Powder Metallurgy
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Lecture – 33
Powder Lubrication and Coating

Hello and welcome back. So, right now we are discussing about mixing and blending of the powder for preparing a powder feedstock for the shaping process. And, you have seen that the powder can be mixed with binder you know in order to aid the shaping process. And, sometime you also may have a mixture of two different powders for different purpose for example, for making alloys and things like that, right.

So, when you have a mixture like this, where there are different ingredients mixed together, it requires some kind of discussion on the theoretical density of these kind of mixtures. So, that is what we are going to discuss in this class today and then it will be followed by the rest of the things which you have for the mixing and blending process towards the preparation of the powder feedstock.

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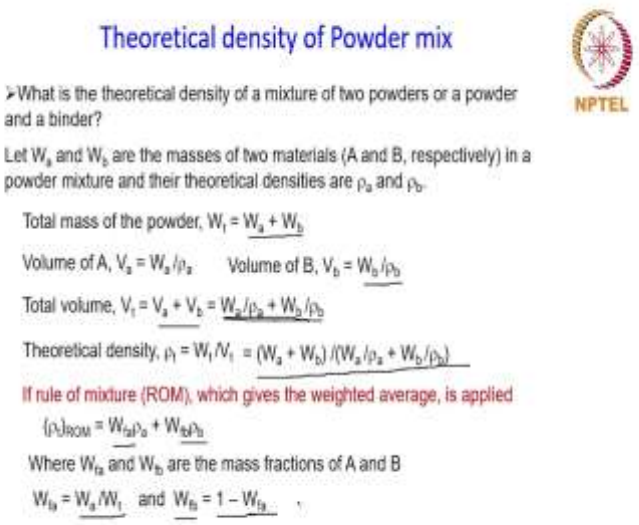

So, let us see: what is the theoretical density of a mixture of two powders or a powder and a binder mixture? So, let us say we are considering a powder mixture having two materials A and B and let **Wa** and **Wb** are the masses of these two materials respectively and let their theoretical densities be ρ_a and ρ_b. So, given this theoretical densities of these two materials, let us try and see how to calculate the theoretical density of this mixture. So, the total mass of the powder **Wt** will be the sum of the masses

$$W_t = W_a + W_b.$$

And now that the densities of these two materials are given, we can calculate the respective volumes, that is volume **Va** will be given by W_a / ρ_a

Similarly, the volume of B will be given by W_b / ρ_b. So, the total volume is

$$V_t = V_a + V_b$$

and in terms of the mass and the densities, it will be equal to . $W_a / \rho_a + W_b / \rho_b$

And therefore, the theoretical density ρ_t which is given by W_t / V_t , when we replace **Wt** by **Wa + Wb** and **Vt** by $W_a / \rho_a + W_b / \rho_b$, the ρ_t will be given by

$$\rho_t = (W_a + W_b) / (W_a / \rho_a + W_b / \rho_b)$$

Now, if we consider the rule of mixture, it is the weighted average of any value that you want to calculate for a mixture of two or more materials, that will give a value like this for the density based upon the respective weight fractions and the densities.

$$(\rho_t)_{ROM} = W_{fa} / \rho_a + W_{fb} / \rho_b$$

So, here W_{fa} and W_{fb} are the mass fractions of materials A and B respectively and W_{fa} will be given by W_a / W_t , the mass of a divided by the total mass **Wt** and W_{fb} is nothing but, 1 - W_{fa} or this can also be obtained in a similar fashion like this, when you divide the mass of b by the total mass. Ultimately, the mass fractions of these two materials is equal to 1 and that is why you get this relationship over here between these two mass fractions of materials A and B.

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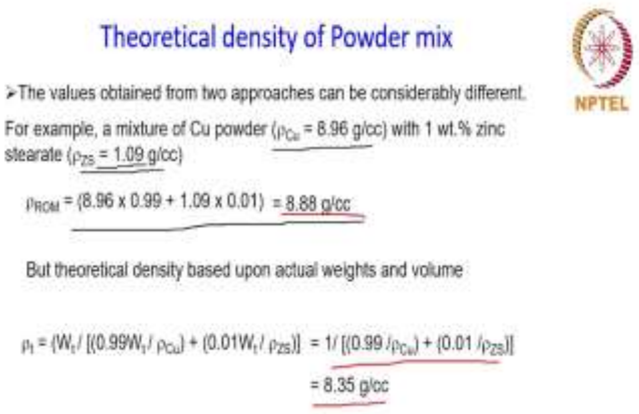

One thing that you should note over here is that, the values obtained from these two approaches can be considerably different. For example, if you consider a mixture of a copper powder and 1 weight percent zinc stearate, which is used as a lubricant. The respective densities are given here for copper and for zinc stearate and now if you calculate the theoretical density based upon the rule of mixture, this will be simply given by this.

