Rheology and Processing of Paints, Plastic and Elastomer based Composites

Prof. Santanu Chattopadhyay
Rubber Technology Centre
Indian Institute of Technology Kharagpur

Lecture 14
Introduction to Paints and importance of rheology in paints

Welcome to NPTEL online certification courses on rheology and process of paints, plastic and elastomer based composites. Today we are in week 3 and lecture number 2 which deals with the introduction to paints and importance of rheology in paints. Of course, rheology of paints we will cover in the next lecture in more details. Today just try to understand what is the paints and how rheology is important while developing and while quality check of the particular paint after development. So, the concepts obviously covered will be what are paints, how do you define a paint and evolution of paints, manufacturing of paints, classification of paints is grossly not into the details of, emulsion paints, polymers used in paints, qualities of paints, several pigments those are used, importance of rheology in paints, that is the most important part. First try to understand the paints and try to understand the complication related to the paints.

And different types of models of shear thinning it is a quick recap that I already talked about and typical shear rate range those are used for paints and coating particularly in the front of storage, during the preparation like mixing, during application like sagging, during the various types of depending on type of paints you develop it can be powder coating like spray method, it can be by brush and in that essence how rheology plays important roles that we must understand. Once again some of the important keywords if you wish to browse through the subject as such, please look through these keywords pigments, additives, solvents, viscosity, again hiding power, thixotropy, polymers and resins, shear thinning fluids, non-Newtonian fluids, geometrical viscometry etcetera. These are the some of the salient keywords involved. Now, let us try to understand what is paints.

See classically paint, is any pigmented liquid or solid mastic composition that after application to a substrate it forms a thin layer and converts it to a thin solid film on the substrate. And it is most commonly used to protect practically. First thing is to protect, second is the aesthetics, it will impart color, it will act as a primer in many instances it will protect it from the corrosion say, if it is a metal body particularly which is very vulnerable or susceptible to corrosion because it will become aesthetically good and it will be soluble, more soluble. So, as that you can understand paint is not made out of a single material as such. It is a classical definition of a composite, it falls under the you know definition, broad definition of composite.

Why? A composite is a material which produced from two or more constituent materials and distinct phases, having distinct phases. So, in that essence paint is absolutely comes in under the definition of a composite material. So, what paint is? I mean if you just see a bottle of paint although every day you use it, but it is a black box maybe for a new person who is using it, but let us try to understand its component. I am not intentionally putting any brand name here, just let us assume we have a bottle of paint. See it has four component actually grossly.

What are those? The very first thing is the resin or polymer which acts as a binder essentially. Then you have a pigment which imparts the colour, you have a solvent that dilutes it and you have certain additives that makes your processing easier, application easier. So, let us try to see quickly what is what. The resin is actually a glue of the paint, a binder of the paint and it used to bind the rest of the components including the pigments, the additives together inside that composite material and give the pigment its adhesive qualities. While the additives it can have a several I mean causes that those additives are used, that should make the paint more user friendly essentially, rheologically.

So, additives are incorporated into to implement a number of helpful qualities, this may include quick drying properties and a resistance to crack and scuffs. So, these are the some of the things which are which are important and in addition to that, some paints can be magnetic, some paints can be anti-corrosive. So, accordingly those additives are added as a minor constituents rather. There is a solvent which is a carrier essentially is. So, as the paint dries, solvent evaporates and there should be a balance.

If solvent evaporates so fast, leaving behind the resin along with additives and pigments, then there may be crack, there may be some sort of a stress concentration points. So, that has to be balanced out, that way you have to choose a particular solvent or combination of solvents say for example. And the pigment is a part which imparts the color. Sometimes some hiding material is also there, say for example, titanium dioxide is also used on top of that you give that color. And color can be in the form of a inorganic pigments or it can be organic dyes also.

It depends on your application, it depends on the performance, it depends on the light fastness, I mean how the stability of the color remains. So, accordingly if you choose a pigment. So, in a nutshell you must understand your paint in general is consisting of four component grossly. One is resin, number two is additives, special additives, number three is solvent and number four is the pigments or the colorants basically. So, as you can understand as such polymer is a complicated fluid material rheologically.

So, you are making it either in the form of dispersion or solution. On top of that you are adding fine particulate pigments and various other additives. So, as such rheology of paints is quite quite complicated, as complicated as a field polymer system is, a composite system is. So, again let us quickly go through the little bit history of paints. And in fact, the paint was known to mankind about 30,000 years ago.

