you nitride now you have to use that, in presence of some amount of carbon you use now your nitrogen gas. So, you can consider that what we have learnt earlier that silicon dioxide can be burnt and can be heated in presence of carbon to giving you the carbide.

So, if you can make some environment or make some reactive process, that your intermediate, which is being formed as your silicon carbide can react quickly with the nitrogen as from your nitrogen gases.

So, that your silicon carbide can be highly reactive, which is formed as an intermediate one to that of your that nitrogen forming your silicon nitride, then silicon tetrachloride we can use S i Cl 4. So, is a simple material, but it is a costly one compared to your silica or the quartz variety, but now what we can use the carbon what is given over here in the second reaction, that particular carbon what we are now not used because this particular process the reaction two is basically a carbon reduction process. So, instead of that now we use something that instead of using di nitrogen dinitrogen gas we will be using ammonia.

So, the hydrogen present in ammonia can function as the corresponding material for the reduction reaction. So, the reduction of silicon tetrachloride can be useful with the invention of your nitrogen of the ammonia so, that basically directly giving you S i 3 N 4.

So, only what we are changing for all these reactions is your starting material or the reacting material. So, in the same way the silicon tetrachloride giving you a different stoichiometric of this reaction instead of producing ammonium chloride, in the fourth

reaction you can produce hydrogen chloride only, but the reaction is again of the same type between the silicon tetrachloride and ammonia.

So, the type of manufacturing process so, the manufacturing processes are also very much important; that means the hot pressing process. That is the high temperature pressure you can use for making this particular material, but in the most cases you use the gas phase reaction. So, the gas phase reactions are there.

So, high pressure is utilized for pressurized gas supply for getting this particular reaction, then pressure less sintering also, that if you go for the typical material which is fused one and the fused material at low temperature is getting sintered, it can be utilized as the pressure less sintering process. And, sometimes the reaction itself give you the corresponding sintering process; that means, the settling of the molten material as a sintered bed basically.

So, that also give you the corresponding reaction sintering process. So, in all these materials, we can also go back to incorporate some of the oxide material also. So, the incorporation of alumina and beryllium oxide, in the material of S i 3 N 4, basically produces another new variety of your ceramic material.

So, this new variety is known as SiAlON or SiBeON. So, further improvement of the quality of these silicon nitride based materials can be achieved again by addition of the oxides, then how we get the boron carbide? So, boron is in your hand, boron starting material from the borax, or any other thing or the boric acid. We can utilize for getting the B 4 C and the particulate the bigger particle sizes you can have. So, the coarse particulate or B 4 C can be achieved by simply utilizing borax, and from that borax the fusion of that borax basically giving you the boron oxide the B 2 O 3.

B 2 O 3 with the carbon reduction process or the reaction typically with that of your carbon which can take care of the entire amount of oxygen, we just present or attached to that boron giving you B 4 C. Then, the boric acid H 3 B O 3 is your simply boric acid H 3 B O 3 or B O H whole 3. So, reaction with the boric acid boric acid is the white material, white powdery material and is we know that is a natural source of the boron also. So, the raw material is a cheap one. So, the cheap variety of raw material even mixed with the some carbon which is also a cheap variety.

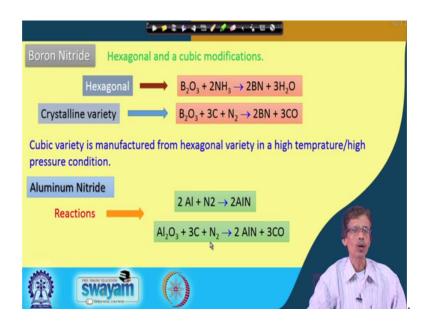
We get something which can be considered as a value added material of your boron carbide. So, two of these material one is the boric acid and another is the carbon in any form. Carbon is the graphite material or carbon and carbon black also these we will also see further, in our future classes that how we get the carbon black or the carbon other type of carbon material even the lampblack also.

