INDIAN INSTITUTE OF TECHNOLOGY DELHI

NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

VIDEO COURSE ON ADVANCED TEXTILE PRINTING TECHNOLOGY

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> LECTURE: 5 MEASUREMENT OF VISCOSITY

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So we continue our lecture series on the thickeners and viscosity. (Refer Slide Time: 00:30)

A step back.....

We had learnt

- What are thickeners?
- What is expected of a thickener?
- Why emulsion thickeners are needed for pigment printing?
- What is the concept of 'Zero' solids?
- Why polyelectrolytes are suitable for pigment printing?

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So in the last time we met we understood what our thickeners, and what is expected of a thickener, why emulsion thickeners are needed for pigment printing, or what is the concept of zero solids, and why polyelectrolytes which in a way are special type of synthetic thickeners are also suitable for pigment printing, this is what we learnt.

So mainly we will be talking about the viscosity, and how is it important to us from the point of view of printing, and how can generally we measure there maybe, not all methods that we are going to be talking about, some of the methods which the textile processing person may use, and that is what we would like to understand.

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So from our point of view, so viscosity as you may have understood earlier also, it's basically layer by layer, there is a shear happening in a system, the way it is defined is so you have a shear stress, so parallel plate model may be represented something like this, so it is assumed as if one layer or one plate is moving, the other may be stationary, so you require certain amount of force to pull this, and it may be pulled by some velocity this particular plate if we consider may have some area, so from simple simplistic point of view the shear stress could be defined as this,

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Viscosity • Shear stress $\tau = F/A$, assuming parallel plate model →F,v kushalsen iitd

and the rate at which this plate is moving would depend obviously on force, but finally there is something called a velocity and if you say shear rate, if you define like this then it may be the velocity with which it is moving, and because going to be sharing this plate will move somewhere there, so this change that will take place would depend on the distance between them also, and this rate shear rate has been also defined on this distance as well.

And so the viscosity could be shear stress by the shear rate, because this is velocity by this, so it is basically second inverse as the shall we say the unit, and here you will get Pascal second, as the unit of viscosity which is sometimes also known as dynamic, (Refer Slide Time: 05:05)

Viscosity Shear stress $\tau = F/A$, assuming parallel plate model Y = a chalcon lite

so because if nothing is moving you don't know how to measure viscosity, they must move relative to each other you see, so unless there is a motion there is nothing, even if you put a ball in a polymer solution, it'll go down, but it must go down, if it just stays there with a zero velocity there is no change, alright, so there is a relative motion.

Now this relative motion means there are molecules in the case of polymer they are long-chain molecules, they can be branched based on their length, they can entangle more and therefore offer more resistance and therefore this force would keep changing, so you have to apply more force to move and therefore you would have more viscosity, and that's how big relief.

In air also there is viscosity as somebody moves as we know, so depends on what velocity you're moving, for example when you talk about automobiles, when they start moving fast then you actually talk about drag, if I keep moving it appears there is hardly any resistance offered by this so-called air, but when you swim in the underwater for that matter then you can feel the drag and you have to really make effort to move forward and that's, it is there but if you just keep floating and you talk about viscosity it has no meaning, alright, so velocity is an important component there, and which will also add to the drags, just so that we don't generally confuse in

case some small numerical comes you should not get confused, so you have force as defined as a Newton alright,

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this is kg meter per second square, because this is mass into acceleration, then you have pressure which is in Pascal's the Newton per meter square there also we use just before a term like this Pascal second which became the viscosity, so Pascal is something important, which is kg meter, per meter, per second square.

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Then this dynamic viscosity which we said Pascal second, so this is like kg meter inverse and second inverse incidentally, this unit Pascal second dynamic viscosity is also in terms of poise okay, so 10 poise,

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so 1 poise therefore is 0.1 kg per meter per second, and then 1 centipoise obviously is again 1 poise 10 to -2 which is 0.001 kg, I think there is a meter missing here, and or millipascal second alright.

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Units...
• Force
$$1 N = 1 \text{ kg.m.s}^{-2}$$

• Pressure $1 Pa = 1N/m^2 = 1 \text{ kg.m}^{-1}.s^{-2}$
• Dynamic viscosity $1 Pa.s = 1 \text{ kg.m}^{-1}.s^{-1} = 10P$ (Poice)
• $1 P = 0.1 \text{ kg.m}^{-1}.s^{-1}$
• $1 CP = 1 P \times 10^{-2} = 0.001 \text{ kg.m}^{-1}.s^{-1} = mPa.s$
• Why cP ?

