New Rheology Testing Solves Operating Problems

Abstract

All coatings processes have an abrupt short duration shear region that controls the application process. Measurements of the force required to make an abrupt increase in shear rate has forecast performance in a variety of applications. Further the valves are the same for a satisfactory process conditions independent of the chemistry used. This force is related to both the chemical associations that break down under shear and the occupied volume of a coating.

This paper describes simple approximations of the process shear rate for a variety of coating methods and reviews case studies where rheology data has solved operating problems. It provides techniques and guidelines for dispersing pigments, eliminating rheology scratches, and the viscous influence on coat weight and leveling.

Surface tension and elastic forces also influence leveling. Indexes for these properties are presented as well as useful values for the process.

Coating Rheology Measurements

The force to enter a very short capillary tube has been found to be a very useful predictor of coating process results. It allows one to mimic the process on a small scale. 250 cc of material is all that is required per condition, making screening chemistries for successful operation easy to accomplish.

At low shear we studied a variety of chemistries with different mechanical configurations to determine if this force is an energy absorption term or a viscous drag term. It is due to the absorption of energy required to break chemical bonds. The metric we report is the Shear Energy Absorption (**SEA**) in Jules/Liter.

At high shear kinetic energy requirements, elasticity, plus the occupied volume affect the SEA. Both the particle volume and any long chainy dissolved polymer influence the occupied volume.

If the shear rate of measurement is higher than the shear rate of dispersion, the measurement itself will further disperse the pigment. In most viscometers this effect destroys the observation of viscosity due to the original particle size. The SEA tester does not have this problem because it is measuring the force to disperse these particles. If they were not there the SEA would be lower.

Chemical associations between components impart low shear viscous resistance. These forces are weaker than chemical bonds and break with shear. These associations can recombine fairly quickly after the shear field is removed and influence the flow out and leveling of a coating. You generally need some low shear viscosity to transport or apply the coating the web but do not want this to impede flow out. On the other hand higher low shear SEA’s will reduce dewetting because they resist flow. Whatever your particular problem doubling or halving the number found will usually fix the problem.

Coat Weight Control
Consider the force exerted by a Meyer rod – a coater with 100% viscous drag. The web floats over the Meyer rod on a thin film of coating so that the mechanical force on the sheet is transmitted through the fluid. The horizontal force on the rod times the machine speed is Newton-Meters/min or power or the energy absorbed by the fluid per minute. As the fluid is being consumed at a flow rate - Liters/Minute -- dividing the power by fluid consumption results in the specific energy or Joules/Liter. We call this the Shear Energy Absorption or SEA. The Meyer exerts a force on the web through the coating layer opposing the direction of movement.

This force is distributed over this thickness of the coating between the web and the streamline that makes the rejected flow boundary. It is the pressure of the coating hitting the Meyer rod. This pressure is set by the sheet tension and speed of the line. If you increase the SEA at the operating shear rate, it will push the web away until the balance of forces is resorted at a lower shear rate. A lower shear rate requires a thicker coating and the coat weight goes up.

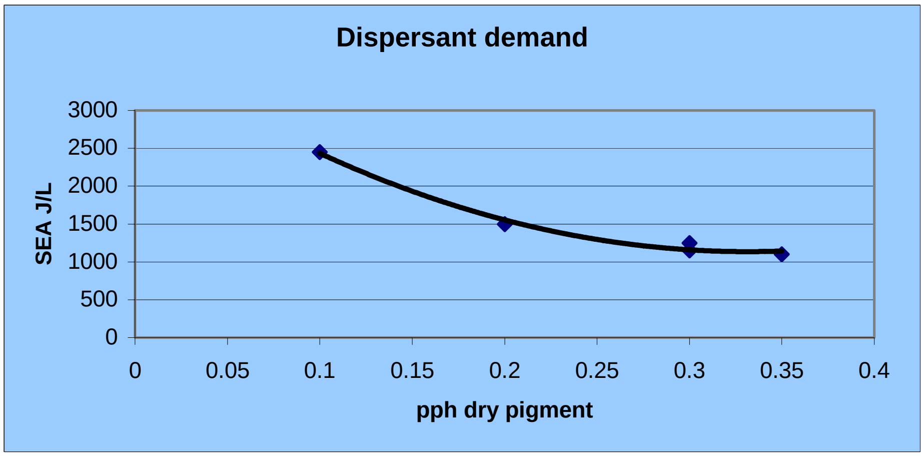
People trying to increase coat weight have used the SEA to screen formulations with predictable results – 20% increase in SEA resulted in a 20% increase in coat weight. This has been one of the barriers to using a smooth rod coater – the visocity affects coat weight in an unpredictable manner.