So, the cheap variety of carbon also can be considered for giving you the corresponding very useful very industrial important boron carbide material, because the boron carbide material has tremendous applications for making some useful material for this purpose. Then, how you get by changing the particle size, if, we go for the fine particulate material or B 4 C. So, the fine particulate of material of B 4 C can be obtained through a different type of reaction where. Now, we will be utilizing magnesium as the reducing agent.

So, use of magnesium for your reduction of the same boron oxide; that means, your B 2 or 3 because earlier we have seen in the first reaction that only, it can go for the direct carbon reduction, the carbon reduction can give you one particular variety show you see, the changing the reaction condition, the solid state reaction condition will tell us that what would be the product formation or the type of the material what will be getting like that what we obtain in solution chemistry.

In solution, in organic chemistry we know that the solution, how we crystallize that particular material through that particular evaporation or the removal of the solvent. Now, in the same process if the reaction condition is being changed we get the different varieties of this as the particle sizes. So, when magnesium oxide is present that magnesium oxide should be removed from there, we get a fine particulate nature of your B 4 C material.

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Then, we go for the nitride variety of boron. So, the boron nitride is there in your hand now and this can have two typical varieties most of the type we know that, the solid state materials either it can be a cubic variety or the hexagonal variety depending upon it is two types of crystal structures.

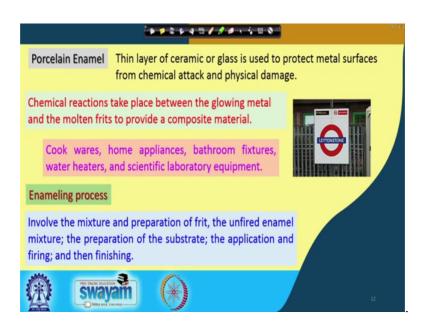
So, we have the two modifications; one is their hexagonal modification and the cubic modification which is there for your boron nitride material. So, hexagonal variety what we can obtained through the reaction again we already know form the silicon nitride, the boron nitride we will just quickly go either of the same type, simply by reaction with ammonia. Then, the crystalline variety the corresponding one having higher crystalinity in it the higher crystalinity can be achieved if we introduce carbon as a reducing agent for the direct reaction with nitrogen of that B 2 O 3.

Then, we can have the cubic variety is manufactured from the hexagonal varieties so, the first we get the hexagonal variety and that hexagonal variety can be converted to the cubic variety at high temperature and high pressure condition. We know that these are the typical things what we know from our solid state structural changes, that one particular variety can be changed to another variety by simply solid state transformation. If we consider that if you have alumina; that means the alpha variety of Al 2 O 3, which can be converted to the beta variety or can be converted to the gamma variety by simply changing the temperature or the pressure.

Because, your solid state structure has to be changed and that solid state structural change can be achieved through the introduction of a higher temperature or a higher pressure in that particular formation.

Then, the nitride of aluminum the nitrate of aluminum the reaction what we can consider is that again the direct reaction with that of your nitrogen into as the nitrogen gas, or the carbon reduction process on the alumina. So, alumina will be there in your hand and that alumina again like that of your boron or any other oxide material reduction will be doing in the same way. So, all these reactions are very simple and they straightforward one, once we consider these things for your making this nitrite processes and all these processes for different ceramic materials.

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So, now we go for that other material which is known as the enamel material. So, we have seen while we are talking about the ceramic material that what is your corresponding porcelain material. So, these porcelain material what you know, now this porcelain type of enamel materials. So, the we known as these are as the porcelain enamel material.

So, what we have we can have the corresponding enameling or the enameling process. So, is basically nothing, but a layering of the deposition of a ceramic or the glass material. So, the thin layer of ceramic or the glass is used to protect the metal surface. So, if you have the raw metal surface in your hand and that raw metal surface can be coated with that of your enamel surface.

So, that enamel surface is there and that enamel surface can be utilized for your that particular coating basically and that enamel surface we can have. So, if you have a raw iron container say or raw aluminum container. So, aluminum can be corroded the iron surface can also be corroded with the moisture with some acid or with the oxygen environment.