Why people use centipoise? Generally if you see viscosity of a paste, viscosity of water, viscosity of other liquids, generally people talk in centipoise, otherwise theoretically you can talk about in dynamic viscosity as Pascal second, you could talk in terms of poise, so I talked about centipoise.

Interestingly at 20 degrees that is the standard temperature pressure, the viscosity of water you know real water, distilled water is approximately 1 centipoise, so people who started saying well water is one of the solvents which everyone uses, so how much you have gone up from there so you can do, otherwise it's a game of decimals here and there, so people have started using centipoise.

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So liquids which is a solvent first then you dissolve something in them, and so their behavior in terms of the shear rate and shear stress and viscosity on one side if you plot, if it is an ideal solution then this is the way it will behave an ideal, alright, so it doesn't matter, at what rate you are pulling, because it appears each layer is independently moving only you worried about how much force I have to require, but very difficult to get an ideal you know solution, so you have two types of solutions which we encounter, one is called the shear thinning, which is represented by this curve where you can see the viscosity goes down as the shear rate increases, this is quite interesting for us from the people who do printing, our printing paste should be shear thinning type, we'll just see why, others could be shear thickening which is also important in some applications, these days lot of people are working on such fluids, solid liquid combines where when you put shear, the viscosity increases and this people are using as if in a body armor, if you put shear thickening kind of fluids when something hits then viscosity increases suddenly, the good application.

When you walk on a sea shore particularly when the water is just gone in, normally you would feel that you put your feet, your feet should keep going down where is the slurry, but that also behaves in a different way that it goes little down and then you, it doesn't go down further, that means so there are examples where by putting pressure that means some shear you want to do you get resistance, and that resistance the viscosity increases and then it go further down you see.

While the other situations are shear thinning which we are interested as a people who are interested in printing, (Refer Slide Time: 13:03)



rheology alright, so when you have the increase the shear rate and measures viscosity, so what you will see is the drop, (Refer Slide Time: 13:37)



this phenomena is seen with the printing paste, this phenomena is seen in polymers which are melt spun, it is seen in polymers which are wet spun, and why it is important is, because of the shear this viscosity does not go down, the amount of force required to push it through the holes or pores will be very high, for example you have a printing screen which is made up of mainly let's say a textile fabric called a bolting fabric made of polyester or nylon, and you have a squeegee which is used to push the paste, now if the force required to push the paste through whichever little holes that we have is very high, then either there will be slackness, extension etcetera of the screen itself, so design can go haywire or you can tear the screen itself.

But if it goes down, so it flows out of those holes very easily, so when you do the squeegee, when you apply the squeegee on the paste which is lying on the screen immediately as goes down it becomes thin and passes through, goes the fabric where it gets absorbed, but the most important part even after this is that when the squeegee is lifted the viscosity goes back, so this is the thixotropic behavior in a way, it's a time dependent, it doesn't happen instantly, but it is not a zero time but there is a hysteresis, but it does reach up, and this is also important for us.

So our printing paste when you apply shear the viscosity goes down, but when you remove the shear force, stress then the viscosities start going back and this is a reversible process, so you again increase the shear rate it will again come down, you did it again go back, (Refer Slide Time: 15:32)



so thinning occurs and then again the viscosity builds up when you work.

So the second part is also important to us, if suppose there are such systems, such pastes where because of shear the viscosity becomes low, and it is helping because it can pass through the screen the design, but it does not come back to this original state, then what would happen? The whole paste which is now has a low viscosity will keep falling down through the holes which you don't want, so what you are interested is? When you apply pressure it goes down, when you remove it should come to the same viscosity and you can keep lifting up nothing will come through the screen, so this behavior if it was not there that was only a simple behavior like it has certain viscosity, when you want to push it goes down if you don't want to push it stays up, then the total force required is high, the stress on the screen is going to be very high, and generally you may be damaging quickly.

