Rheology and Processing of Paints, Plastic and Elastomer based Composites
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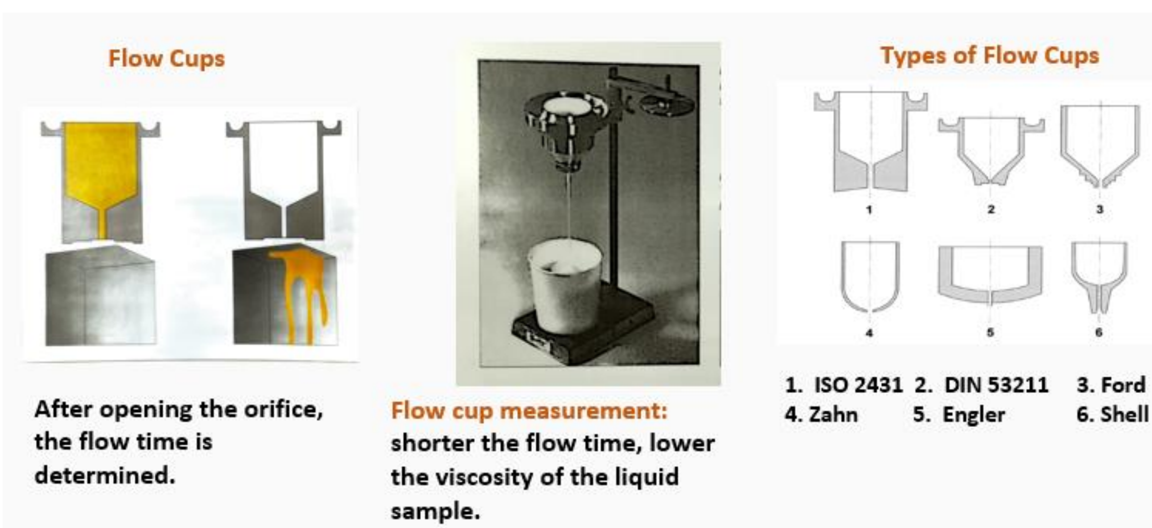
Lecture 15
Rheology of paints 1

Welcome to NPTEL online certification courses on Rheology and Prosthesis. Today we are in week 3 and lecture number 3 which is titled as Rheology of Paints is the number 1 part 1. So, once again today we will be covering some of the concepts including viscosity measurement techniques, various rheological studies in general, rheological characteristic of water based coating, shear thinning flow behavior, Thixotropic behavior and how to capture long term storage stability. Once again if you want to have a parallel studies you can refer to this following keywords including this plastic properties, LVER, complex viscosity, zero shear viscosity, glass transition, kinematic absolute viscosity which I talked about earlier already, Newtonian non-Newtonian fluids, shear stress, shear rate, Stokes law, terminal velocity, torque effects, strain amplitude, storage and loss modulus, oscillatory shear and rotational shear, extensional deformation, dynamic modulus, shear rate and shear stress for example. Again I already talked about detail about viscometry and rheometric measurement technique, but today we will be very specific to application in paints and coatings. See when you take a paint after diluting it also how do you test it? You simply take a brush or spatula and try to put the paint or coating and try to see how it is flowing.



Say for example in this cartoon here, see first case you see it is a thin one, so it is flowing and second one is sticking here actually you call it thick, but that does not really quantify how much is that, one or the other very close proximity of viscosity variation, you would not be able to discriminate. On the other hand the very first thing as I was talking about you do for a paint or coating is particularly adhesive material, you try to stick it between two fingers and try to see, expand it. See if this forms a very tacky material, forms a long thread, okay it is called tacky and when less tacky you see it is a less elongation you can have it and it separates basically. So that is another qualitative test people make it for initial assessment.

So another technique which started becoming a little quantification of it is a flow cups. Today also it is being practiced like plastometer, even though it is a fast thermometer it is still practiced in rubber industries. In paint industries also the flow cup is still people practices, what you have essentially you have a cup and you have a capillary and you can give with a given volume of the coating or liquid material how much time it takes to come through the orifice or capillary. So the flow time is determined, so longer time it takes more viscous the material as obvious. So this is the flow cup measurement technique you can see through the cup it flows and you note down the time, lower the I mean shorter the flow time again the lower the viscosity of the liquid you can assess.

So accordingly depending on the viscosity and depending on the type of fluid you are handling with there are different types of flow cups available. And it has also ISO as well as other international standards. So for example ISO 2431 refers to one of the cup and orifice geometry. So similarly DIN the German standard also refer to 53211. So there are local standard or company standards say for example Ford, Shell, Zahn, Engler they have their standards and accordingly it is devised I mean what is the cup size and what is the capillary size.

In many cases you see for example here you have a sharp edge here, you can understand there can be some vortex may form. But if you look it at in this particular one, fourth one, Zahn one it is a it is a it is a devoid of any sort of a sharp angle basically. So depending on type of measurement it can be little wider here compared to here over here. So this minute differences are there but principally that the same given volume of liquid how much time it really takes to flow through a given orifice. So the time is a determinant of the viscosity of the material as such.

And let us try to be very specific I mean more quantitative way we would like to assess, we would like to see even its viscous vice versa elastic response as I exemplified for a proper rheometric measurements. There are in general two different types of measurement techniques available. One is a tube type like I mentioned, it flows through a tube like say cup method, glass capillary method, capillary viscometer I already talked about. If you say for example trying to assess only the resin part of the paint say. Then falling ball methods, these are already elaborated earlier in the rheometric classes earlier week.

