Technology of Surface Coating
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Lecture 23
Mechanism of Wetting

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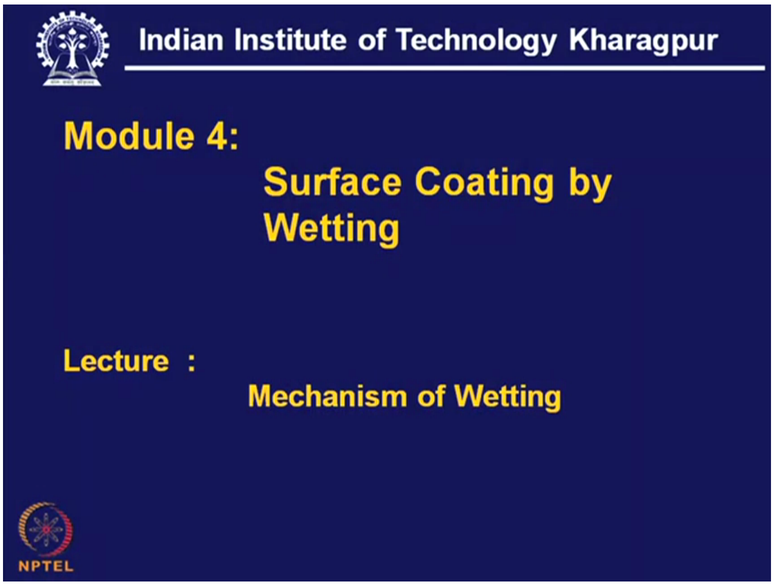

Okay, so today we shall discus this mechanism of wetting in the broad area to be covered is surface coating by wetting.

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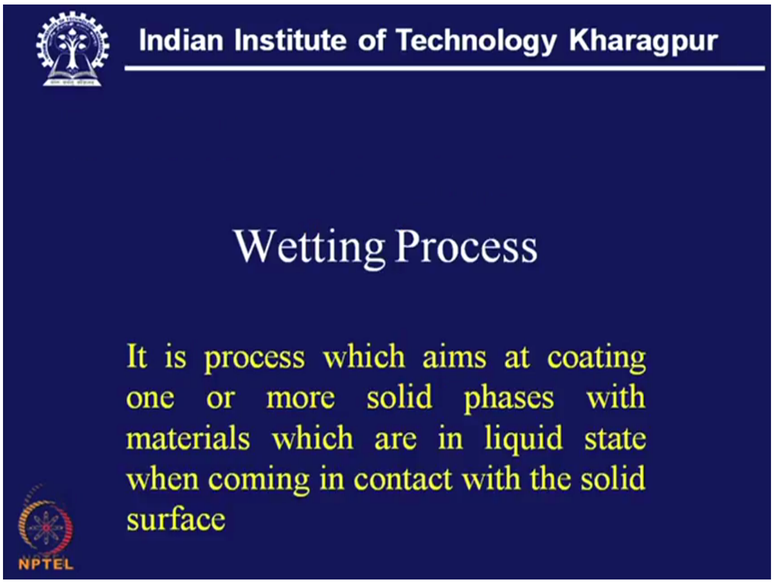

Now what is mean by wetting? It is a process which aims at coating on one or solid phases with materials which are in liquid state and which comes in contact with the solid surface. So it basically means the spontaneity in spreading of the liquid over the solid surface once it is brought in contact with that solid.

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Now the application of this wetting process which can lead to a surface coating, immediately we can see that coating on metallic sheet and where and it is commonly used for putting some resistance against corrosion this is a very common use of this wetting process then comes the manufacture of composite materials. In this case what happens? The hard material that is the dispersion of hard material that is done in a metal metrics and this metal should be able to form a fine coating or one encapsulation over the composite material.

Then Manufacturing of cermet, it is basically a composite material where the ceramic particles are dispersed within a metrics of metal, properly chosen metal and in this case also the metal holds the ceramic surface by putting a coating and this coating is done by the mechanism of wetting. Then very important use of this wetting process is metal ceramic joining where the Ceramic surface needs to be coated with a metal and this metal serves like a brazing or bonding alloy which can get attached to the metal base to be joined.

So this metal layer which adheres to the basic ceramic that is also done by this wetting process.

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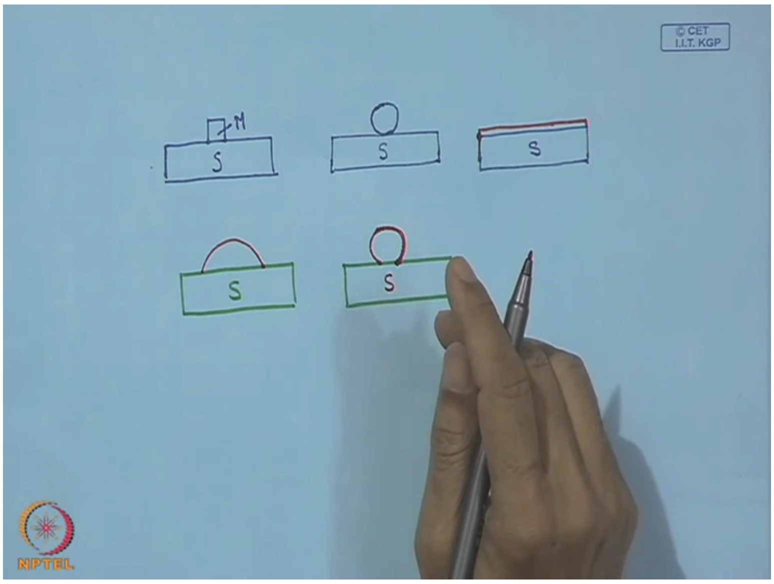

Now comes wetting and spreading. Now when we have a solid surface for example like this and over which a small block is placed and which can be later on melted over this solid surface then we may arrive at four situations, number 1 this is the solid surface and just after complete melting of this small block, this molten liquid can assume the shape of a sphere or a ball that means it is to dewetting on non-wetting situation this is one extremity.