Even some of the ancient things including Egyptian mummies, they are painted with several types of paint that protects it from the natural degradation say for example, mummy is a classical example where lead pigments are used inside the glue material. That glue can be egg yolk, water, oil etcetera, etcetera. And the colorants initially could have been charcoal even plant based dies basically, that is the beginning of it. Then subsequently human civilization was going through the renaissance in terms of business and industrialization. And in fact, first recorded one even if there are I mean which are not recorded actually there are many many many steps by which it evolves.

And in 1700 to 1867 about more than a century over century the first paint was established in Boston in 1700 and by Thomas Child later in 1867 which is recorded D.R. Averill in Ohio patented the first ready mix paints in USA. So, that is the business with the paint started by the industrial users. Mid late 80s paint factories began, but problem was again transportation.

They made it a centrally placed how to really really transport it. So, a centralization was very difficult that way because the galons and galons maybe was the requirement and that time that transportation was not that user or industry friendly that way. Then early 1900 industrial revolution took place both Europe and other part of the West America and Japan and new markers of paints and coating as established. So, that becomes a separate industrial sector as such. And from the latest model of Ford to the latest model of television those days they are they need a very special type of paints special requirement, but nonetheless the bottom line is that if you look at the anatomy of any paint you make that has four components maybe the components will be different.

Anyway, so before World War II people started realizing the lead pigment when I talked about even Egyptian Mummy they had a lead. Lead had a special property like to stop the bacterial or microorganism activity at the same time it was proven to be carcinogenic to mankind and the environment. So, with that lot of other invention happened and actually consumer product safety commission band-led in the consumer paints essentially. And then today you have a market up in 2020 I mean 26.1 billion is the market in paints and that paints improved several new generation paints when antifungal paint, anti corrosive paints, water based single phase epoxy based paints to name a few.

And so you can understand it has a very challenging and evolving type of a market it has industrially. So, let us quickly try to see at a glance the manufacturing of paints. So, it starts from the inspection of raw material any industrial things you need to have a standard quality of the materials you are using and selection of additives. So, once you have a formulation then next is weighment. So, dry raw materials are wetted such as pigments additives and resins.

Next step is a pre-mixing step, particularly pigments are insoluble in binder as such specially so if it is a inorganic pigments. So, they are mixed in the form of a paste and this leads to a fine distribution in the long run. So, next step is your grinding of the pigments normally a triple role is used. Over which depending on the nip gap of those ,nip gap is the basically gap between the surfaces of the roles and you can pretty much decrease the size of it. So, pigments particles must not get damaged at the same time may result in change.

So, the color shape and size of the pigment is very important, shape of the size in a dispersion stage is very very important because light scattering depends on the shape and size of the particle. So, that way you have to conserve at the same time lump has to be broken. If lump is not broken this color, will be opaque kind of a opaque translucent sort of a color it will come. So, it will not be reflective good attractive color you will get at the I mean even if you do not realize it during this when it is dispersed in the paints, but when you apply when solvent goes away diluted concentrated system there it may form lump and that may give you a not aesthetic appearance at all. The next stage is a fineness of the color inspection this is very very important stage as I mentioned it to you.

And the next step is stability inspection. So, now, you are you have mixed them you made it in the form of a paint. So, viscosity say for example, is very very important I will come back here I mean viscosity again across the shear rate at low to high shear rate how it is important. Drying time once you apply how fast or how slow the solvent is going out again I mean I will come back there your paint can be like water based it can be even high volatile solvent based paints also. So, requirement or time of evaporation monitoring evaporation at different different tune for different paints cases.

Bleed resistance and density this should must be and then you are very ready to pack it the it filled in the container and there your concern will be the storage stability. So, if you put it in a container it should not sediment it should remain in the form of a dispersion state. Remember it most important or crucial one is a dispersion of the pigment inside the solvated polymer resin that is what is the bottom line. So, that must be conserved. So, your pigment which comes under the gravity say it will try to settle down.

So, this has to be maintained somehow. Once again quickly look it at the paint as I mentioned it can be water based or oil based. In water based one it can be one category distemper it is a very classical sort of a you know paint material and then also the emulsion. And in distemper there are one broad categories acrylic base or other synthetic varieties of it. So, that way your paint can be grossly classified.

But we will try to see a generalized depiction over here. So, paint I am not going into not expect that I am going to a particular type of paint and I am throwing light. Again it is a different perspective learning the basics from here you have to extend based on your application end of the day that is most important. So, emulsion paint as I mentioned it is a very I mean as you can understand it is a water is the base in emulsion. So, it is a that way very green material compared to the oil based one.

Where you have a significant amount of solvents and solvent hazard is also another part of it. So, emulsion paints are so called as they are made by the process of emulsion polymerization. And in which the liquid monomer to be polymerized and first dispersed in water as an emulsion. And the polymer produced typically in the form of emulsion is 5 to 10 lakhs average molecular weight if you consider the weight average molecular weight here. So, that is the typical range you polymerize it.