Similar is the case of the melt spinning or wet spinning when polymer is pushed, solution is pushed through the spinneret the viscosity around the spinneret and through the hole becomes very low and just passes through that, and after that of course there are other processes which solidify, our aim is different, so this thixotropic behavior of the, are printing paste is an important characteristic of the paste, any polymer which does not give us this also is not so good, alright, so difficulty for example somebody is saying last time that can we use polyelectrolytes synthetic thickness for every printing? Theoretically yes, as long as there is no PA change, if because of any addition, any type of anion cation combinations happen suddenly viscosity will fall and you will not be able to do anything what you want to do, so this is one precaution as long as you say we are neutral nothing is going to change as far as the ionic concentrations are concerned then you may be able to print anything and everything, so that the sensitivity towards this, but this sensitivity is every type of a polymer that we would require for printing, this is not pH dependent although we all understand viscosity is temperature dependent, so if you increase the temperature then

things will be different so whenever you measure you will have to say at what temperature did you measure,

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not only that what temperature you measured people would like to know how did you measure, this is like when you say crystallinity of a polymer, do you say how do we measure? Say I use wide angles X-ray diffractometer, very good, other one can say I used a DSC to measure the viscosity, so you have to actually tell or density to measure crystallinity you have to say well this is density crystallinity, this is x-ray crystallinity and this is the other method that we use, so you have to talk about the method.

And similarly viscosity measurements despite all the fundamentals looking very nice, but because there is going to be relative motion, how do you do this motion? How do you observe this behavior is what's going to actually, also say that well I use this method to do this at this temperature and of course hopefully pressure is going to be atmospheric pressure.

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Basics

- Relative viscosity
- Specific viscosity
- Intrinsic Viscosity



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So some terms which you may like to revise, one is called relative viscosity, the relative viscosity means that you have a solvent,

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let's say in our case it was water and then you have a polymer or it could be any solute for that matter, or it could be any other thing which you're dissolving, so you measured viscosity of one and the other, so eta 0 is the solvent, the eta is your actual measured, so this term is defined as a relative viscosity, which is sometimes used more often than the actual values alright, so you know the solvent for some reason, use a measure viscosity and say well this is the relative viscosity, so if it is more or less and you talk about certain numbers and then you can say well

the paste that we were actually making one week before is not exactly same what we're making today and they do something else, so what can you do, you can't change the molecular weight very easily because it is what you got it, but you can change the concentration.

So in some ways we said the molecular weight and concentration both can change the viscosity, but you require a certain viscosity, so you may have to do that, but this type of a study is normally done to, by those people who are doing research in the sense that they're looking at a molecule itself, they change the molecule, they have modified the molecule and they want to know what has happened or they were idealized, so molecule rate has gone down, how much has gone down? So theoretically from viscosity measurements you can get to the molecular weight as long as you know certain constants.



The other is called the specific viscosity, which is also from the same values but defined as the change, change that has happened and this is you can measure which is derived from the same thing, so basically they will be related you know they are related, but why we talked about this? The intrinsic viscosity is very specific to the molecule, so what people will do and it also has another term called concentration, (Refer Slide Time: 23:06)



so you measure specific viscosity of a certain concentration then dilute it, and then measure and dilute it, and then measure and dilute it and measure, if you can go almost to the zero concentration limit where the concentration is very close to zero, that almost is the property of the molecule itself.

In other cases there are one molecule may be interacting with the other, and therefore giving a different value, entanglements could happen, but here is almost like so dilute then we're not really looking at the entanglement, we are looking only interaction, so this is also people who do research they would like to know about their molecule and so they may like to measure intrinsic viscosity, alright, anybody who makes a new polymer, tries a new polymer, does something to the polymer would like to study intrinsic viscosity, so if you are actually dealing with relatively dilute solutions,

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relatively dilute solutions, then this type of viscometer which is called the capillary viscometer can be used, so this is one typical viscometer which is called the Ubbelohde viscometer, so you can use any such device, it doesn't have to be this device.

What you're looking at is that there is a capillary here, so if your solution is here so there are markings, if the solution is let's say filled up to this point and then allowed to go down and you measure time, because the volume is fixed between let's say there are two bulbs, this is just to have some more additional solution here, and then you allow it to go down, flow down, and the capillary is dimension of the capillary is fixed for example, once it is fixed then the flow rate will be decided by the viscosity alright, and so they measure time from let's say point this particular point and to this marking, how much time does it take? Of course the whole thing can be submerged in a bath so that you can have temperature control, (Refer Slide Time: 26:25)



so there is a bulb which is reservoir, in a kind of reservoir, so it also says well you fill it up at this point, you can fill from here the measurement, then you suck by sucking device, you can use a sucking device the solution will go up, you take it up, remove it, then it will keep coming down, so you have enough time with a stopwatch you can measure the time, and so this will done.