The sum of the products of the respective weight fractions and the densities will give a value of (ρ_t)**ROM =(8.96 x 0.99 +1.09 x 0.01)** =

8.88 gram per cc. But, if you calculate the theoretical density based upon the first approach, that is using the actual weights and the volume of the materials, then the theoretical density ρt will be given by

$$\rho_t = Wt / [(0.99\ Wt / \rho_{cu}) + (0.01\ Wt / \rho_{zs})]$$

wherein **Wt** is the total weight of the powder mixture and these are the respective densities that is ρ_{cu} and ρ_{zs} as you can see over here.

And this can be simplified to

$$1 / [(0.99 / \rho_{cu}) + (0.01 / \rho_{zs})]$$

Since, Wt is common in the numerator and the denominator and now if you put the values of densities of copper and zinc stearate over here, then it will give a value of 8.35 gram per cc and as I said in the beginning, this can be considerably different from the one that you will get by using the rule of mixture. So, this is something that has to be kept in mind whenever the theoretical density is calculated for a powder mixture.

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So, with regard to the preparation of the powder feedstock for the shaping process, there are few more things that we need to discuss and these are as follows. Deagglomeration of the powder, powder lubrication and powder coating. So, let us go ahead and discuss about these aspects of the powder feedstock preparation.

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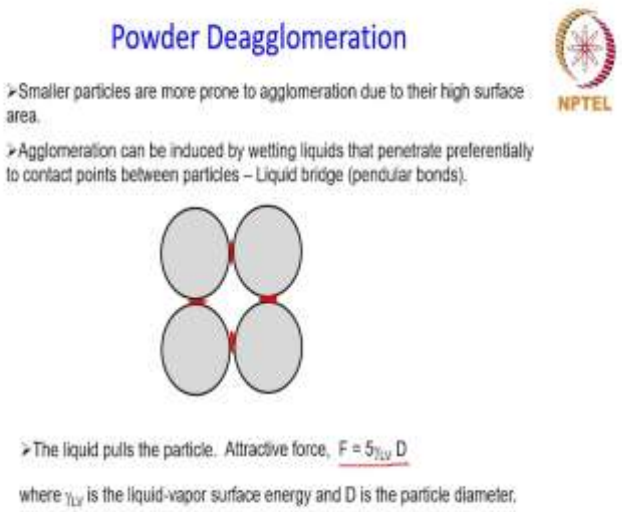

Talking about powder deagglomeration, first thing is the smaller particles are more prone to agglomeration due to their high surface area. And, the other thing that you would have noticed before also is that the agglomeration can be induced by wetting liquids, that will penetrate preferentially to the contact points between the particles, right.

So, during transportation and during handling of the powder, there are chances of the moisture from the atmosphere being absorbed by the powder. And, as a result of that moisture the liquid will penetrate particularly to the contact points between the powder particles and this will form a liquid bridge. For example, if you consider this spherical particles over here in this diagram. These are the contact points between the particles.

And now if this powder is exposed to moisture, then the liquid will penetrate along this contact points and form a liquid bridge along . And, this liquid bridge is also known as pendular bonds because what happens here as we can see, this wetting liquids between the particles is kind of creating a bond between them, right.

As a result of this the liquid will pull the particles and the particle will tend to stick to each other forming the agglomerates. So, this pull or the attractive force is given by the particular relationship

$$F = 5\gamma_{LV} D$$

where γ_{LV} is the liquid vapor surface energy and D is the particle diameter.

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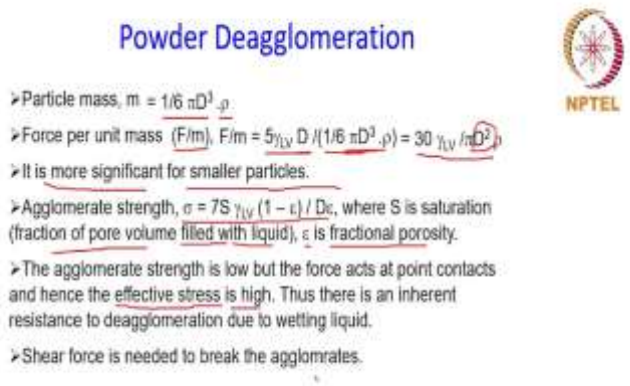