And the next as such they are useful only as dispersion since they would they are extremely viscous if they are carried out in solutions and they would make them unusable. So, let us quickly have a look if it is in the form of a dispersion like in the form of a emulsion you see viscosity if I try to check it with the relative molecular mass it says only relative I am gradually increasing it. You see dispersion has a continuously low viscosity. While if you make it happen to make it a solution then after a critical molecular weight you know molecular weight and viscosity they are not simply proportional directly proportional they are proportional to the molecular weight to the power 3.

4. So, that way there is a abrupt change in viscosity and that way high molecular weights you know solution will be difficult to process. It has extreme high molecular weight some of the applications say for example, spraying, brushing where you need to have a very low viscosity during the application. Even if your polymer is a shear thinning type that will not come to that tune from the initial viscosity which is quite high. When I am talking about the viscosity with the molecular weight that proportion I am talking about zero shear viscosity. And remember the polymers either polymer solution or polymer bales are shear thinning type.

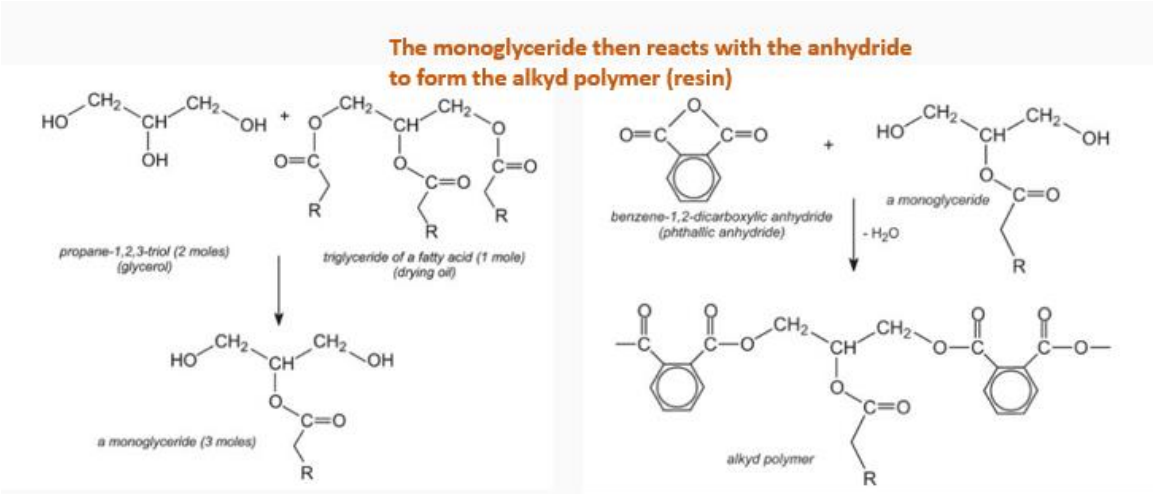
So, you can expect the viscosity will go down at a high shear rate, but if the initial viscosity is way too high and its dependency is not that you know high it will not come down to the

tune of viscosity as you desire for that particular application like spraying or brushing I will come back there. So, now in terms of polymers although there are several polymers used classically people used to use egg yolk people used to use several cellulosic products as a polymer initial days. But these days in synthetic paints you have grossly three different types of polymers which are used including acrylic, alkyd and epoxies. So, let us try to see quickly into the chemistry I am not going into the details again at this stage.

So, acrylic polymers is one of those special category acrylic basins may be used in the industrial paints either as a water brone emulsion or all solvent based both way ok.

The paint frequently comes in two components which are mixed together just before the use and the main paint portion typically consists of a acrylic resin produced by the polymerization of a propionate ester and from a polyhydric alcohol diols or trials. And the resulting polyester has numerous hydroxyl group pendant. This hydroxyl group react with the other component often consisting of polymeric isocyanate. So, it is like two component things. So, you just before use you try to put inside the pre polymer you try to use the isocyanate here and such as hexamethylene diisocyanate it is aliphatic in origin most often.