Shear Rate Approximations
The shear rate is the velocity gradient of fluid. Below is listed a number of approximations used to calculate shear rate. These approximations are simple but only a ballpark estimate. They will put your measurements in the right region to solve a problem.

- Smooth Rod. The shear of a sheet running over a smooth rod the difference of the sheet speed verses the roll speed divided by the gap. Ft/min/Thou = 1/sec   Gap is the wet film thickness of the coating. A Meyer rod has a variable gap – use 1/3 the wet film thickness.
- Curtain Coater landing Zone 2 X wet film thickness / sheet speed
- Curtain Coater Die Lips 8V/D
- Pipe 8V/D
- Wiping Die Applicator   Speed / ½ wet film thickness
- Nipped Roll under pressure loading Difference in roll speeds / ½ wet film thickness
- Nipped Rolls Gapped   Difference in roll speeds / Gap

Dispersing Pigments

SEA 200,000 is a good measure of the degree of dispersion. Most pigments are only dispersed to an SEA 200,000 of 2400J/L. Increasing the solids during the dispersing process and adding surfactant to minimize the SEA will result an SEA of 1100 to 1200. As a reference, water is 650 J/L. Historically the surfactant demand is 0.04 to 0.06. The surfactant demand to reach 1200 J/L is at least 5 times that, indicating a significant increase in surface area.



Optical properties and coated smoothness have been significantly improved.

Rheology Scratches

Rheology Scratches occur as the speed is increased and work out as the speed is decreased. This usually it is a pigment or latex particle agglomeration under shear. The SEA nozzle will plug if there is agglomeration. At a lower shear where agglomeration does not occur, it will flow. The metric is to gradually increase the shear rate and record the rate where agglomeration just starts. Improving the stability of the dispersion by increasing the shear rate of initial agglomeration will result in higher line speeds.

Dynamic Surface Tension

We have yet to measure extensional dynamic surface tension independent of rheology. As elastic and viscous forces affect the force required to draw out a fluid element, it is unlikely we will ever have such a measurement. Therefore we use the term Stretch Index to report the combined effect and rely on other measurements, specifically SEA and the Elastic Index, to sort out which phenomena is in control of a problem.

The Stretch Index was developed to simulate the surface tension and rheology effects on a falling curtain with a falling round stream. The minimum stable flow rate of a round stream forecasts the minimum stable flow rate of a curtain. Reducing the dynamic surface tension and increasing the SEA lowers the minimum flow rate and lowers the Stretch Index. The numbers of the Stretch Index have been calibrated to be in the same range as surface tension. Since they are the combined effect of initial surface tension and SEA, they are not surface tension numbers.

The Stretch Tester monitors the end of the falling stream where surface tension is able to squeeze off the stream into drops. Most fluids take between 8 and 18 milliseconds to squeeze the stream into drops. The Stretch Index is, therefore, affected by the initial surface tension curve as it falls from 72 dynes/centimeter to its lowest value at the end of this time period. The Stretch Index looks at the dynamic surface tension.

The Stretch Index of surfactants in water will rate the ability of a surfactant to provide low surface tension quickly. It is a measure of dynamic surface tension.