So there are certain measurement technique as I mentioned earlier also are called rotational type. In rotational type of viscometry it includes parallel plate, cone and plate. I guess I already told you what is the difference between parallel plate and cone and plate. To have a precise air rate measurements you go for cone and plate rather than a parallel plate measurements. Also this parallel plate and cone and plate has some limitation because from the age it can get separated that also I highlighted earlier.

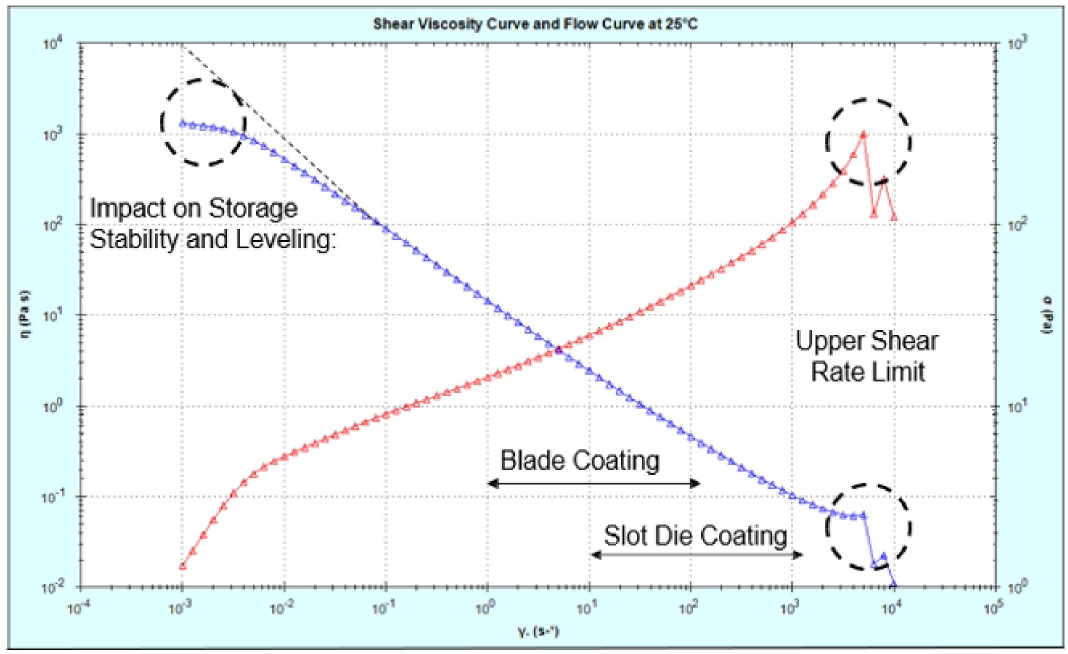
So that correction can also be done accordingly. There are other methods in order to avoid those issues concentric cylinder methods. And of course the mixture and mixture is simply you have a I mean stirrer that rotates you try to measure the torque required to make a constant rotation at a constant temperature say. So rotational type of rheometry always has certain advantages over the capillary type of measurements, tube type of measurements to be very precise. Number one is more efficient than capillary viscometer.

Why? They can be used a wide range of materials because opacity, settling, non-Newtonian behavior those difficulties can be I mean overcome. And then the shear stress as a function of time also can be measured. Why shear stress as a function of time? Many of the type of coating we would like to see the gelation time. We would like to monitor the curing so that only you can do if you happen to measure it as a function of time and try to see when you have a G prime G double prime crosses over or when is the viscosity suit of phenomena happen. So that is what precisely will be well captured by rotational type of this kind of energy.

Then the both viscous and elastic property if you do in a oscillatory mode you get two components of it. However, it can be modulus, it can be viscosity that means G prime G double prime and eta prime and eta double prime respectively. So that will give you the idea about how much it is viscous, how much is elastic. So on top of that as I mentioned normal force also directly you can measure if you happen to do it in a rotational type of measurement. So these are some of the advantages of rotational viscometry over tube type of geometry technique.

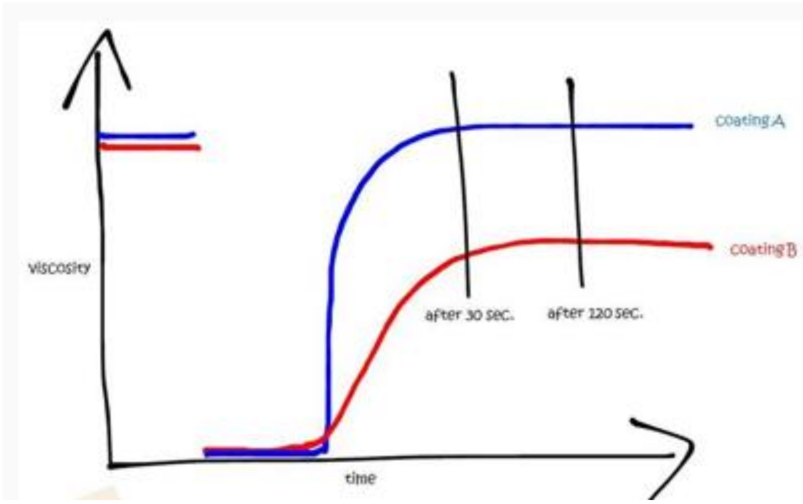
Let us try to take it from other angle also, application angle as well. See this is the typical measurement where we have plotted the viscosity the blue line the viscosity as a function of shear rate this is gamma dot. And other part is giving you plot of the stress, stress as a function of the red one. See one thing for shear, if you increase the shear rate your shear stress ideally should shoot up. See if you see some form of fall off here, sudden fall off that means that defines your limit of the measurement.