This flow also because of concentration, at whatever concentration you have if you are looking at a solution which may have a different density, so N nita eta, so you have, which is also related to time and density of the solution or a solvent, so T naught and rho naught for the solvent and rho and T at density and time required for the solution, if it becomes more and more dilute then this may be approximately equal to the density of solution and the solvent may become same, so what it means is this particular thing can be almost equivalent to the ratio of the time taken, right, so therefore you can use this method, simple, (Refer Slide Time: 28:31)



nothing to be done just keep sucking it and keep putting that, and dimensions don't change, only thing here to make sure is that you have to have the capillary clean, if something gets stuck then the dimensions change, and then you don't know what results will get, as long as you know how to clean it and everything is good, so this method can also be used to keep diluting the solution, and then later on plot whichever way you want to plot and get to a value which looks like as if the concentration is going to be zero, then this is kind of the value and you can get to intrinsic viscosity also, alright that's what it is.

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So when you have print paste, now when we are looking at printing we are more concerned about the viscosity of the paste rather than the intrinsic list of viscosity of the molecule, so this is the practical situation, can we use this viscometer, the capillary viscometer for this purpose? So we cannot use this because nothing will pass through, and so you have to have different methods of measuring viscosity,

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Rotational viscometers

Torque required to turn a spindle, in a fluid indicates the **viscosity** of the fluid.



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so you can have your viscous liquid here, hoping that this one have less effort, but anyway one has to calibrate and every time you make any instrument you have to calibrate, you calibrate and that would depend on what? The diameter of the spindle, the diameter of the vessel in which you have put your viscous solution and then want to rotate, so energy required to rotate can be related to the torque and therefore you will get to the shear rate, then you will also know what is the mass being rotated, what is the area or volume of this particular thing, and that can be related to viscosity, you can appreciate if you do not turn at all you will see note reading no change, the moment you start turning there will be some value, so what people do is they turn at a certain RPM, of course temperature and other things should be constant, the dimensions hopefully of a particular rotational viscometer will remain the same and so based on that this can be correlated to the actual viscosity of the paste, so if tomorrow you decide to make your own instrument, so you will have some other way or one other way of measuring viscosity then you will say well I am measured viscosity and these methods, and these are the values which are coming, and now in a dynamic viscosity I am doing, and the moment you change the RPM the viscosity will go down at least for our pastes, and so keep rotating faster your value will go down, then you make it slower the viscosity will start coming up.

Now in this case the distance between the inner portion of the container versus the outer surface of the spindle could be very small or very large, if it is very large then it's a story which is different because here there is a material which is very closed which does not move at all, and therefore resistance offered will be different, so the distance between them also going to be factored in calculation of whether the viscosity is whatever you are measuring or otherwise is different, so for one instrument this will be constant, so the constant for that will be given and theoretically the torque can be calculated by the amount of energy being supplied to rotate anything at a certain RPM, so you retain anything at a certain RPM you are applying energy, if suppose you put a more viscous material, so you say therefore to run, rotate it at 10 RPM for example, then you are supplying more energy, otherwise is rotating at less, so you want to fix the RPM so you have to keep applying the energy, and once you do that, yes it will get the value then you can correlate and that constants will be there.

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Brookfield viscosity



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One of the popular viscometer is called the Brookfield viscometer, and the viscosity measured by this viscometer is also known as Brookfield viscosity, because this particular instrument or the, it's like you know you say Worcester evenness, so evenness is an evenness, why is it Worcester evenness, it was because this value became so popular everybody wanted to use that and therefore you can almost correlate, oh if this viscosity is this much I know what we are looking at, it's become almost like a standard, so they would be having for example based on the range of viscosities, they may be having different spindles which will have their own constants, and theoretically here you can have a large vessel and you just dip or push this in and you can still measure, so you can correlate that means the effect of the walls can be avoided, you're looking at the effect of only the neighboring layers of the polymer solution which was effect, so this is one way of looking at it, so they would have different types of spindles, all of them have different constants, they will be in a way useful for a certain range of viscosity so based on you know that well this is my printable viscosity, this is something else, you may use a different spindle and get to that, so there's that, they would be in your table available that this spindle, if this is the kind of rotation is coming at a particular RPM then you go.