Now, if you consider the force per unit mass, let us say we are talking about a spherical particle. The mass of a spherical particle will be given by

$$m = 1/6\ \pi D^3.\rho$$

this is the volume of the particle and if you multiply that by the density ρ that will be the mass and therefore, the force per unit mass F by m will be given by

$$F/m = 5\gamma_{LV}D / (1/6\ \pi D^3.\rho)$$

This is the force as we have seen before and this is the mass and if you simplify this, it is given by this particular relationship.

$$F/m = 30\gamma_{LV} / (\pi D^2.\rho)$$

And, here we can see that this is inversely proportional to the square of the diameter or in other words we can say that as the particle size decreases, the force per unit mass increases. So, for smaller particles this becomes more significant and as a result the smaller particles are more prone to agglomeration. And, the agglomerate strength is given by this particular relationship,

$$\sigma = 7S\gamma_{LV}(1 - \varepsilon) / D\varepsilon$$

where S is the saturation which is nothing but the fraction of pore volume filled with the liquid and epsilon is the fractional porosity.

The agglomerate strength as such is low, but as you would have seen the force acts at point contacts; that means, the contact area over which the force is acting is very small. And as a result of that, the effective stress is very high because stress is force divided by the area and since the area is very small in this case, the effective stress becomes high right. And therefore, there is an inherent resistance to deagglomeration due to the wetting liquid, right.

And, in order to break such agglomerates induced by such liquids shear force will be needed. And this shear force can be induced by the blades and employers of mixers, which are used to mix the powder or if the powder is subjected to milling, the milling media like the balls and the rods can also induce the shear force and break the agglomerates.

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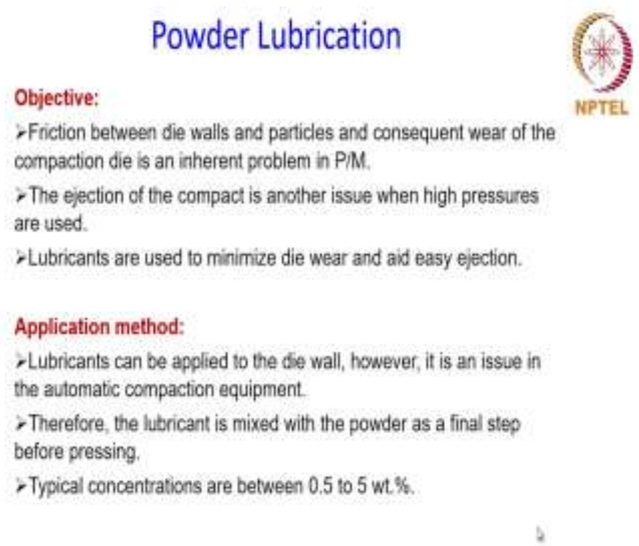

Powder lubrication is an important aspect of the powder metallurgy process. So, let us see the details of the powder lubrication process as to how it is done and what are the materials used and so on. So, let us first see the objective of powder lubrication. The objectives are as follows.

The friction between the die walls and the particles leads to wear and tear of the compaction dies and this is an inherent problem in the powder metallurgy process. Lubricant is used to reduce the friction and improve the die line by reducing the friction between the die walls and the particles.

The ejection of the compact is another issue when high pressures are used during compaction and application of lubricant also aids the ejection process and makes it easier. So, the two main objectives of applying lubricants are to minimize the die wear and aid the ejection process at the end of compaction.

Now, let us see how the lubricant is applied. Lubricants can be applied to the die wall; however, it is an issue in the automatic compaction equipment. And therefore, more often than not the lubricant is mixed with the powder as a final step before pressing. And the typical concentrations are between 0.5 and 5 weight percent.

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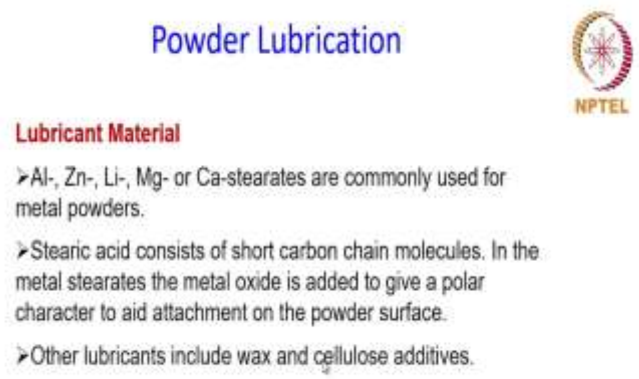

And now let us see, what kind of materials are used for lubrication. The stearates of metals like aluminum, zinc, lithium, magnesium or calcium are the most commonly used lubricants for metal powders.