We can have another extremity also, we have another extremity also where this metal block after melting it can have spontaneous spreading over the solid surface that means this is the solid surface and this block of a metal which after melting can have instantaneous spreading over the surface and we can get a layer and this layer is actually a coating over the surface by this wetting mechanism.

However we can have a situation, at least 2 situations in between these 2 extremes absolute non-waiting, instantaneous spreading there is a spontaneity of spreading of the liquid and we have another one situation this is the solid and after melting the liquid assumes this shape and here this is the wetting is somewhere in between these 2 extremes situations and now we have the fourth one where this liquid after being melted it takes this shape, this shape.

So this is absolute non-wetting, spontaneous spreading and wetting, this is a favourable situation for wetting and this is unfavourable situation for wetting more towards this extreme situation and this one is very favourable approaching towards this end. So this way we can understand the wetting or spreading of a liquid over a solid surface.

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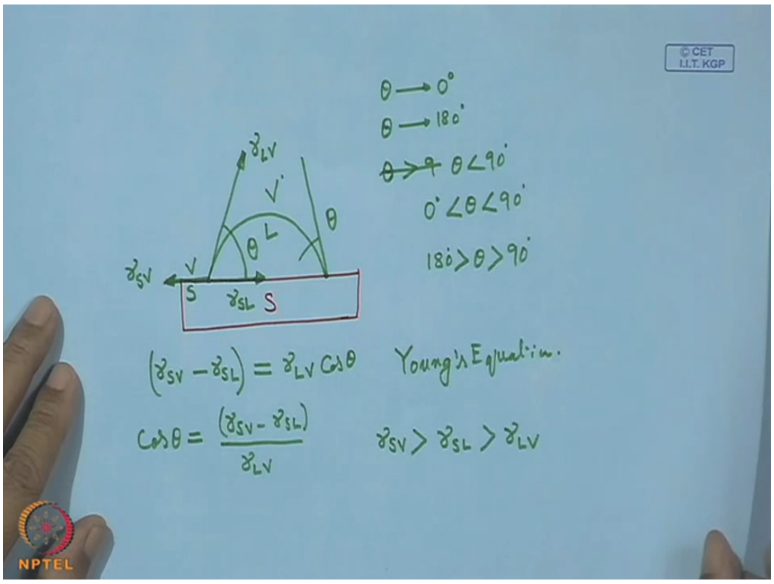

Now here more important is the term Contact angle and by this Contact angle we can assess the degree of wetting of a liquid over a solid surface. So this is the solid surface and here this liquid is in equilibrium with the solid surface and making such a shape which is a part of a sphere like thing. Now here what we can draw? At this point if we draw one tangent that this angle is Theta and that is called the contact angle.

On this side also it is Theta, so that is the contact angle. Now this contact angle is a measure of wetting, so when we see that it is spontaneous spreading than Theta is almost equal to 0, it is approaching 0 and when it is like a sphere that means like a ball resting on a solid surface it is approaching 180 degree and when it is favourable wetting then we can find that this Theta is less than 90 degree that means we should say here that Theta is in between 0 and 90 degree. So that is favourable wetting and it is more towards a wetting characteristics.

We can also would this way the value of Theta that means it is somewhere between these 2 and this is actually the sign of non-wetting. So absolute wetting, very satisfactory wetting, totally non-wetting, this is a favourable wetting and this is unfavourable or say it is more towards non-wettability. Now here if we consider the equilibrium of this liquid with the solid surface we can find out, identify 3 interfaces.

One is here between this liquid and this vapor then we have one with solid and vapor and another one between this liquid and solid. So what we see here? That this film is equilibrium on this solid surface under the action of various forces which are known as interfacial tension force. Now here along the line of tangent we have one force that is actually the surface interfacial energy per unit area at this vapor liquid interface and that we can put as gamma LV.

Similarly in this direction along this surface we can also have gamma SV that is the interfacial surface energy per unit area at this vapor solid interface which is gamma SV. Also we can see another force very much prevalent at this liquid surface interface that is known as gamma SL. Now under the action of these 3 forces, of course there is some gravity force this whole thing is in equilibrium.

Now we can balance this force in the horizontal direction and from there we can find out that gamma SV minus gamma SL that is equal to gamma LV cos Theta. Here we can see that to have satisfactory wetting or spreading this liquid film has to be stretched in this direction and for that there must be a driving force and this happens to be the driving force which is balanced with this cosine component of the interfacial tension between the liquid and vapor.

However considering the dynamic state and if we want this continuous spreading of this film, this part should be greater than gamma LV cos Theta. So this is actually known as Young's equation. Now this equation gives us a clear message that means we can write cos Theta is equal to gamma SV minus gamma SL by gamma LV, so this is the term. Now when we have to have a spreading leading to 0 Theta then obviously this value should be very high and under that condition this gamma SL should be as low and gamma SV should be quite high.

So in this case when we consider this as a favourable case of wetting we can write gamma SV is greater than gamma SL and that is greater than gamma LV. So that is the condition which must be met in order that this liquid has good or favourable wetting characteristics. Now here one thing also we understand that this gamma LV that is the surface tension of the liquid that is actually the resisting force which opposes this spreading or wetting and the numerator is a driving force.