Interpretation of Shear Viscosity Curves of Coatings



So similar so in the viscosity also if you see a sudden downfall or fluctuation say so that you have to decide that geometry has that limit of maximum shear rate that you can assess. So now from the paint point of view if you see at the lowest shear rate regimes that means 10 to the power minus 3, 10 to the power minus 2. So what information it gives? It gives you idea about the impact of storage stability and leveling say. See when you are going to the higher shear rate regimes it gives you idea about as I mentioned it gives you idea of blade coating or slot die coating say for example. So this is the shear rate this double headed arrow represents what is the range of shear rate the viscosity data is so important from that point of view.

So two things one is the lower limit you have to decide whether it is stable data you are getting so that gives you the lowest possible shear rate regime you can capture using that particular technique. And second thing from the other extremities of the curve that means here so that is how the boundary will be decide for the particular geometric technique and within the data you try to see from your application point of view. So in a nutshell what I mean to say here the lower shear rate data do stability analysis try to fix it from this point onwards my data is reliable. And similar so at a high shear limit what it is I mean corresponds to the application like say coating different types of coatings there also you have to do the stability analysis and not any raw data you can take it forward as such. So that is will be your point as a rheologist there.



So let us try to be more specific let us try to pick choose one paint which use normally painting a wall. So the number of available rheological test has been steadily increasing actually especially the user and users in the research and development as well as in the quality and process control. Quality is a quick check you do not have much time to assess whether this paint you should take it forward or not. So let us try to understand a rheometer can be used to evaluate phenomena such as yield point. So if you happen to have a Bingham plastic sort of a thing you have a yield point after that only start flowing.

When determines the structural strength so it is related to the structural strength. So you have to cross it over and then only it will start flowing basically. And shear thinning behavior you see after a while it will try to I mean decrease with the shear rate and extent of decrement. Say for example here if you see viscosity versus shear rate data let us take two wall paints wall paint number 1 wall paint number 2. Red one is 2 let us take red one is 1 and blue one is 2.

See both paints shows a decrease in viscosity with the increase in shear rate that means it is shear thinning no question about that. From the elementary understanding you can conclude that. But you see degree of shear thinning the way the blue has dropped down to this initial value to the final value within the given range and compared to red, red is quite sluggish in that decrement. So that also matters. And another thing is also important is the thixotropy.

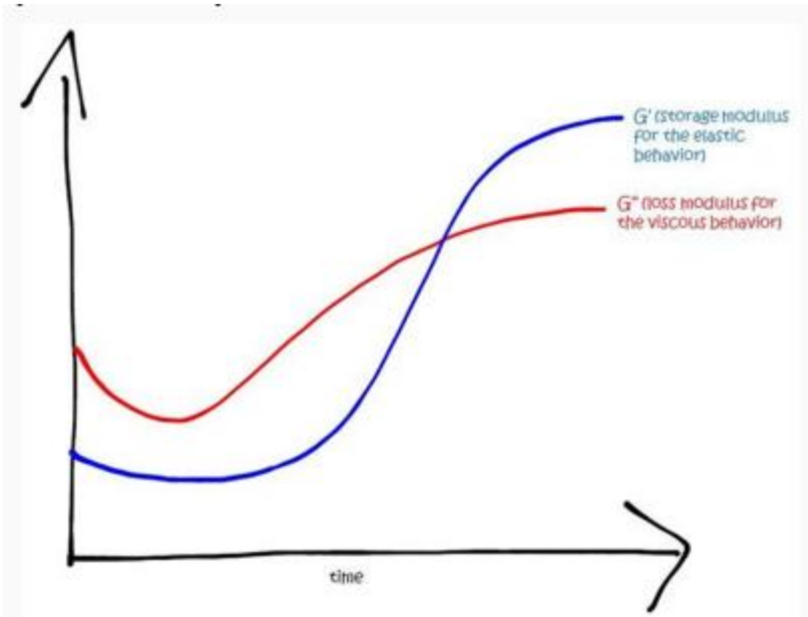
Thixotropy once again for your you know to recapitulation thixotropy is the change in viscosity as a function of time. So in that is in the thixotropy when analyzing the time dependency is important in terms of the recovery. So that actually reflects which one gives you more structural recovery after application. You understand you applied it at a very high shear rate then it comes about almost 0 shear rate and you are allowing the time and try to see whether the viscosity is further decreasing or standing tall there itself.

So that is what it matters. So most paints shows shear thinning flow behavior with a decrease in viscosity once shear rate is increased. That I told you it is true for any polymer solution any polymer melts in general. Only in some special cases when you have some special type of a filler you may have a shear thickening behavior also. Otherwise in general it is a shear thinning type. And therefore the faster you stir you just apply a polymer solution or paint or coating solution and you increase the rpm of the stirring and the viscosity goes down.