So anyone of you used Brookfield viscometer? So you should get a chance I think in the lab you have viscometers, you can use them because although there is no lab here, but I am sure you should be able to go there and see, make your own stuff, measure it and even check whether by increasing the RPM anything else happens, (Refer Slide Time: 36:55)



different spindles will have different dimension and therefore different constants that you should know you can specify that also, normally people believe that if you are saying Brookfield viscosity therefore the equipment and instrument that has come has got certain standard sized spindles so everybody has the same standard size spindles, and then you talk about RPM and temperature, so you can say that your results are as good as anybody else's results.

So calibrated to measure the centipoise the viscosity, (Refer Slide Time: 37:43)



because this C should be small and so you can measure your viscosity of the print, but that also means that you got to have a Brookfield viscometer wherever somebody's doing a printing, but most people may not have this viscometer.

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So there's another thing called a Ball fall, so you take a solution and put a certain amount of

steel ball for that matter in a jar and again measure the time required for this ball to move from one point to another point, so in the capillary it was the solution which was moving, here the solution is no, container obviously doesn't move, it is the ball which is moving relative to each other, and therefore there will be some resistance, so therefore there is resistance therefore there is going to be some time difference based on the viscosity, and then you can correlate that as well.

So people sometimes say well there's a ball fall method I have used in the time is this, and so they just keep talking about time, time required is too much that means more viscous less, less viscous and so one can work around,

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so one can fix up some time markings point 1 to point 2 and then as quick and simple as long as you can see the ball, you just put the ball and that's it, and you want to take more readings, if there's enough space at the bottom you can keep putting one ball after the other, you will have more readings you can have the averages and work around.

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What happens?

Drag and terminal velocity....



Why this is important is, there is a term which is terminal velocity, this is a ball which wants to go down, let us say so there are streams which would be there all around the ball as it keeps moving, so gravity is going to pull it down, but there is a drag force because of viscosity which will in some sense keep it up buoyancy,

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What happens?

Drag and terminal velocity....





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and this will depend on of course the mass well in fact the volume and density they're going to be related, so density of the ball versus density of the fluid are same what will happen? If the density of this ball and density of the fluid are same, then what would happen? It will just stay wherever it is, it will not change any position, so if you just push it by something whichever position you push it, it remains stationary there only, that'll give you nothing, so will give you nothing, you do not know what is the viscosity is, okay, viscosity will not know, you only know that the densities are same.

Have you done any experiment on a density gradient column? Have you heard about, do you know that how people measure the density of a fiber, how do you measure the density of fiber? Density of a fiber measure, so that's called a density gradient column, and density gradient column you use to partially miscible solvents, those densities are different very carefully and you create a column where the density from the top to the bottom is gradually increasing very nicely the column has to made, you do shake it everything is gone, so you make one type of a density mixture, and the heaviest it goes down then very slowly pour the lighter one, then the lighter one, then the lighter one, and you say you can actually create a density gradient as you move from top to bottom.

And then you put a polymer chip or a fiber it will start sinking till the time where its density is equal to the density of that point and just stays there, you can come next day and measure the height and say well this the density of this fiber because I know the density gradient of the column, right, but we are not interested in finding density, what we are interested in finding the drag and then the viscosity, and knowing how they are connected, so if you drop anything like this it accelerates alright, if it accelerates then it is very difficult to measure depends on from where it started and where it's gone time becomes along, but fortunately does not happen, there's something called a terminal velocity, the two forces where if we call this as a drag force pulling up, and the force due to gravity pulling down they do get balanced at some point, and when they get balanced it doesn't accelerate, it just moves with a constant velocity, it's a Newton's law anything at the state of rest will remain at rest, anything which is moving will keep on moving, so that's the kind of thing.