So, in order to make these stearates, stearic acid which consists of short carbon chain molecules can be mixed with metal oxides and this will give a polar character to aid the attachment on the powder surface. Other lubricants include wax and cellulose additives.

So, apart from metal stearates alternative lubricants like this wax and cellulose based additives can also be used.

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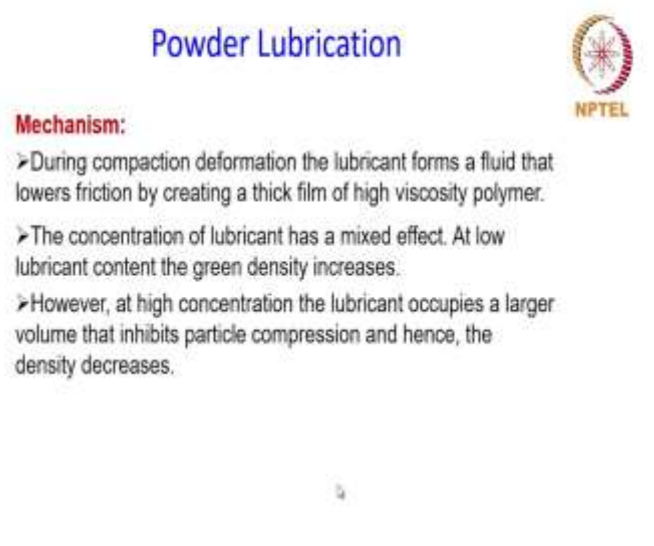

Now, lets see what is the mechanism by which the lubrication happens. So, during compaction as the pressure is applied, deformation will take place and the lubricant will form a fluid that lowers the friction by creating a thick film of high viscosity polymer, ok.

So, when the lubricant is subjected to deformation through the application of the pressure it creates this high viscosity polymer and that will lower the friction between the particles and also between the particle and the die walls. And the concentration of the lubricant has a mixed effect. At low lubricant content the green density increases.

However, as the concentration is increased at high concentration levels, the lubricant will occupy a larger volume and this will inhibit the particle comprehension and hence the density will decrease. So, at the lower side it is beneficial at low concentration, but when the concentration is high, the lubricant actually becomes detrimental for the density of the compact.

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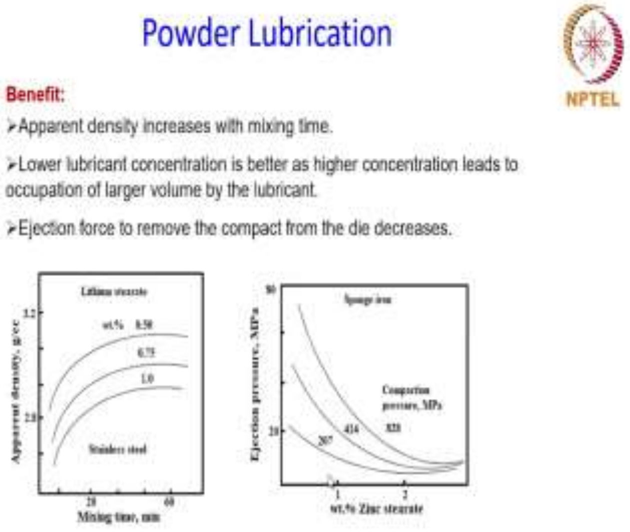

Now, let us see what are the benefits of powder lubrication. First of all the apparent density will increase and you can also see that in terms of the mixing time, which is shown over here in this diagram. The apparent density increases with the mixing time, the mixing time that is allowed for mixing the lubricant with the powder.

And here again you can see the effect of the concentration of the lubricant, as I said at the lower concentration level, the benefit is more and you can see that in terms of the apparent density and as you increase the concentration of the lubricant, the apparent density decreases, as you can see here for this stainless steel powder, where lithium stearate is used as the lubricant.

And as I said the other objective of using the lubricant is to ease out the ejection process at the end of the compaction. So, during compaction you apply the pressure through the dies and at the end of the process the compact will come out from one of the ends of the die. So, it will provide some resistance while coming out because there will be some dimensional changes and all that.