So this test I have normally performed with a rotational rehometrics technique basically. I will come there, there are certain viscometric technique which will readily offer you those sort of an information. So again once you apply a coating many a times you have a primer then have a top coating. Primer has a different characteristics top coating has a different characteristics from the application point of view. So that assessment is very very important.

And that too when you test it however in a rotational or oscillatory mode some different types of test protocols you have to decide. Some routines you have to decide. Let us try to take a look on that on the top four. In rheology thixotropic behavior is defined as reduction of sample structural strength during the test interval with a constant shear load. And the complete regeneration of the structure during the subsequent interval of the test.

So generally it is performed the test is performed the test routine is three interval thixotropic test. How? The first one is rest interval. In the rest interval evaluation of structural and rest at rest by pre-setting a very low shear load that gives you idea whether my coating or paint will settle sedimentation will happen or not that idea you get it. Second thing load interval then evaluation of the structural decomposition behavior during application under a constant high shear load that is what I was talking about. And thirdly structural recovery that means there you have to observe it as a function of time.



So evaluation of the structural regeneration over time after application and the preset measuring conditions are exactly the same as the rest interval. The first one and second one is same in between you applied the high shear rate. So that is that the viscosity versus time measurements for coating A and B. Let us take two examples blue and red once again. The red one you see there is a distinct difference between as a function of time where you build up.

So you see the two boundaries is mentioned after 30 second after 120 second in between 90 second you try to observe it. And then coating A a rapid structural regeneration and less sagging but not enough for leveling. This one high viscosity is developed here. For leveling you need little bit low viscosity as I mentioned it to you. But the second one you see leveling wise it is better because after setting it as a low viscosity but at the same time if you observe it you can see that it is leveling I mean it is storage part is because slow structural regeneration happens and better leveling behavior but not stronger tendency to sag.

So that is why you define resulting in insufficient layer thickness and tears running off. So that is what it happens. This is a three interval thixotropic test as I mentioned. One is rest interval then you go up to very high shear load try to see and then again you stop it and try to see the structural deformation how it is happening. See if we take an example here the viscosity versus time two coating system A and B blue one as you see it is a very rapid very fast development of the viscosity it happens.

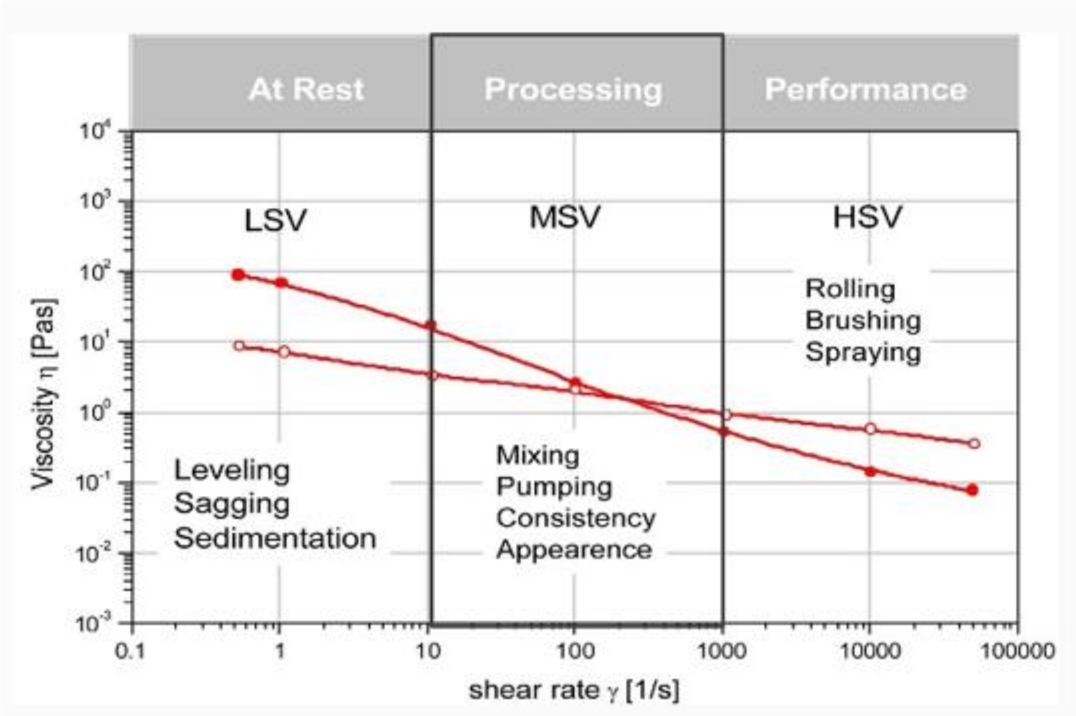
So that means in this case there will be no sagging it will stay there but leveling will be a problem. At the same time if you look it at the second one in that case it is a slow wielder. So leveling will not be a problem in this case but there will be obviously a sagging tendency of sagging. So that is the difference you can make it from the rheological studies that way on the top coatings say.

Primaries underneath of it. So when I talk about the rheological test on powder coatings this is also important. Powder is a molten state and then it is a particulate form it is sprayed on a substrate kind of a electrostatic way it actually forms a continuous film on that. That is the powder coating. So cardboard is for example is coated by the powder coating techniques. So powder coating coatings are an emission free alternative to the coatings in liquid form as they do not contain any solvent.