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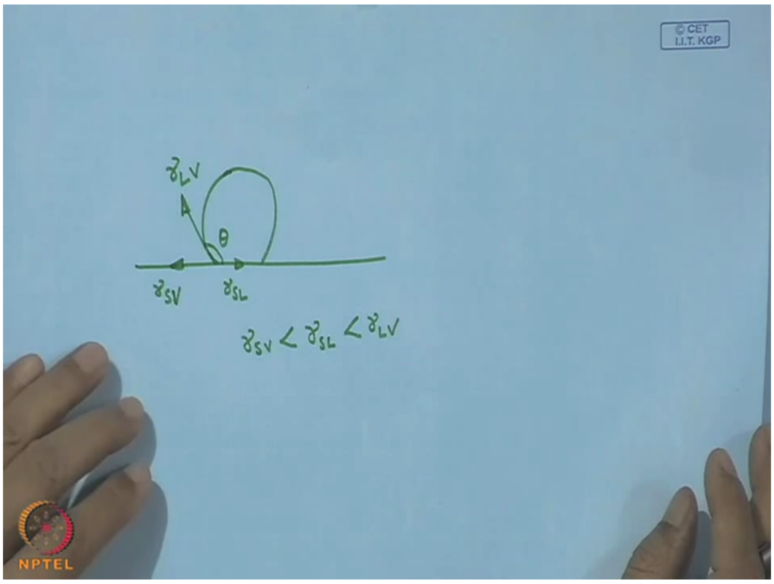

Now when it is nonwetting, we have little different situation this will be gamma LV and in this case, this is gamma SV, this is gamma SL and this is Theta. So in this case what happens? Just the situation changes this way gamma SL and gamma LV that means in this case liquid tension is quite high compared to the surface energy of the solid surface though the interfacial tension is in between these 2 extreme values.

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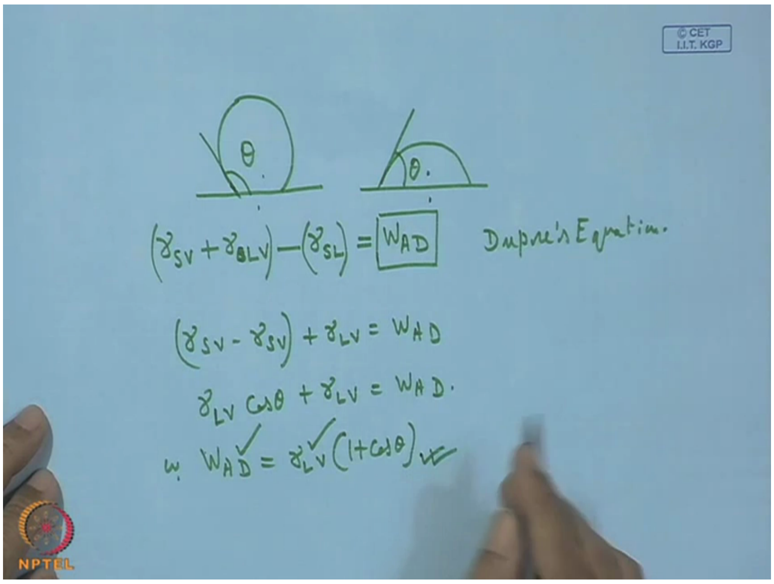

Now with that we can find out another term apart from Contact angle that is called work of adhesion. Now this work of adhesion means that when we create this interface which is having a contact angle which may be obtuse or we can have a Contact angle which may be also acute. The main thing here is that if we like to break this interface than certain change in free energy will take place, this can be expressed this way.

So we can have gamma SV plus gamma SLV minus gamma SL that is given as WAD, now this we can see in the form of change of free energy per unit area of this interface that means this is the final state, this is the initial state that means the change is taking place from splitting of the interface and transforming it to 2 surfaces that means one liquid solid interface is now changed to a solid surface and that of liquid surface and in this process of change in free energy is taking place and that is given by this term work of adhesion.

Now lower this value of interfacial energy, higher will be the work of adhesion that means this is actually the energy per unit area one may require to break this bond. So this is actually known as Dupres equation and putting this Young's and Dupres equation one can find out that gamma SV, this gamma SV minus gamma SL is plus gamma LV that is equal to WAD but this can be substituted for substituted by gamma LV, cosine Theta plus gamma LV is equal to WAD.

Or finally we arrive at this relation gamma LV is equal to 1 plus Cos Theta, so this one this is an index of cohesion and this is the index of adhesion. So by looking at the surface tension of the liquid that of the contact angle some estimation on the work of adhesion or the adhesive force which is prevailing between this liquid solid or this liquid solid interface that can be estimated.

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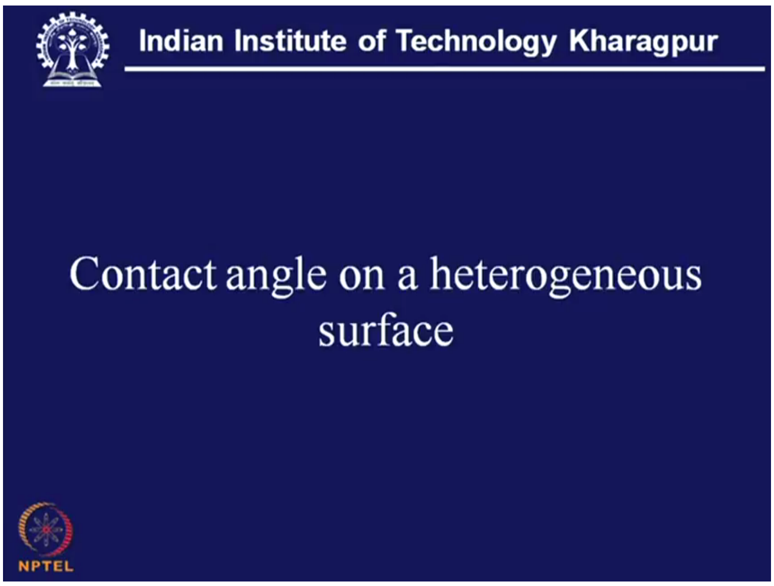