And, the lubricant will also help in ejecting the compact, because you know the friction between the compact which is now already given a particular shape and the die wall is reduced due to the presence of the lubricant. And that will in turn aid the ejection process, when the compact is coming out from one end of the die at the end of the compaction process.

So that we can see here from this particular diagram, which is for sponge iron powder, that is compacted by mixing with zinc stearate lubricant, these numbers that you see over here, these are the compaction pressure in mega Pascal. So, here you can see as the concentration of the lubricant increases, the ejection pressure decreases.

So, that is how the application of lubricant will also aid the ejection process and that is important because if there are difficulties during ejection; it might even lead to breakage of the compact and whatever is done before the compaction process will be lost, right. So, that is why it is also important to make sure that the ejection is as smooth as possible and application of the lubricant will make sure that, the process of ejection is smooth.

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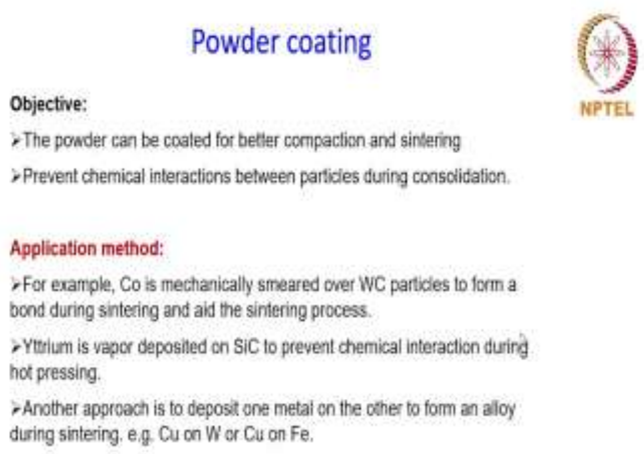

Now, let us talk about another process which is used in order metallurgy and this is about powder coating. So, let us first see, what are the objectives of powder coating. The objectives of powder coatings are as follows. The powder can be coated for better compaction and sintering. And prevent chemical interactions between particles during consolidation.

So, there are chances that the particle can interact or react with each other or if there is a second constitute present in the powder; there are chances that there may be some chemical reactions between the powder particles and those constituents.

So, if you can coat the powder particles with some other materials, this kind of chemical interactions can be prevented. And if there are coatings on the powder particle, it will also aid the compaction and the sintering process as well. So, let us see how the coating can be applied on the powder particles. For example, cobalt can be mechanically smeared over tungsten carbide particles to form a bond during sintering and aid the sintering process.

So, in this case the coating is actually helping in the sintering process in terms of helping the powder particles to bind to each other and give rise to a solid dense compact at the end of the sintering process. The other methods of applying could be vapor deposition for example, yttrium vapor can be deposited on silicon carbide and this can prevent the chemical interaction during hot pressing.

So, hot pressing again is a process of sintering where compaction and sintering happens simultaneously. And, since there are high temperatures involved in this case, there can be chances of chemical interactions between the powder particles. And therefore, if some other stable material is coated about the powder particles, the chances of the chemical reactions can be minimized. So, this was one example, where yttrium is coated over silicon carbide particles.

Another approach of applying powder coating is by depositing one metal over the other to form an alloy during sintering. For example, copper over tungsten or copper over iron can be coated and when these coated powder is sintered at high temperature, this can form an alloy because one of this will be dissolved in the other metal leading to formation of an alloy.

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Another method is to use bonded particles which will hold the alloying additions by an organic glue. For example, this iron phosphite particles can be glued to iron powders, by be coating over the iron powder with the help of an organic glue. And this will also carry an alloying element, which is in this case phosphorus that will be added to the material in the final stage when it is sintered.

And this process of adding a alloying elements in this manner, will also delay the alloying until the final stage which is sintering. So, that the compactability of the elemental metal powder can be utilized for better densification, because any alloy will have higher strength compared to the elemental powder. And therefore, you know compaction is little more difficult for alloy powders compared to elemental powders.

And therefore, if you could delay the alloying process, the compaction will be easier and that is what exactly is achieved in this case, when the alloying element is added in this manner to the powder. So, that the alloying happens only at the final stage during sintering and during compaction; the elemental powder is only present and leads to a better compatibility in the powder. A similar process would be to use partially pre-alloyed powders, where the alloy is yet to form.

So, there again you know the compactibility of the elemental powders can be utilized during compacting the powder and this is used for low alloy steels for example, low alloy steel, which contains molybdenum and nickel as the alloying elements. And another example of this pre-alloyed powder process is the abradable seals used for jet engines.