And that's very important if the raindrop is coming from such a high point like almost half a kilometer if it keeps on accelerating and hits anything, impact will be interesting, it doesn't happen, because at some stage because the drag it actually attains a velocity which is called a terminal velocity,

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Stokes's law

Drag force (F_d) Pulling force (F_g)

At Terminal velocity, $F_d = F_g$ Therefore,



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so if this is what happens is we have a law which governs this, and so it gets related to the viscosity, so because this was also talking about a spherical ball and not any other object because if any other object is there, there are corners, there are other things and the calculations becomes much more difficult, and so Stokes calculated and found that this is how it will be related alright, so this is the viscosity, so you have radius of the ball which you will be putting down, viscosity, so this drag force will be more if the viscosity is more, and then the velocity with which is moving also related and the radius.

The pulling force which we talked about before which is the one here is related to the volume and density, okay, and the density is the density difference let us say this of the ball and this of the fluid, and of course G, (Refer Slide Time: 46:43)

Stokes's law

Drag force $(F_d) = 6\pi\gamma \sqrt{R}$ Pulling force $(F_g) = \frac{4}{3}\pi R^3 (J_b - f_f) q_f$

At Terminal velocity, $F_d = F_g$ Therefore,



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so when you put the ball, the ball start accelerating because a zero velocity, will start accelerating till the time these two become equal and where you can say the terminal velocity if you equate would be like this, density of ball - density of fluid, right, so what do we see here? If the R is more, the mass will be more and therefore velocity will be more alright, if viscosity is high, velocity will be less of the moving body,

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if the density difference is high then it'll move faster, if the density difference is less it'll move slowly, if the density difference is 0 then a 0 no move, so in this situation when you put this ball as I said initially it will start accelerating you don't measure time when it is accelerating, so in a

standard equipment people would have found that this type of a ball or this ball or that ball or that ball depending upon viscosity you use them it will move down, accelerate, but after a certain point it would have attained the terminal velocity and therefore you start measuring time, if you start measuring time from here it will be not a good thing because it is related to terminal velocity, and not to any velocity, the terminal velocity is a constant value alright, so this is how I can measure that.

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can see the ball, if it's a dark black you see nothing, if you make the dimension of let's say jar almost equal to that of ball so that if you want to see the ball then the values will be different because it'll be either touch the ball or the wall of the container is going to affect this ball as well, so it should be away also.

Then what do we do? I leave it, you think about that, (Refer Slide Time: 49:32)

A glimpse of viscosity of pastes

- 1% sodium alginate
 - ~ 2000 cP
- 1% guar gum > 5000 cP
- 25% corn starch ~2000 cP



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generally a starch would require almost 24%, 25% to get to some 2,000 centipoise viscosity, your guar gum at 1% could give you more than 5,000, because you can go to 10,000 you see all this or you can say natural compounds and therefore molecular weight is not a fixed one, so you just looking at approximate values while a 1% this may give you 2,000 centipoise, you may require more than that for printing viscosity alright, so you will have to keep adding more alright, so that is how some work, so what I did not answer you will do it yourself, (Refer Slide Time: 50:13)

Design

 A ball fall viscometer for determining the viscosity of coloured printing pastes



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design an equipment, the ball fall viscometer for determining the viscosity of a coloured printing paste, what will you do? In your own ways, okay, then do it yourself, you don't have to submit anything anywhere.

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Find out

- The chemical structure of starch.
- How is it different from cellulose?
- Chemistry of different thickeners
- The approximate concentrations required with different thickeners.



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Also whenever you get time find out structures of various compounds, start cellulose you know quite a lot, but you can still revise them, chemistry of different types of thickeners, they modified gums, modified cellulose, sometimes the starch modified and + synthetic thickeners, so some of the chemistry you can know, hopefully I will probably upload one or two papers for you, you can read them also but you can work around.

And approximate concentration required with some thickeners if you can get hold, so that you have for printing purposes, that's just to revise, (Refer Slide Time: 51:19)

Activity

- In lab mix different ratios of kerosene oil (white spirit) and water and stir. Note what happens.
- Add a little soap solution (emulsifying agent) to the above. Observe. Measure viscosity and effect of shear on viscosity- check if this is reversible?



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whenever you get a chance in the lab you can do this type of things also, that is mix different ratios of kerosene oil or white spirit or whatever you get, and stir see what happens when you add a bit of a soap solution emulsifying agent then what happens, then the viscosity whether it changes with shear and also if you reduce shear, does it come back, is it a reversible process, you can check it yourself whenever you get time, alright, so that's all for today, we'll meet next time.

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