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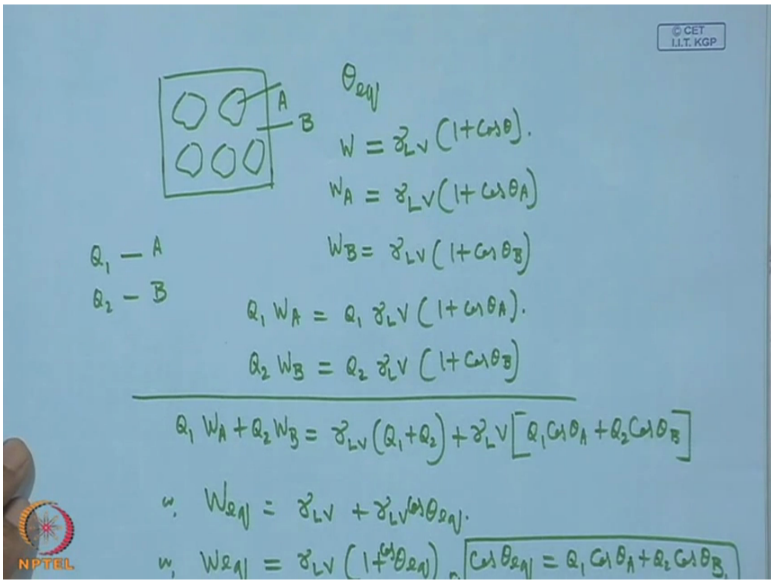

Now contact angle on a hydrogenous surface, now so far what we have discussed that is the contact angle on homogeneous surface but the surface may also have 2 phases. Say we consider this as the unit area there we can have 2 phases and this is just like a dispersion in a metrics. So if this is A there is dispersion and B is a metrics then we can also make some attempt to find out what could be the resulting contact angle?

That means equivalent when we have a heterogeneous phase consisting of A and B, so basic equation is say W, we write W as work of adhesion into 1 plus cos Theta. Now this can be also written as WA as into, had it been totally the dispersion material? That means the material which is dispersed, if it contains 100 percent then we can write it is like this one plus cos Theta A where Theta is the contact angle, had it been hundred percent of A?

Now following the same logic we can also write gamma LV plus 1 plus cos Theta B and this is considering that the metrics is actually 100 percent over this unit area. Now let us consider that over this unit area Q1 fraction that is occupied by A and Q2 fraction that is occupied by B. So in that case we can write that Q1 into WA that gives us Q1 gamma LV into 1 plus cos Theta A and Q2 WB that means the work of adhesion for A and work for adhesion for B.

So this will be equal to gamma LV into 1 plus cos Theta B, so it is now a portion meant by Q1 part and Q2 part. So if we add then we get Q1 WA plus Q2 WB is equal to actually gamma LV which is the surface tension of the liquid plus into Q1 plus Q2 plus gamma LV into Q1 cos Theta A plus Q2 cos Theta B, so it is Cos Theta and Cos Theta B. Now this one Q1 plus Q2 equal to 1 because it is the fraction over this unit area.

So this is the equivalent work of adhesion, so if we replace it by W equivalent then we write here WLV, this is also WLV and this is also equivalent to the resulting contact angle which we can write as Theta equivalent, what we have shown here? And this is in the same form as the combine form of Young Dupress equation that means 1 plus Theta equivalent.

So this one actually this is coming as cos Theta equivalent so from there we can write or cos that equivalent is equal to Q1 Cos Theta a plus Q2 Cos Theta B. The summary of this whole exercise is that, if we have component A and component B over a solid surface and if their proportion is Q1 and Q2 and if Theta A is a contact angle for the surface A and if Theta B is the contact angle for the surface B than the equivalent contact angle when we have a dispersion over a metrics that will be given by this relation. So for a heterogeneous surface we can have one attempt, we try to find out the equivalent Contact angle.

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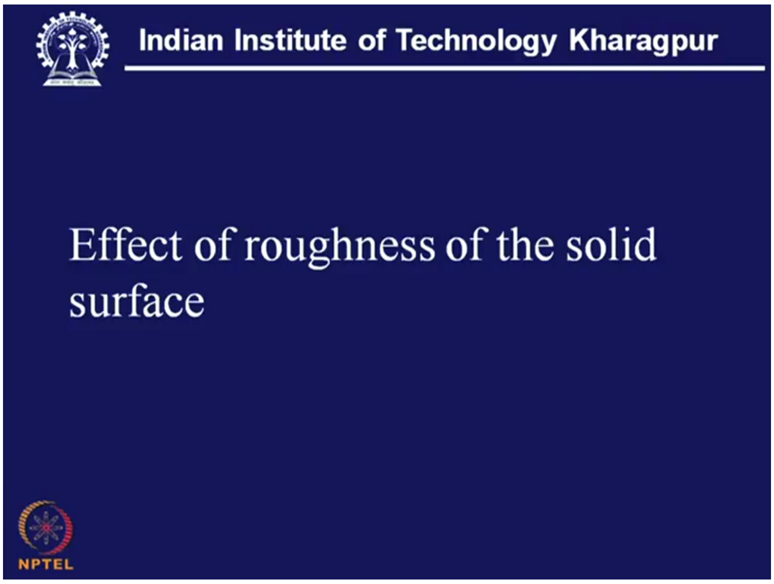