Thickening agents will reduce the rate surface tension can squeeze off a drop, lower the minimum curtain flow rate, and lower the Stretch Index. Increasing the rheology acts to retard the contracting flow induced by surface tension. Our tests show the aspect of rheology that correlates best with the drop forming flow condition is the Shear Energy Absorption at 2,000/second.

While the Stretch index has been helpful in curtain coating, it has rarely contributed to the solution of other elastic problems such as turkey tracks or banding. Surface tension does play a role as well as the elasticity in these defects. Apparently, the elastic forces are a more common cause of these defects than differences in surface tension. The exception case was a coating that had variable amounts of internal surface area. The degree of wetout of CMC was varying from batch to batch. If dissolved CMC was present the surface area would be high, the Stretch Index was also high and poor leveling would occur. Increasing the shear and time for wetout of the CMC eliminated this batch-to-batch variation.

Extensional Elasticity

All coating methods have an extensional flow field. As a fluid is stretched out, the long stringy molecules responsible for an elastic force uncoil, untangle, and can slide past each other. If the elastic force is strong enough stringy defects will occur as heavy bands in the coated product. At some point the above extensional orientation can be reach a totally untangled state and no further elastic forces can be generated. If that happens before the coating escapes the influence of the metering element, banding will not occur. Elasticity is question of extent.

A common tool to measure elasticity is an oscillating viscometer. The position of the oscillating element is plotted versus the force on it. Since the fluid is storing and giving back some of this force, the two do not line up. The extent of elasticity is measured by the size of the angle offsetting the peaks. Generally it is reported as the tangent of the angle.

Unfortunately, unless the flow field mimics the process one wants to simulate and the measurement is directed at the controlling condition, the test may not measure an important property. The oscillating viscometer does neither and is not a universal index. We want to know if the coating can fully extend and the elastic force drop to zero before causing a defect.

Elasticity is measured with the Stretch Tester in an extensional flow field using a falling round stream. As the stream falls the elastic force decreases if it can. We examine the stream for the presence of elasticity by deflecting it sideways and looking at the corner of this deflection. If the coating is elastic, it will be pulled around the corner and the corner will be round. The falling distance where the round corner disappears is measured and used as an index. This is a measurement of how quickly the elastic effects can be worked out. We have chosen physical dimensions and procedures that give this index good correlation with the performance of the curtain coating.

One would not think this metric would be universal for any coating method but so far our experience is otherwise. We have solved elasticity problems with curtain, gravure, Meyer rod, and air knife coaters to this point. The index ranges from >0.1 to 4.0. For the above coating methods, a value above 1.0 is always unacceptable. A value of 0.2 always runs well. Between 0.2 and 1.0 the critical value varies with the speed. One can get out of elastic defects at slow speed and get right back into them at higher speeds. Elasticity is a question of extent. A larger % elongation/sec (higher speed) is more demanding.

Leveling

Making a level coating or achieving a smooth coating lay is a complex subject involving all the above properties. The SEA, dynamic surface tension, long term surface tension, elasticity, and degree of dispersion can play a role.

Dispersion is often overlooked, but it can be important if the size of the particle approaches the wet film thickness or specifically $1/10^{th}$ the wet film thickness, then there is not enough room for the particles to flow paste each other and you can develop a grainy appearance.

Elasticity can also cause a lumpy appearance. Elasticity can be present and one would never know it as without an instrument it is often undetected. A fluid is not elastic at the low extensional rates we impart with visual methods like swirling the coating in a beaker or pouring it.

High surface tension is another culprit as surface tension always wants to draw things into a bead.

Solving these problems takes a bit of detective work – taking measurements, coating different properties, and observing the results. If you have a good and bad coating sample, testing these is always very discerning.

These tests and performance prediction techniques are covered under US Patent 6,845,653; 6,701,778 and other pending patents