And usually a powder coating is applied electrostatically as I mentioned and afterwards a film is formed by melting the individual powder coating particles in an oven. And the time and temperature required for the film formation are of great importance and require low temperature and short time for film formation. So what is important here try to see do the oscillatory test here why? In order to determine the curing behavior of the powder coating a temperature test with an oscillatory rheometer is performed. So an oscillatory test simultaneously determines both viscous behavior described by loss modulus as I mentioned it to you it is other way round. When I talk about viscous behavior eta prime or G double prime that is what I meant.

And elastic behavior that represented by the storage modulus which is represented by G prime. And thus when curing behavior can either be determined as a function of time dependent behavior at a constant test temperature it is called isothermal test. And as temperature dependent behavior within a certain temperature range so both way that test can be done. Here is a isothermal test is represented. Here you see two modulus G prime and G double prime you monitor as a function of time.

And you see as it cross links obviously it is G prime is dominant over G double prime. So you can really see when the cross linking is happening. Same as when I talked about MDR it is the same principle when you do rotational rheometric test here. And so long as G double prime greater than G prime coating is in molten state that means it is a liquid behavior. And the curve minimum shows the onset of curing process.



And after crossing over G prime G double prime becomes equal and this point is called gel point. This is exactly same when I talked about for the curing of rubber. But I am just looking at from the point of view of powder coating. So in order to sum up can't we define the range of shear weight from different different applications say for example if I try to capture leveling sagging and sedimentation behavior of a paint that regime is generally called low shear viscosity or LSV and that is typically ranging from 0.

001 to 1 second inverse. Then you have a medium shear viscosity regime which actually corresponds to mixing, pumping, consistency, appearance those aspects of a paint. And this is represented by MSB medium shear viscosity range 1 to 1000 second inverse. The higher regimes the high shear viscosity regimes which is 10 to the power 3 to 10 to the power 6 you know second inverse shear rate it demands. And it takes care of rolling, brushing, spraying depending on type of coating you are applying or type of paints you are applying this is the HSV. So the consistency of a coating appearance, pouring, mixing behavior is defined by MSV the medium range.

So this gives you aesthetics, ease of manufacturing say. And there is a dedicated viscometric technique available for the paints which refers to ASTM D562 you can always refer and it is called Stromer viscosity. It is same as the rotational viscosity applying different when payload on the rotor and see the effects basically. And that way you cover the entire regime of MSV. And corresponding DIN standard which is a German standard is also available you can always refer to.

Once again I will repeat on this slide. You get a plot of viscosity versus shear rate it is a master mode of a master curve. And you can see here that low, medium and high you know two different paints are water based coating systems are represented here. One the this one unfilled one in the legend you see is lower here that means this will be vulnerable to sagging compared to the this one. But this one also is a lower viscosity here and that is that means that it is rolling brushing will be easier. And that way I can always refer the first one if I put it first this one second first one is superior at least from the point of view of leveling sagging sedimentation as well from the point of view of rolling brushing and spraying the application point of view.

So that way you can discriminate by simply doing the rheology across the shear rate and which I always refer it to as a master curve in terms of rheometry. It can be viscosity versus shear rate if you do it in a simple rotational way. If you do oscillatory way you can have a same representation. Your viscosity turns out to be that complex number and if you can have it you can have it. So accordingly you will be getting another additional information which is nothing but how much viscosity is how much elasticity is as simple as it is.

So let us try to consolidate it in a table. Typical profile of a good thin film water based coating is given below. In terms of storage I always refer to as shear rate 0 or 1 second inverse very nominal one. So it demands from that application point of view from the storage point of view the viscosity must be at least greater than 50 Pascal second. This is a arbitrary figure but close to that.

Whereas instress should be greater than 1 Pascal. So that gives you assures you good storage. You can store that particular paint over time self-live is going to be very good. At the same time when you transfer it to brass without dropping, without dripping rather. So then you demand a measurement at 0. 0 is not possible but you always have a chance to interpolate it, your viscosity data as I mentioned it to you.

There the viscosity must be nominal. It should be just simply greater than 2.5. Less than 2.5 it will drip like water.