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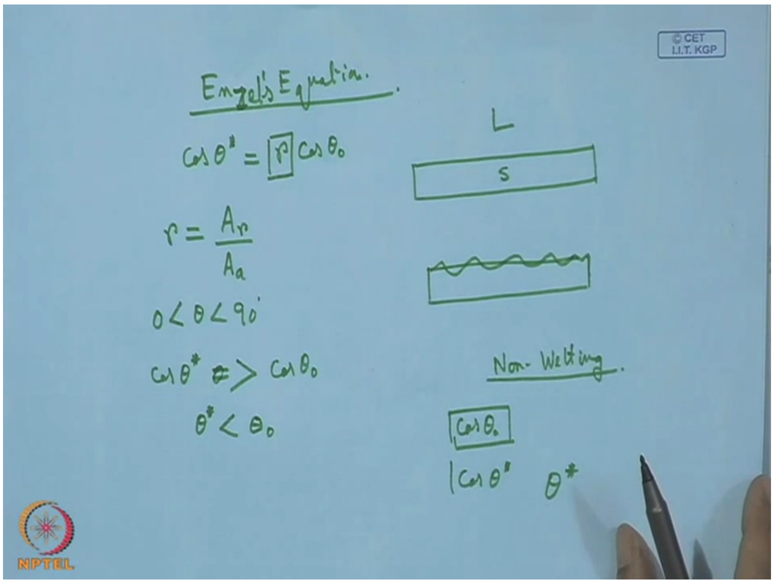

Effect of roughness of the solid surface. Now roughness of the solid surface can also affect wetting characteristics and this is actually given by Engels equation. Now the equation states that this cos Theta star that is given by r into Cos Theta o. Now Cos Theta o is a normal wetting angle of the surface is absolutely flat and smooth. So if it is a flat surface with sufficient smooth this then Theta o will be the contact angle of a liquid over this surface.

So the liquid and solid they are same only according to Engels equations, what happens? Now the surface is no more smooth but it is slightly rough and this roughness is given by this factor r and this r is actually it is given by Ar by Aa suffix. So Ar means the real area of contact. So if the surface is rough it can be machining mark or grinding mark or can be scratched over the surface.

So naturally real area of contact with the liquid that will increase and obviously this ratio will increase, so if it is a advancing liquid that means there is a spreading, normal spreading or there is normal wetting that means in a situation where Theta is in this zone that means less than 90 degree that means it is a favourable case of wetting, under that condition if we have a rough surface that this rough surface favours wetting according to this law.

Because in this case Cos Theta star that means the equivalent or apparent wetting angle this will be more than one, so naturally this value will be greater than that of Cos Theta o and naturally if it is a higher value of Cos Theta star. So in this case this Cos Theta star is going to be more than Cos Theta o and therefore this Theta star will be less than Theta o that means wetting is improved by this roughness.

However if it is the nonwetting situation that means in that case what we see? That value of, so this is for situation where we have normal wetting but nonwetting in that case what happens? This Theta o this is normally it is negative that means greater than 90 degree, it is normally usually negative and by putting this equation here, what we find?

That Cos Theta star will become more negative, more negative means it will approach more towards 180 degree, so this will be more negative that means Theta star will be greater than that of Theta o because of the simple reason that Cos Theta star is more negative than that of Cos Theta o. So we also come to this conclusion that if the liquid drop is basically if it is nonwetting in character then because of the surface roughness this angle will keep on changing and that value will keep on changing and it will be more towards nonwetting. So nonwetting character will keep on increasing because of the surface roughness, if originally the liquid is nonwetting in nature.

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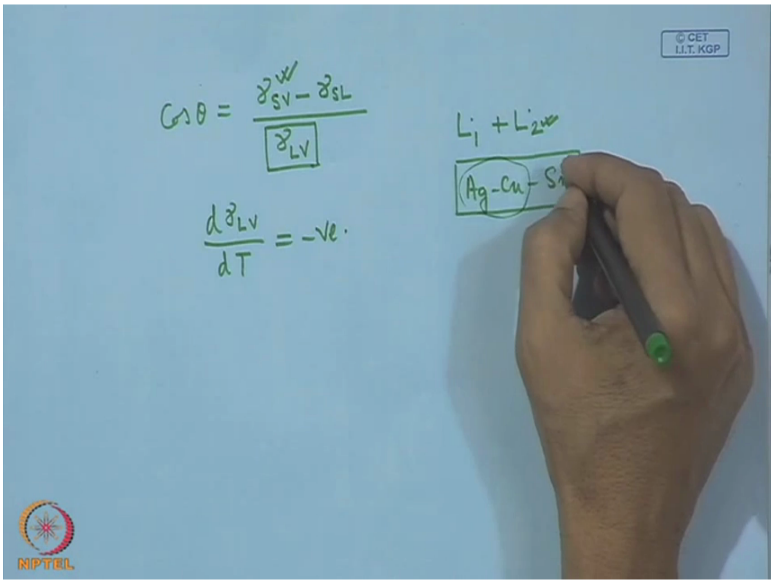

Effect of temperature on surface tension of liquid. Now if we recall the basic equation of wetting which is given by this gamma SV minus gamma SL by gamma LV then we find that this gamma LV has a role to play though it is understood that the predominant role will be played by this surface energy of the solid and interfacial energy between this solid and liquid should be as low as possible.

But at the same time if by some mechanism we can reduce this value of the surface tension of the liquid that will go in favourable direction. So from this point of view we can consider the effect of temperature on surface tension of the liquid and here this is the common experience that means if we put in this differential form dT which is the temperature this happens to be a negative quality.

That means with increase of temperature we have lowering of this value and by lowering this value we can have an affect positive effect on the value of cos Theta that means the cost Theta value will keep on increasing and as a result the Theta value will also improve a lot that means more it will move towards wetting characteristic. So this is the effect of temperature.

Now surface tension of liquid solution, so this is actually if we have one liquid L1, we can add another liquid L2 in certain proportion, of course these 2 are totally miscible. So in that case we can find out that there is a resultant effect of this liquid and in this case what happens? That is particular liquid can also reduce the surface tension of the original liquid and by this addition if we reduce the value of gamma LV, so in that case we can also get a favourable value of cost Theta that means higher value of cost Theta means low value of Theta.

So here the basic idea is to add one component in the parents liquid only to reduce its surface tension for example in silver, copper, alloy if tin is added that can have a positive effect of reducing the surface tension of this parent liquid and that can have immediate effect, a very positive effect on this value of Theta.