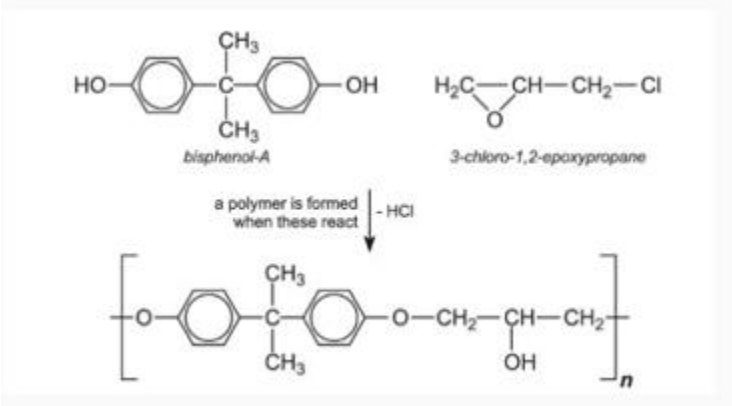
So, this is the chemistry. So, you have a pendant hydroxyl group from the main acrylic polymer pre polymer and that reacts with the isocyanate ultimately gives you the cross link structure which gives the stability of the base that is being formed. And remember in this particular base your pigments every things are actually dispersed ok. So, that is the beauty of acrylic paints many a times.



Another typical resin which is used traditionally used to be used for the decorative gloss paints typically are alkyd resins ok. What is that? A typical alkyd resins is prepared from a triol, polyol basically that is glycerol is one of the classical example with dibasic acids such as phthalic anhydride.

I mean anhydride way also you can use not directly acid sometime ester also you can used ok. And a drying oil, which is linseed or soybean oil is used ok. Let us try to understand very quickly what is there in chemistry. First of all this triol you do react with the ok triglyceride of a fatty acid and that is the typically what I say is a drying oil and that reacts it form a mono glyceride. And this mono glyceride eventually react with the phthalic anhydride and giving rise to final alkyd polymer.

This is the chemistry and the relative molecular masses in the range of 10,000 to 50,000 are usually carried in organic solvent and in the case of solvent grown paints in particular ok. And once the alkyd resin is applied the paint and oil drying groups react with the oxygen in the air and forms the cross link and a thermosetting coating is formed. So, that is how the chemistry evolves I mean revolves around.



The latest one is a epoxy variety ok. Once again it is mostly used in industrial primers all the primers anti corrosion paints and sometimes you know single phase sometimes I mean multiple phases two phase or two part or one single part ok.

So, in the in the in the anti corrosion paints to to protect your steel structure ok. So, they give the paint with the excellent addition together with the high resistance to chemical corrosion ok. And physical resistance necessary for example, in the sieves big structures, sieve holes in the bridges, storage tanks etcetera etcetera those are used mostly. So, epoxy this then let us try to see the chemistry. Chemistry is simple you have a bis phenolate and you have the epoxy monomer here and this is how the polymerization the n value you can manipulate.

The value of n can be controlled to give a range of resins varying from the viscous liquid to solids with the high melting temperatures. So, that is how you can manipulate based on the your polymerization process basically. So, epoxy resins can be carried out in solvents such as in aromatic hydrocarbons although aromatic hydrocarbons are these days people are trying to get rid of it as much as it is possible. Alcohols is relatively friendly ketones and esters and also in the dispersion in water. And water grown or water grown paints are becoming more and more popular more and more I mean people are giving governance are giving more importance to using water based one because you you get rid of essentially the organic solvent part of it which has lot of hazard.

Not only from the safety point of view while manufacturing there are chances of fire, but also while application that inhaling those organic components can cause lot of diseases to the users basically. So, they are not normally used in top coats for the outdoors because of the susceptible to UV degradation, but they are excellent interior coating and exterior primers. So, most often the that is that is the fate of epoxy based coatings are. So, there are of course, various as I mentioned other types of resins I just discussed the chemistry of three important ones, but they can be saturated polyester and saturated polyesters. It can be vinyl, polyacetals, polyurethane, amino acids, phenolics, rosin based, malic based resins, ketonic resins, isocyanate, polyamides, silicones also often used even including the chlorinated and fluorinated polymers are also used to add fire and you know those are the concerns and oil repellency is concerned.

So, qualities of good paints, good hiding power first of all, I mean as I mentioned it to in this context titanium dioxide paint is very important role. So, that it should not be transparent the material should you should not see the base of it. It should be capable of covering the existing surface of the material and it should be uniform. The color after its use on the outer surface they expose to atmosphere, even sunlight UV and oxygen and due to the exposure to the atmosphere it may be affected by rain, various types of radiations from sunlight which can cause the bad effects on its color. So, color fastness is as I mentioned it is another taste that you must assess.

I mean you use it today after two days, the color is gone now it should be assessed in such a way that after this many years the color should not fade away. So, that much of guarantee you have to do and accordingly your development or uses or selection should go evolve around that. Resistance, the paint should be chemically inert to the atmosphere and this is essential if it had to protect the under length surface of a metal in particular. So, if it gets exposed the surface and from that point the corrosion will start. It is a physical barrier and many a times it can be have chemical active components which can combat against the corrosion also.