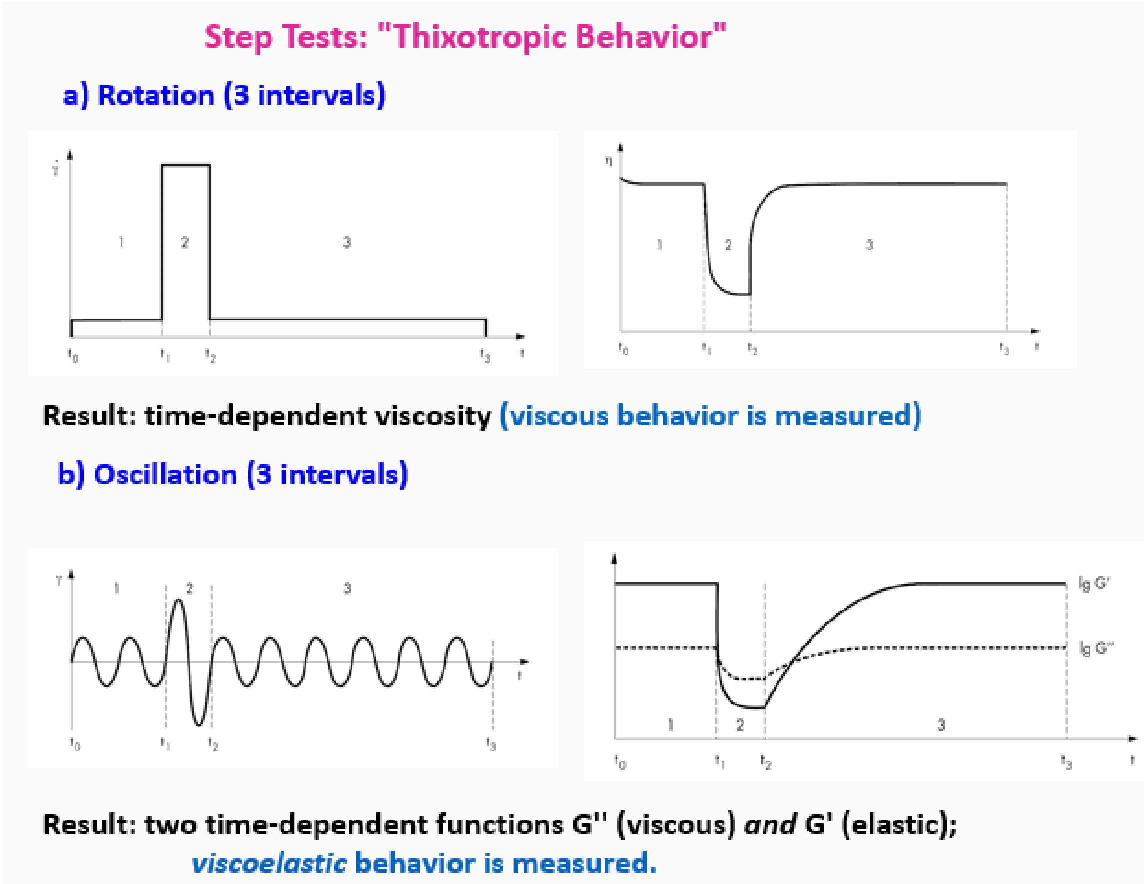
And then you should have a instress again or greater than 1. So I am talking about a transfer to the brass from the can. Then transfer to the substrate while application. I mean I am taking a particular brushing or rolling shape for example.

So 10 to the 4 second inverse and viscosity must be between 0.1 to 0.3 Pascal second. And here you do not need that much of instress obviously. If it is a you know big-ham type of a body it is nominally greater than just greater than 0.25. And for drying point of view which is corresponding to 1 second inverse shear rate and your viscosity has to be again drying and leveling.

It should be higher than when you apply. Obviously it is 5 to 10 but not as high as when you store it. And instress is greater than 0.25. So that is a typically figure just to set your mind set from the application point of view.

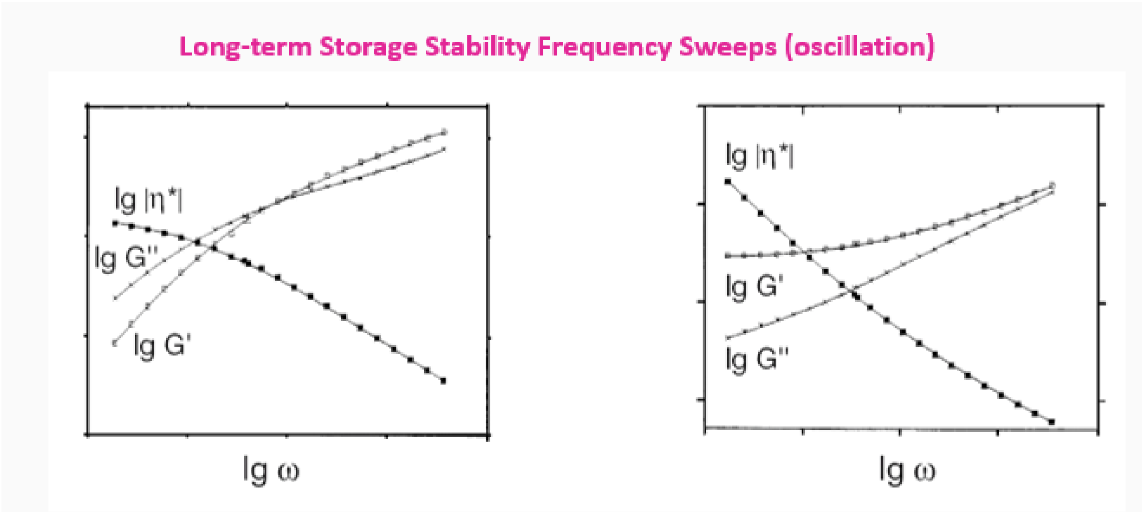
Nothing more than that. This number may vary grossly from here to here. So instress larger than 1 Pascal and a LSB about 50 low shear rate viscosity obviously up to 1 as I defined is a are typical values to prevent settling and during storage operation. And this is a thumb rule you can take it as a thumb rule. Now your paint is not only about the resin another material which has is a pigment and which is dispersed and some special additives maybe. Now we will try to understand why shear thinning happen.