So, how to protect these things? So, if we are able to protect with a coating of the ceramic or the glass material. So, the coating will be in such a way because we have seen that the ceramic material is with[stand]- can withstand the corresponding acid or alkali attack. So, withstanding that particular thing; that means, the resistivity to the acid or alkali attack can be achieved on those metallic surfaces, through layering or deposition of the ceramic material in it which is nothing, but the enameling process.

So, basically the physical damage can be avoided or the chemical attack can be avoided with that particular thing. So, you can think or you can just can be recognize this particular thing is basically nothing, but your sign. So, the sign earlier we are utilizing all these things, earlier we are used very much now with the plastic days are there and the plastic we are not using much of these things, but still the life of this material the ceramic material; that means, the porcelain enameling material.

So, the enamel sign this basically the enamel sign in the corresponding thing where we get the corresponding coating of all these things. So, basically is a tube of the tube service in UK. And that tube service one station name is there and the station name is given in this fashion with that particular material of enamel.

So, you have the iron seat and on that iron seat basically the coating of that particular ceramic or glass material is achieved such that you have a protected iron seat with that of your enameling. So, what do we require there basically is basically the chemical reactions, that is why we are considering these as the typical inorganic industrial reactions. So, chemical reaction can take place between the glowing metal.

So, with a high temperature you have the glowing metal surface and the molten frits basically; that means, the powder which can give you the corresponding that frit material

the sintered bed material. So, the frit material the fine particle materials of the ceramic type or the glass type and you can get these as the molten frit and provide a composite material.

So, whatever we are talking about the enamel is basically a huge area where we consider as the composite material, because learning of all these things in terms of the composite material what we know that, the polymer the modification of the polymer, when we add some amount of fillers in the polymer material, we get basically a composite material of different variety of different property, because the we can increase the strength increase the longevity and all these things.

Here also the simple iron seat where the rust can take place which can be degraded can be protected through enameling. So, we get a nice variety of a composite material. So, historically is also very important, still we are using this thing little bit of this business has been down now with the introduction of plastic material and all other thing, but it can have a lifetime good lifetime. So, in terms of this material so, material utilization for the new purposes can be achieved through this particular composite material.

So, what we get we get the cook wars we get the home appliances, and the different types of bathroom fixtures the water heaters basically because it can have a high temperature withstand. And, the most important one is your scientific laboratory equipment's. So, scientific laboratory equipment's whatever we are using so far for the different types of laboratory, whether you have a teaching laboratory or research laboratory mostly of the glass material.

But, the glass materials are fragile in nature, we can have some loss through breakage, through degradation, but if you consider this enamel material for the laboratory equipment we can have good strength and we can have the good longevity for this material. So, for the bigger thing; that means, if we just go for a huge reactor material.

So, the reactor material is made up of some metallic iron say. So, you can have an iron container huge iron container. So, that iron container can be your typical reactor material and that reactor basically you can have, and that reactor can be coated with that enamel material. And this enamel material can give rise to the corresponding enameling process and that enameling process is basically achieved, that will see how a typical reaction

material or the corresponding equipment or the corresponding container can be achieved with that particular enameling process.

So, what is that enameling process that we discuss in our next class in detail, but right now what basically the material is involved? So, the thing is that we should know a particular terminology we are using is the preparation of the frit. So, preparation of the frit is nothing, but the corresponding material what we will be obtaining from the ceramic or the glass material. So, is a mixture and preparation of the frit then unfired enamel mixture? So, before firing we can have the corresponding enamel material which can be coated.

And, preparation of the substrate basically the substrate material will be in your hand and on that substrate will be utilizing that particular coating. And, the application for that how you coat that material and then we go for the firing. And then finally, the finishing; that means, the polishing and all other thing. So, stepwise we will consider all these thing getting the frit and the finishing process for making this particular porcelain enamel material ok.

Thank you very much.