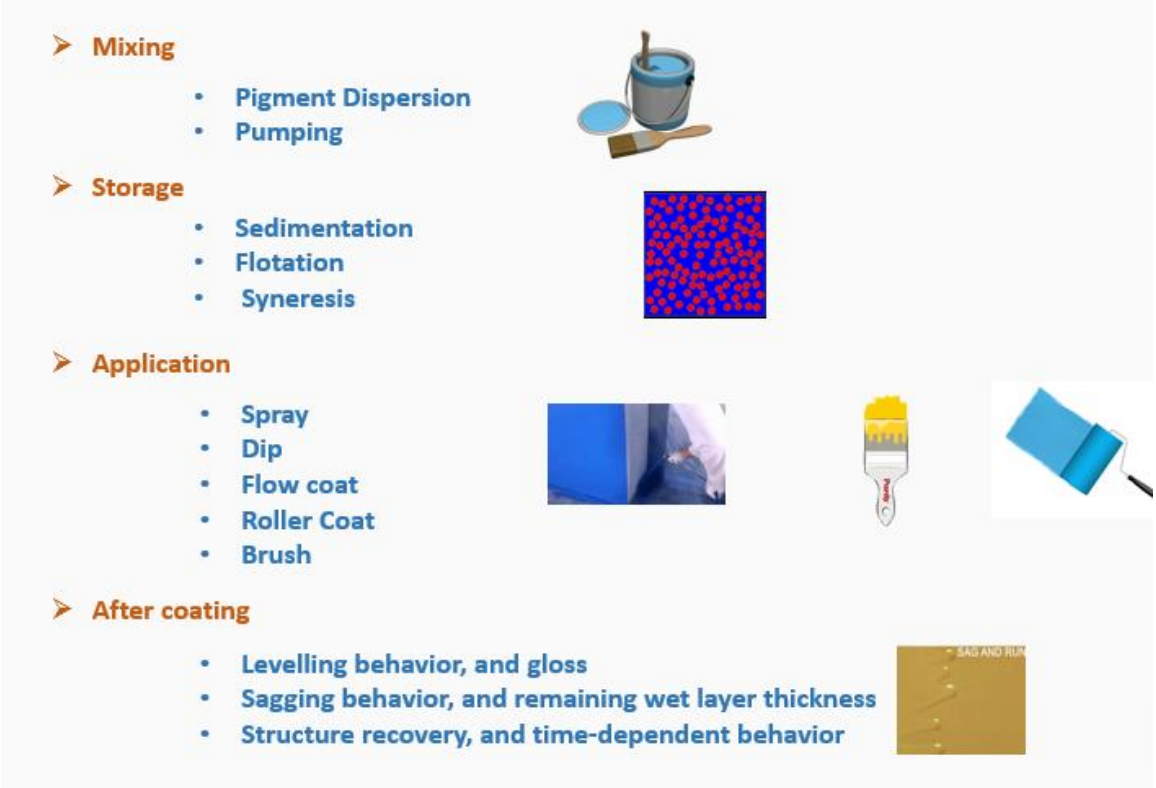
And the easy application this is very, very important in that essence your rheology plays very, very important role. It is therefore necessary that it should be such a nature that it can spread easily and while spreading it should not sag at the same time. So, at uniformly it should it is supposed to cover the surface of it. There are pigments which are giving a beautiful colors and choosing them based on certain criteria, certain physical properties including refractive index, hiding efficiency, color, pH, bulking value, then density, hardness, oil absorption and impermeability of course. Many a times you want your coating to be impermeable to gases and you know moistures.

The idea behind the pigment is to provide color and protect the substrate and to give color to a coating the pigment must create a opacity on the coating that is what the hiding capability means. And when a coating is opaque the pigment particles present scatter or absorb light sufficiently to prevent it from reaching the substrate. And whether or not the pigment imparts opacity is depends on the two characteristics as I mentioned it is inherent why titanium dioxide is used. It has a very, very high refractive index.

Second thing is the particle size. Color depends not only on the material chemistry but also it depends on the size of the particles basically and that disperses. That is why your gold particle of different you know gold you know it is a golden yellow color. But if you make it sufficiently small size this part it can be even violated. So, that is what the size matters. And one important component in a pigment is a pigment volume concentration PVC is very, very important.

And this is why it is important to have a pigment particles with high refractive index. So, that is how you have to manipulate the surface. So, you see here schematically the hiding efficiency is shown. See in the first case light scatters with this small volume element.

Well here the light can then scatter maximally. And so you do not see that much of gloss I mean in the latter case. It is a poor hiding efficiency is here. So, anyway that is a altogether optics you must understand bit on optics. But before we wind up today s lecture we must understand four important areas where geology plays significant role. Number one, the first place when you manufacture mixing the pigment dispersion and pumping.