At rest your polymer chains are entangled which has resistance to flow. We apply a shear rate you see it will try to align with the flow come out of the entanglement that is why the shear thinning major shear thinning behavior happen. A droplet emulses apparently with a spherical or globular shape you apply this force it will try to elongate and try to align itself with the flow direction. If it is a secular in nature which is random apparently while flow it becomes almost parallel. So this is what it exactly happens. Now let us try to understand the thixotropic behavior that is also important many a cases many a times for application from the point of view of application.

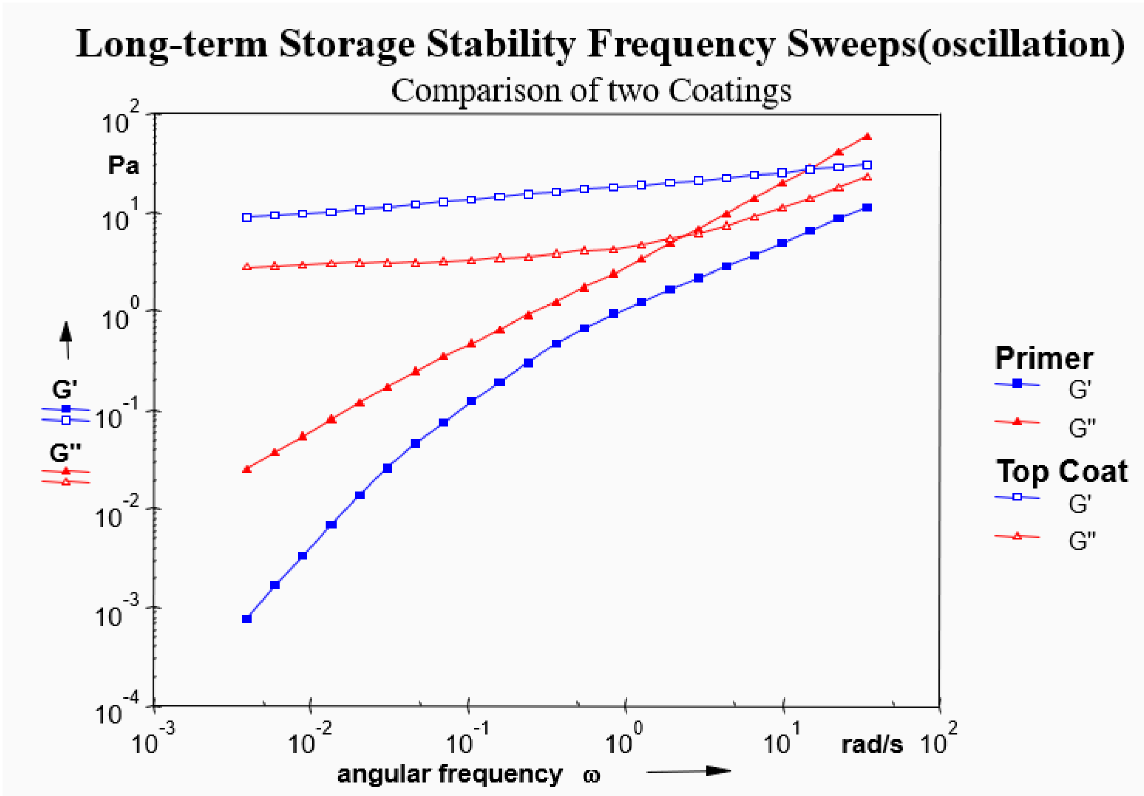


See many a times you do either rotational or oscillatory test but with some intervals. Say you do rotation you have to do apply here shear rate as a function of time is a step shear rate you see initially shear rate was very nominal and then you increase it quite a bit as a step function and then decrease at a time say t2 and then keep it and then you come to end your test this is the end of the test t3. And you try to monitor the viscosity behavior. So as it is a shear thinning fluid initially viscosity at a low shear rate was high and then you see as a function of time how it is going on and then when once you withdraw or increase decrease the shear rate is trying to recover. So that is how it is a three interval test and that gives you idea as a function of time how the structural recovery happens.