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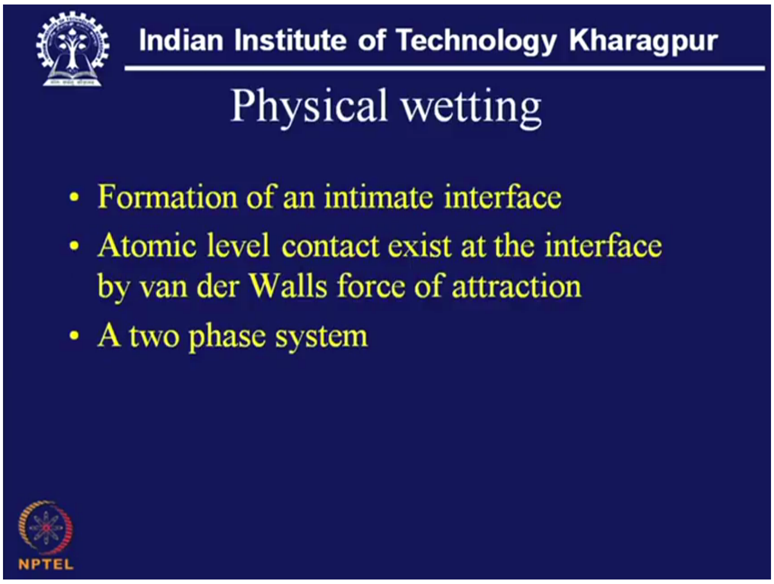

Now physical wetting, so far the discussion we have made and the equations those governing equations whether it is Young's equation or Dupress equation or combination of that, so this is a guiding equation. So what we have observed here? That means it is actually the basic requirement of formation of interface an intimate contact that is basically requirement to be met to have the wetting.

Then comes an atomic level contact that mass exists at the interface and that is only possible by Van der walls force of attraction and this is just a 2 phase system that means here we have, so this is liquid and this is solid and at this the phase that must be an intimate contact and this can happen by virtue of very presence of this Van der walls force of attraction and this is a 2 phase system that means liquid and solid and there is no presence of any third element in between. So this is actually known as physical wetting.

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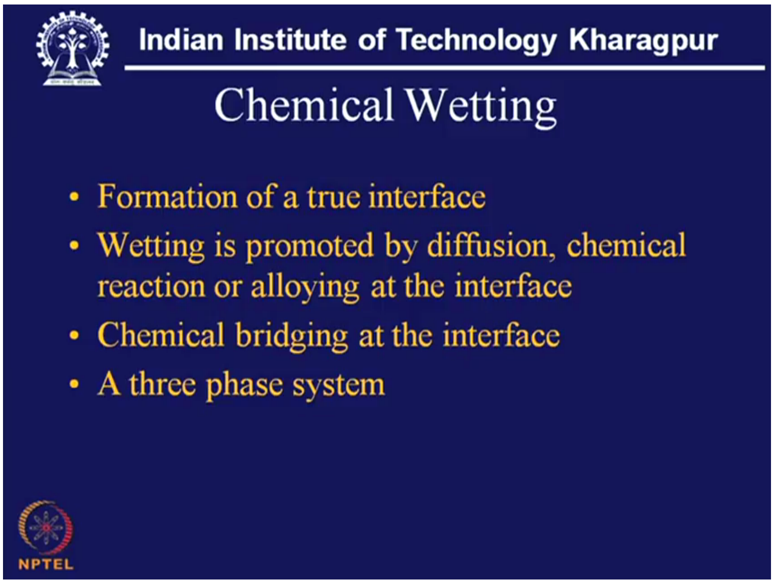

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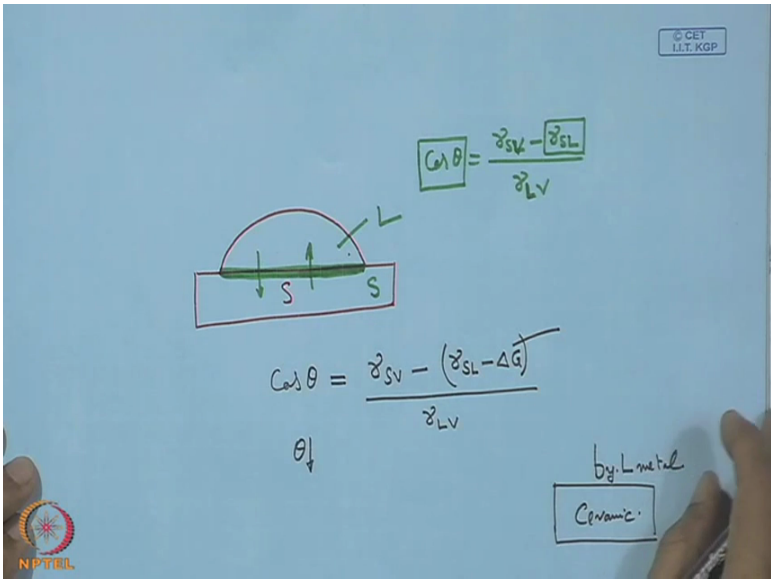

Now comes chemical wetting. Now in chemical wedding also we must have a true interface. However in this case it is not only Van der waals force of attraction that promotes wetting but more importantly here it is the diffusion across that boundary that means this is the solid and here we have the liquid, more importantly here you have transfer of the material either by the process of diffusion or by chemical reaction or alloying at the interface that means there is a chemical bridge that is established at the interface and as a result it is no longer a 2 phase system but it becomes say 3 phase system.

So you have here a diffusion layer or a reaction layer or earlier because of the alloying, this layer can be very thin or very thick, it depends upon the chemistry of the liquid, chemistry of the solid than the prevalent temperature. So these are the 3 parameters which dictate what should be the reaction layer or the layer as a result of this alloy formation or because of the diffusion.