When you automated one you pump it there. So, in that case the geology of that entire system plays very, very vital role. Second one as I mentioned already sedimentation. So, once you prepare the paint not necessarily you are making it today tomorrow it is going to be used. It may stay together on on self for one year two year. So, you have to give a guarantee it should not undergo sedimentation like this case from the cartoon says.

It should have a flotation I mean that that characteristics and seneses. So, this three I will again explain in details in the next class. And in application front I mean once you have a mixed prepared one stored and then you are going taking it to the application. And then depending on type of coating it can be either used by the process of spray say for example powder coating, it can be a dip, it can be flow coat, it can be roller. Whether application of roller you apply on the substrate or most I mean frequent application you are familiar with is brush. So, all these things they they they they refer to or they corresponds to certain shear rate of deformation.

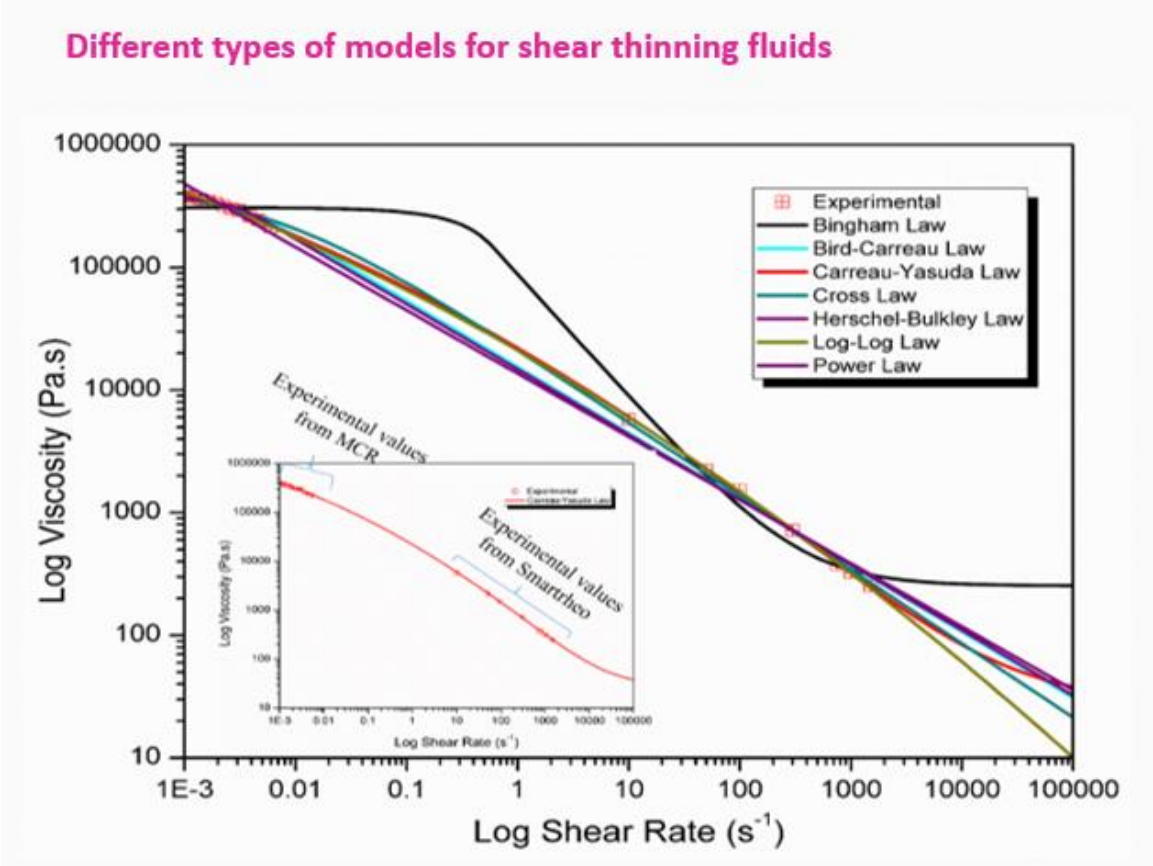
And in that deformation rate of deformation what is the viscosity that matters I am coming there how. And after coating few things you have to look it at you coat it your job is over not like that. It may so happen the leveling and gloss after after leveling what is the gloss it is giving. Sagging you apply it you see it is coming down down down down here it is not good it should give you a level glossy surface end of the day after application. So, layer thickness should be very very uniform and the structure recovery see polymer you are applying it after solvent goes it becomes a concentrated polymer solution then

eventually it becomes a solid composite mass.