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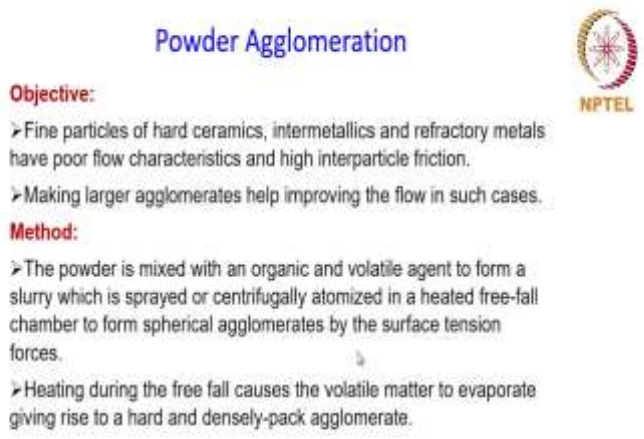

Finally, we will talk about this powder agglomeration, but as you have seen before we have been talking about deagglomerating the powder.

So, suddenly why there is a need to talk about the agglomeration or you know, what is the need of making agglomeration again, because as we have seen before agglomeration is detrimental for the powder metallurgy process as such. But, here we are not really talking about the particle agglomeration like how we have discussed before. Here we are talking about agglomerating the particles into a particular shape which is good for flow and packing.

So, you can say this is particularly useful for powders which are very hard, like hard ceramics and intermetallics or the refractory metal powders, which are again very hard or powders which have poor flow characteristics and high interparticle friction. For example, the irregular shaped particles which have high interparticle friction and poor flow characteristics. Those kind of powders can be agglomerated into a shape which is more favorable for flow and packing.

And we have seen before that spherical particles are known for their good flow characteristics. So, the objective of the agglomeration in this case is to make large agglomerates to help improving the flow . And, as I said this will be achieved by giving this powder particles a spherical shape by agglomerating the powder particles together, .

So, this agglomeration process as I said is very different from the particle agglomeration that we have talked about before. So, here you mix the powder with some binding agent. So, that the powder particles bond together and form large clowns which are more or less spherical in shape.

So, that you know as I said the flow property can be improved. So, the way it is done is the powder is mixed with an organic and volatile agent to form a slurry first, which is then sprayed or centrifugally atomized in a heated free fall chamber to forms spherical agglomerates by surface tension forces, right. So, while being heated during the free fall this volatile matter will evaporate leaving behind hard and densely pack agglomerates.

And, these agglomerates as I said now will be in spherical shape and the powder will be easier to pack and densify into a solid product. So, that is the objective over here, making the powder from non-spherical shape to a large aggregate having spherical shape, which will aid the flow and packing of the powder.

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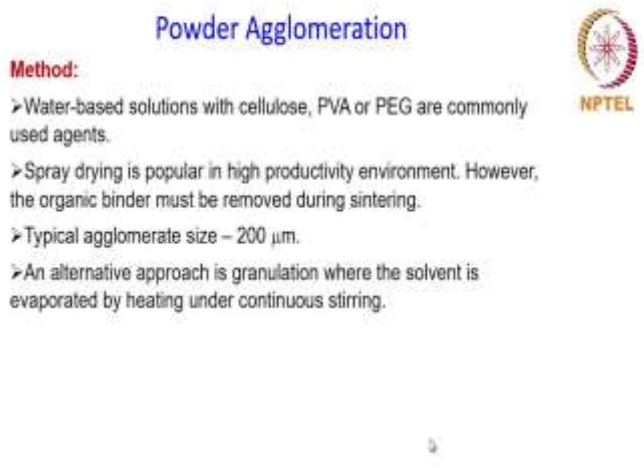

So, far this spraying or the atomization process, water-based solutions with cellulose, polyvinyl alcohol or polyethylene glycol are commonly used agents. Spray drying is popular in high productivity environment. However, the organic binder must be removed during sintering.

If it is not then the evaporation of this binders will lead to gas evolution and that in turn will lead to porosity in the sintered compact and it will hamper the density of the product. The typical agglomerate size that you obtained by this spray drying process is around 200 micrometer, there are alternative approaches of making these agglomerates.

For example, granulation where the solvent is evaporated by heating under continuous stirring; can also be used to make these agglomerates in spherical shape. And, with that we come to the end of this class.

Thank you for your attention.