The interesting thing here is that, the equation that governing equation showing that this is gamma SV, gamma SL and this is LV these just cannot be directly used in this case. So here what is important? To also consider this gamma SL that means this interfacial tension at this interface and that will be affected because of this chemical reaction that means this wetting angle is not just affected by Van der waals force of attraction but the affect of diffusion, Cross diffusion or a reactivity or even alloying effect can have an overriding influence over the overall value of Theta.

And this can be rewritten, little bit modified just by writing because of this chemically augmented wetting, we can write this as SV minus gamma SL minus Delta G and that will go inside this parenthesis and LV. So by this, what we can achieve? That original value of gamma is L that can be drastically reduced if we have some kind of reactivity between this liquid and this solid thereby changing the surface chemistry of the solid.

And as a result of this reactivity there will be a change in free energy which must be negative and this negative change in free energy that can act in a very favourable way by just reducing the value of the interfacial tension and thereby the net gain would be a very low value of Theta and this is actually known as chemical wetting and this is extremely suitable or this is essential for wetting of ceramic surface by a liquid metal by liquid metal.

And unless this reactivity is there we cannot achieve the spreading or even a meaningful wetting otherwise this most of the metal they will act like a passive one and that will not lead to any meaningful wetting or spontaneous spreading. So this reactivity is must for wetting of those materials where there is a discontinuity, in terms of mechanical discontinuity or physical discontinuity or even chemical discontinuity across this interface.

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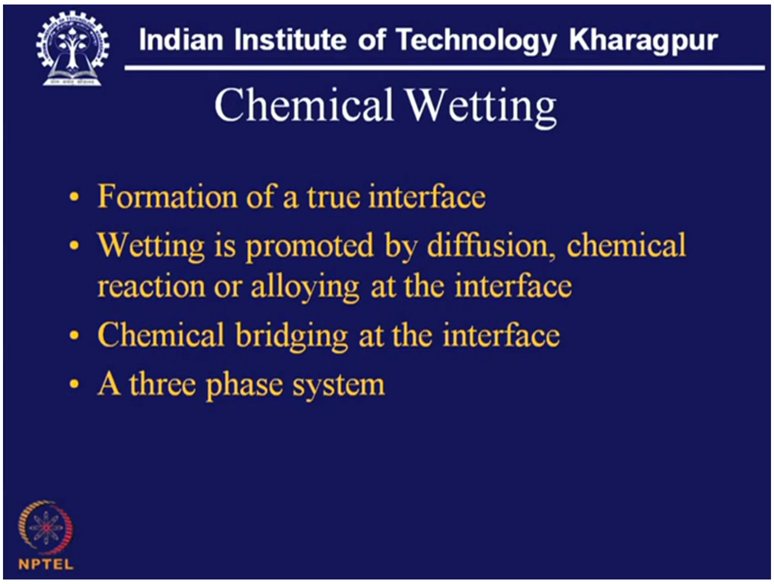

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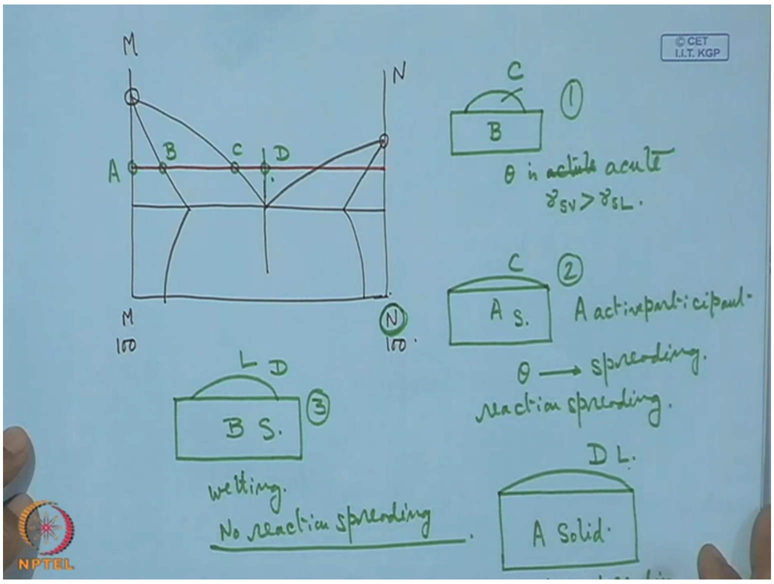

Now this can be well illustrated by one wetting characteristic and this can be illustrated here. Let us consider one binary system, binary alloy and which forms one eutectic at certain temperature, this is a melting point of element M and this is the melting point of element N. Here M is 100 percent, here N is 100 percent and this is actually the eutectic composition and what we can have here?

Say few cases; say this is the prevailing prevalent temperature where we are going to examine the wetting characteristics. Now what we have here? Four compositions of this alloy is 100 percent this is A, this is B, this is C and this is D that means following this diagram we come to conclusion that M is 100 percent M and B means that is a limit, that is a limiting the marriage of up to which B can hold itself in the solid form.

Similarly C is also one limiting position where it can also assume the liquid form and D is also in the liquid state. Now what we can examine here? Very interesting thing say we have one solid which is B and we have a liquid which is C. Now in this case participation of B or C in spreading the liquid that will not take place because of the simple reason that B is having a saturated composition and C liquid that is the liquid C that is also having a saturated composition.

However angle theta that is acute and in this case gamma SV that is greater than gamma SL, so this is called a passive interaction between B and C there is no sign of change of composition of C or B when they are brought in contact. Now if we have another situation where C is in contact with A, what is going to happen let us look into? That in this case A will dissolve this element in from C.

And so A serves, A though it is a solid, A here it is acting like a solvent and this composition of the liquid at C that is like a solute, so A will dissolve some component N from this composition C and as a result the chemistry of surface A that will change and because of this change, what we can say here? A is a active participant in this wetting activity and is active participant will reduce the value of Theta drastically and it will lead to spontaneous spreading that means we can call it reaction spreading.