The shrinkage is a factor structural recovery is a factor which is time dependent phenomena. So, this the visco-elastic property of the fluid as such. So, polymer no more you have to consider as a Newtonian fluid it is more of like a visco-elastic fluid then. So, this after coating also so you have distinctly 5 different 4 different stages say for example, mixing storage application and after coating. Quickly into that what I said what is the knowledge of I mean across a difference here rate what is the viscosity and even if you know the viscosity well at all the material is time dependent or independent I already talked about many times and this stability also plays very very important role.

So, what theologically, geometrically you must you know evaluate, calculate the amount of shear rate which will affect the paint or coating sample during application. Evaluation the viscosity value of the paints or coating will fit in the requirements for the applications and most importantly measure the long term storage of that otherwise you make the paint tomorrow you have to throw away the paints. Just quick recap like any other solid material a paint which is a dispersion or a solution in the state it can be either being harm plastic with a ill stress if you plot shear stress with the shear rate it can be shear plastic, it can be dilatant, it can be Newtonian. Newtonian is a very ideal case often you do not get it a Newtonian behavior. Again from the time point of view it can be you know again viscosity if you plot it Newtonian stays constant.

Pseudo plastic it decreases with as a function of you know shear rate increase the shear rate and then you have a dilatant and which is not shown here whether it is a thixotropic or reoptic ok. So, it is time dependent way how it matters. So, ultimately what I mentioned it to you in the reometric case not no reometer is available which actually measures from the 10 to the power minus 3 to C 10 1 lakh second inverse. So, you need in certain cases a wide range that is what it is called mass curve ok. And then what you do you try to fit in with some parameter equation as I mentioned you already to you care about or it can be two parameter model like pseudo plasticity or power law type.



It can be like three parameter, it can be four parameter even it can be five parameter model depending on the complexity of the fluid you get in ok. So, this is end of the day you need it for different types of model for C and thinning fluids basically. Let us try to understand before we conclude and these are the some of the already as a quick recap this is a power law, this is the Burt Carrow cross, this is the Herschel-Brockle and this is your Carrow-Yashida model which I emphasized last time also I mean for a many fluids like rubber like EPDM it fits very very well ok. But again it you have to figure out where it is giving you better regression that you can carry it forward for your simulation or CFD sort of a work. But before I conclude the day one second let us try to see what I told you already in a summary as a shear viscosity and shear rate plot is a master curve ok.

Power law

$$\eta = K(\lambda\dot{\gamma})^{n-1}$$

Bird - Carreau law

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)(1 + \lambda^2\dot{\gamma}^2)^{\frac{n-1}{2}}$$

Cross law

$$\eta = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^m}$$

Bingham law

$$\eta = \begin{cases} \eta_0 + \dfrac{\tau_0}{\dot{\gamma}}, & \dot{\gamma} \geq \dot{\gamma}_c \\ \eta_0 + \tau_0 \dfrac{\left(2 - \frac{\dot{\gamma}}{\dot{\gamma}_c}\right)}{\dot{\gamma}_c}, & \dot{\gamma} < \dot{\gamma}_c \end{cases}$$

Herschel - Bulkley law

$$\eta = \begin{cases} \dfrac{\tau_0}{\dot{\gamma}} + K\left(\dfrac{\dot{\gamma}}{\dot{\gamma}_c}\right)^{n-1}, & \dot{\gamma} > \dot{\gamma}_c \\ \tau_0 \dfrac{\left(2 - \frac{\dot{\gamma}}{\dot{\gamma}_c}\right)}{\dot{\gamma}_c} + K\left[(2-n) + (n-1)\dfrac{\dot{\gamma}}{\dot{\gamma}_c}\right], & \dot{\gamma} < \dot{\gamma}_c \end{cases}$$

Log-log law

$$\eta = \eta_0 10^{a_0 + a_1\left[log\left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)\right] + a_{11}\left[\log\left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^2\right]}$$