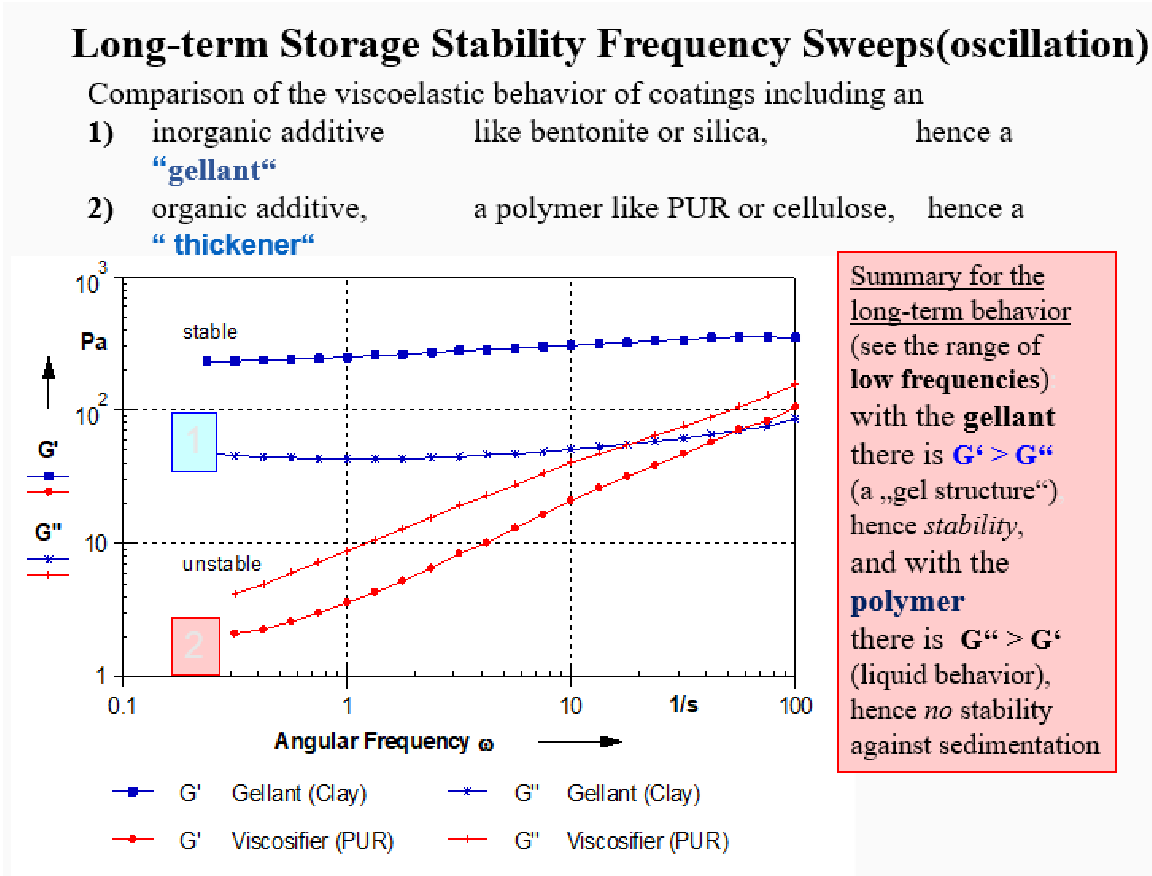
And similar so you can do the test in a oscillatory wave also only thing is that you change the amplitude here at a given interval between t1 and t2. t0 remember is the starting test and then low amplitude high amplitude or frequency also you can vary. So this is the step and try to capture the response of it in terms of course you have two components g prime and g double prime and you try to monitor the process over and that gives you idea about the structural you know regeneration reformation as a function of time structural recovery. So that is what I meant by thixotropic behavior you can well capture with certain test module which is elaborated here again what I told you is written point by point and this is how you capture.



Once again long term storage you can do a frequency sweep as well. So you see this particular case low frequency regime you see high viscosity its test gives a like a plateau and then it decrements while in the other case you see the sharp increment. So what is the difference the first case is a unlinked molecules its untrusting molecules in the second case you see a clustering molecule see by frequency test clustering molecule case unlinked molecule case which is not cross linked you have g double prime is greater than g prime that means more liquidus behavior. So as I mentioned if you monitor the complex viscosity of it it gives you a plateau type of a behavior here of course the crossover you can monitor as I mentioned as earlier while for cross linked molecule you see this thing increases abruptly here at a low frequency regimes and you see the behavior between g prime and g double prime and it signifies the gel structure of the material. Again the same thing you can see between two coatings if you compare primer and top coat say for example. So two things has a two different requirement top coat has to be more elastic than that of the primer which has to cover the whole surface primarily.



See you have a primer which has this behavior while you see g prime and g double prime is almost going hand to hand in case of the top coat across the frequency regime frequency sweep. So these are the some of the ways while you can monitor different types of coatings what should be the characteristic properties and you have to impart such properties in order to make a top coat vice versa make a primer one. Again long term storage stability you can determine you can have a inorganic pigment you can have a organic pigments you can have a inorganic additives like mentolite, laponite or silica which you call it gelant in paints language. You can use some organic additives like polyurethanes or you know polyurethane rubber or cellulose those are called thickener why this discrimination. You just have a test again oscillatory I mean g prime and g double prime as a function of angular frequency for these two cases.



And you see the what its summary of the results if I can summarize here low frequencies with the gelant g prime greater than g double prime gelant means that inorganic part g double prime is greater than g double prime. While with the polymer if you add a polymer like polyurethane or cellulose into that g double prime is greater than g prime which is a liquid type of a behavior you call it more of a thickener rather than a gelant. And that geometric measurements you can always do and you can see in case of the clay see this the field one you see the behavior while for the other case you see a whole lot different behavior you see for the case two which is actually a polymer which is used and which you always call it more like thickener than a gelant. So I will continue in the next class further from here but once again only one references I added on what I talked about so far is a surface coating science and technology by Swarajpal where you get a good depiction of that and applied rheology by publication is Anton Parr that also is a good you know reference you should always refer to. So quickly to conclude today I given the lecture of viscometry of rheometry in terms of paints and coatings only.

I have given you some case studies from rheological characteristics of water based coating systems shear thinning behavior and particularly how to set your test protocols particularly to capture the thixotropic behavior as well discriminate between you know top coat and primer how to probe into the curing behavior of a powder coating say for instance and finally I talked about long term storage how do you monitor and nonetheless once again I will repeat I define three regimes in your master curve one is a low medium and high in terms of shear rate and that corresponds to certain application some storage and certain preparation or manufacturing relevance. With that thank you very much in the next class again we will be touching upon some more about the rheology of paints. Thank you.