So A changes its surface composition just by dissolving some of the element N from this liquid which is at the composition C. Now we can consider another situation where the solid B that is in contact with D, so liquid D and solid B. Now in this case also we don't see any active participation of the solid D though the liquid at D can dissolve some of the element M from B that means this D can dissolve some of the element in from the composition B.

However B composition as such it will not change because this is already saturated level. So in this case also we can say that it is just a wetting case of wetting, no reaction spreading. However there is no reaction spreading. So what we see here? That considering this particular case and this case the first one, number 1, this is number 2 and this is number 3. If we consider one and 3 only the difference is that D can dissolve some of the component M from B thereby its composition may change but the composition of B is not going to change its surface composition is not going to change because it is already saturated at that point, so there will be no reaction spreading.

Now we take another example which is, okay. We consider another example which is actually 2 extreme situations, here we have A is the solid and D as the liquid D as the liquid, this is the liquid. So what is interesting thing? That both A and D both are unsaturated, so in this case what is going to happen? A will solve some of N from D, at the same time this liquid D can also dissolve some of the element M from A that means there will be change in composition of both liquid and solid at the interface across this interface and in this case we can see that both liquid and solid both are actively participating in this wetting spreading activity and we can call it reaction spreading.

So what is important? What we find from this example? That to have spontaneity in spreading there must be some kind of reaction and this reaction should lead to a change in surface chemistry of the solid surface unless that is done the liquid cannot be chemically activated towards the surface of the solid and we may not achieve the spontaneous spreading or wetting.

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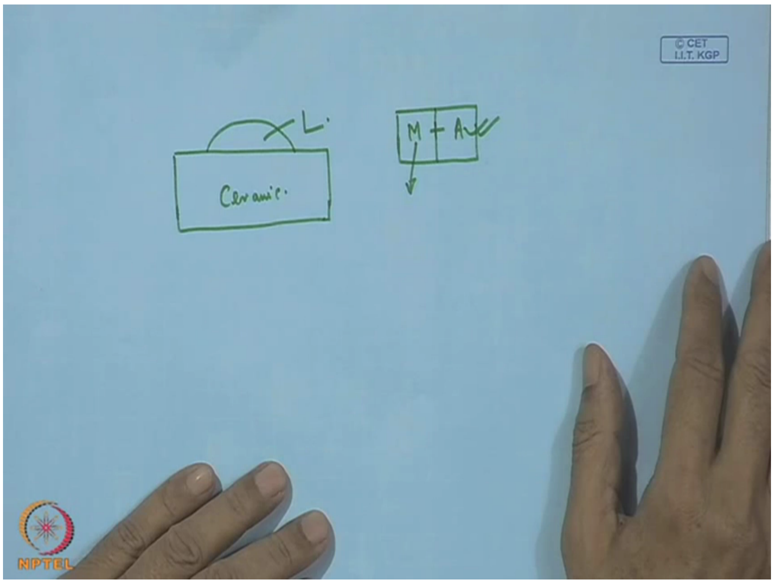

Now this thing can be also be extended, this idea can be also extended in joining of Ceramic where we find that, a serum it known for its ionic nature or covalent nature and it doesn't have the free electron to share and to bridge a continuity across this interface, so when it becomes a ceramic and this is a liquid metal, so unless this ceramic is reacted with this liquid that means this liquid should be able to react on this surface of the ceramic to change its chemistry we cannot achieve this spreading over this also, ceramic.

And that's why the conventional alloy must have some additive that means this alloy must have some additive which can enhance the reactivity of this liquid over this ceramic and as a result this additive will be segregated towards the surface then change the chemistry of the ceramic making that surface wettable by the conventional metal M. So this is also one of the very important aspects of metal ceramic joining by the activation of the conventional metal by this addition of a strategic material and these strategic materials are mostly, we find from this transitional elements which are known as Carbide former, oxide former or boride former or even nitride former.

So these materials are strategically chosen and added to the parent material to make the surface quite active and that can increase the wettability.

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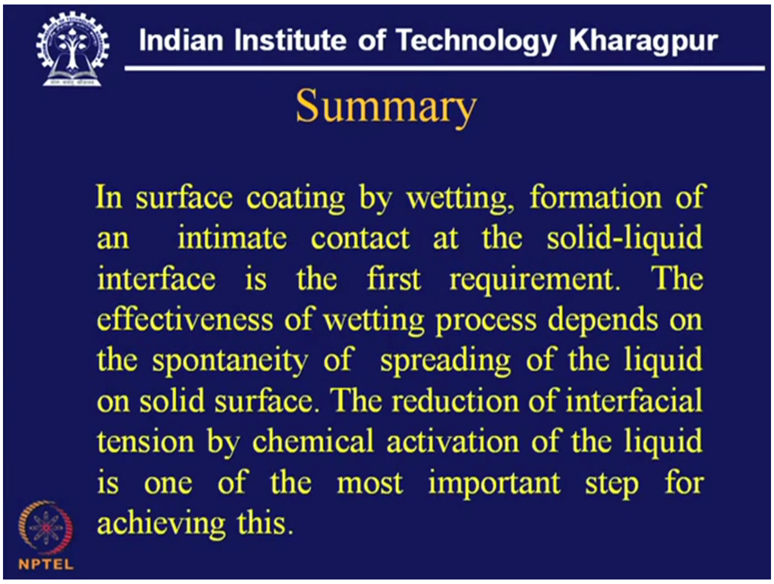

So what we see? That in surface coating by wetting, formation of an intimate contact at the solid liquid interface is the first requirement. The effectiveness of wetting process depends on the spontaneity of spreading of the liquid on solid surface. The reduction of interfacial tension by chemical activation of the liquid is one of the most important step for achieving this.