Carreau-Yasuda law

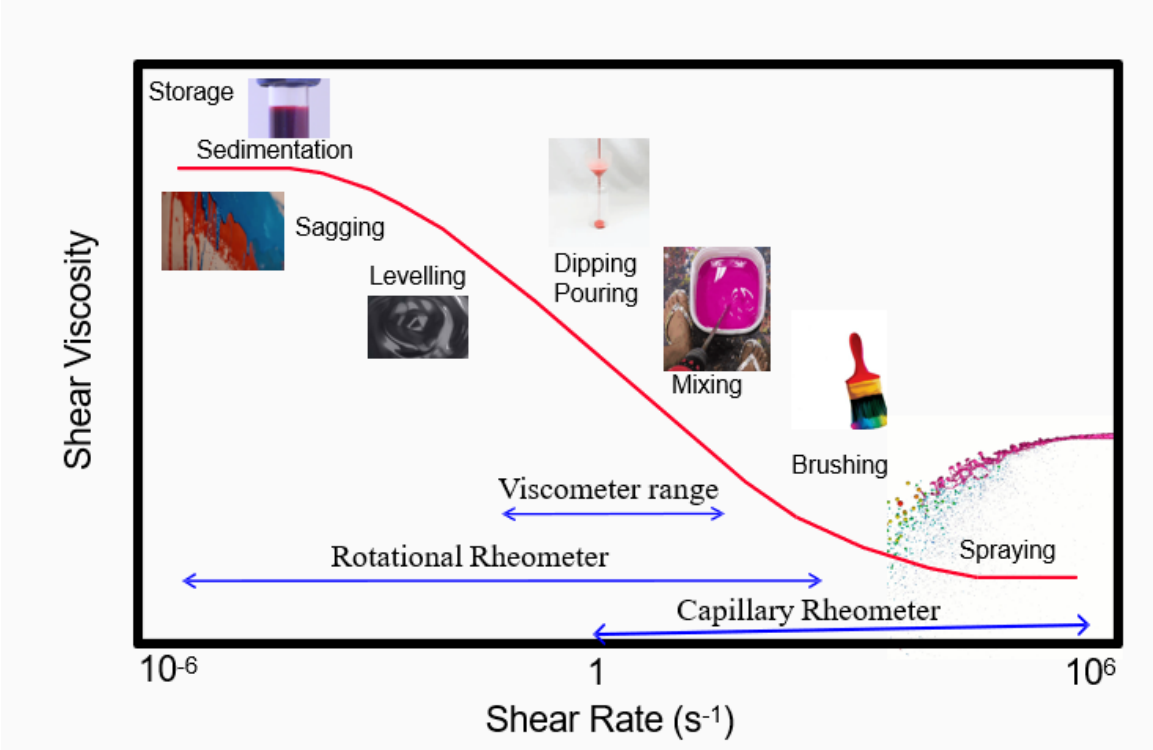
$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)\left[1 + (\lambda\dot{\gamma})^a\right]^{\frac{n-1}{a}}$$

η_∞ = infinite-shear-rate viscosity
η_o = zero-shear-rate viscosity
λ = natural time
a = index that controls the transition from the Newtonian plateau to the power-law region
n = power-law index

So, you see rotational viscometer gives you some Brookfield or Oswald viscometer gives you some range capillary rheometer gives you some range say 1 to 10 to the power 6. So, now ultimately you have to either use time temperature superposition principle or else you have some specialized methodologies like Cox-Merz rule different rheometric

measurement you fit it into a master curve. Now, why master curve is important let us try to understand here. See as I mentioned it to you when you prepare a fluid sedimentation.

So, it demands very high viscosity so that it will not allow pigments to settle. At the same time sagging at a very once you apply the shear you know paint on the wall it should not sag ok. That also demands high viscosity which is around here shear rate involves ok. On the at the same time when you spray it by powder coating it needs a very low viscosity because it has to pass through the nozzle and try to you know cover up the wall surfaces or surface of the body you want to cover on. Blushing on the at the same time needs little bit higher viscosity if it is very way too low viscosity after blushing it will fall down everything will fall down. Mixing or dipping or dreveling say for example, it is a intermediate shear rate it involves not as low as my 10 to the power minus 6, but at the same time it is something like close to 1 or close to you know 10 to the power minus 1 second inverse sort of a shear rate.



So, these actually similarly dipping or pouring or mixing require different level of viscosity and that not only that ok. It is it is a pseudo plastic sort of a behavior and say for example, I have a very high viscosity ok. So, sedimentation I am not bothered about it will give you a good good storage and sedimentation stability, but at the same time my viscosity if it does not come out up to this it is say for example, time dependent way comes up to that this is very bad for spraying operation it cannot be good for you know powder coating operation. So, that way rheology becomes very very important. You can use the rheometric

tool either way you develop a paint try to assess the quality check its master curve whether that paint at all will be good for your perspective or else you try to develop a coating in such a way that it should fulfill your master curve and then you do the further development or modification in terms of material.

Hope it gives you a good picture about the paints as a beginner ok, but again paints and coating is a is a vast area you need to read more on that. See in addition to this in paints in particular there is a book by Swaraj Pal S W A R A J probably P A L ok. So, that book is a classical book that you can refer to ok in addition to this purely rheology oriented books. Again quickly conclude I gave you a gross definition of paints its anatomy ok and then the rheological parameters which are important specially from the you know preparation point of view, storage point of view and application point of view ok. Next class we will try to see more details about the rheological paints considering each and every segment of it considering the storage, considering the you know other things which I already talked about till then. Thank you.