Thixotropy of Solder Paste Impacts Repeatability and Reproducibility of Rheometric Results

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The widespread use of SAC-based (SnAgCu) lead-free solder paste drives the industry toward a smaller process window. This is due to higher reflow temperatures as well as the limited thermal resistance of the current generation of electronic components. Furthermore, differences in the wetting performance of Pb-free surfaces not only require reduced variation in all process steps, but also in the soldering materials.

SPC data has shown that the solder paste printing process is the primary source of soldering defects in SMT assembly. Consequently, verification of the specified printing properties of solder paste is of paramount importance in the pursuit of higher quality goals and higher overall yields. Process variations such as temperature fluctuations in the printing area, changing printing speeds, and varying stencil life have been recognized as important factors in the characterization of solder paste.

In recent years, quality management standards such as ISO/TS 16949 have been driving the development of a reproducible rheometric methodology to characterize and quantify the aforementioned solder paste properties.

In the course of this development, we have learned that the thixotropic history of a solder paste has a major impact on the repeatability and reproducibility of its rheometric characterization.

This paper describes the differences in this respect between the various measuring principles such as the spindle, spiral pump and plate/plate method. It also introduces the development and implementation of a sample preparation method to reduce the impact of the thixotropy of a solder paste in conjunction with enhanced plate/plate rheometry.

The Rheology of Solder Paste

Rheology is the science that defines the flow behavior and deformation of matter. Solder paste is a complex composition of metal particles and multiple polymer species ranging from relatively simple, slightly modified wood rosins to larger molecular-weight resin systems, solvent(s), activator(s), rheological and numerous other property modifying additives.

Rheological additives alone do not determine the overall rheology of a solder paste. All constituents make their contribution to the flow properties of a product.

They form a complex of short-chained linear substances, long chained linear and even branched molecules. Some of those substances will truly dissolve in the solvent system, while others will swell and form a colloidal structure.

Upon full development of the mix of substances in the solvent system, the molecules will entangle and form a rheological network (also identified as the superstructure).

The short-chained fractions in the network are only physically and relatively weakly entangled. Another category of relatively weak bonding is the hydrogen bridging that occurs with adjacent hydroxyl-groups of neighboring molecules. This, in particular, is the case with solder pastes with a distinct yield point. In those cases, the rheological network has a more physical nature characterized by dipole forces, hydrogen bridges, electrostatic and/or Van der Waals forces.

The bonds are easy to break and will rapidly restore the structure of the network. This is typical for pseudo-plastic flow behavior such as may be found in well-formulated solder pastes. The efficiency of hydrogen bridging is strongly correlated to the hydroxyl-content of the various substances in the rheological network. Whereas it is obvious that derivatives of natural rosins will show variations affected by the vintage and their geographical source, the variation in hydroxyl content of synthetic resins has to be explained by the fact that these product are made in bulk. Bulk chemicals have bulk tolerances. For a resin in wall-paint this apparently is not a problem, but for a solder paste it is. The key to reduce variation in this respect is the manipulation of the hydroxyl content in order to increase homogeneity of the substances.

Each rheological network has specific requirements with regard to its processing temperatures in order to develop its optimal degree of entanglement. The processing temperatures required are related to the solvent system that is used. The rheological network is a function of the required printing properties. The solvent system predominantly is a function of both the required stencil-life and tack-time of the solder paste, as well as the solubility power required with regard to the substances selected to form the rheological network. Furthermore, the heat profile in the reflow equipment and the post-reflow properties of the organic residue are determining factors in the selection of the chemistry that builds the flux vehicle for solder pastes.

Usually, low processing temperatures during the production of the flux lead to incomplete development of the rheological network. Excessively high processing temperatures during production or during storage and/or transportation may partially dissolve some of the groups in the rheological network, and will cause disentanglement and the formation of agglomerates, causing inconsistencies in viscoelastic behavior of the solder paste. Therefore, production equipment with computer control over production time, shear-forces, frictional heat, delay times in conjunction with adequate provisions for storage and shipping of the solder paste are required to reduce the variation of printing properties.

Pseudoplastic &Thixotropic Properties

As with toothpaste, solder paste is a pseudoplastic material with a distinct yield point. This means that the material only begins to flow when the external forces (squeegee pressure, vibration,, gravity, etc are stronger than the internal forces of the rheological structure. Below the yield point, the solder paste shows a plastic behavior, hence the characterization as a pseudoplastic. With pseudoplastic flow, viscosity decreases as shear stress increases. At any given shear stress, viscosity is constant. As shear rate increases, the rheological network breaks down and viscosity drops. When the shear decreases, the rheological network restores itself and the viscosity remains constant for any given shear rate. This means that the solder paste with a true pseudoplastic behavior upon shearing by the squeegee, becomes more fluid, rolls over the stencil, and flows into the apertures. When the squeegee forces stop, the rheological network of the solder paste ideally restores almost instantly.

Whereas the application of shear forces on the solder paste will partially or completely break down the rheological network, the removal of these forces will result in a recovery of the same. The complete recovery, however, will follow a logarithmic time-pattern. This property is referred to as Thixotropy. The challenge to the solder paste formulator is to develop a network that features a quick recovery of the network to the extent that enables proper printing at adequate speed without slumping and smearing.

In order to achieve reproducible measurement, it is important to know exactly on which point on the recovery time-line the test sample is. Another option is to make sure that the recovery has reached the point beyond which small differences in relaxation doe not affect the rheometric measurements in a significant way.

The Rheometry of Solder Paste

Rheometry comprises the techniques to characterize and measure rheological parameters. One of the basic challenges in rheometry is to define an application issue into a rheometric concept. For solder paste, it is important to study the deformation and flow of the material when different forces are applied: atmospheric pressure and vibration by conveyor belts (slump) and the forces of operations such as printing (rolling). The different forces applied to the material are referred to as shear forces. Besides these forces, the deformation and flow of a solder paste – but also its recovery – are time and temperature dependent.

Often, the study of the flow behavior of solder paste has been simplified through the use of a single point viscosity determination, or with a viscosity profile. Viscosity is defined as the resistance to the Newtonian flow of a substance. Depending on the level of sophistication, equipment for rotational rheometry is capable of characterizing the viscous behavior of a solder paste by the determination of single point viscosity values, viscosity profiles and yield values. The equipment ranges from the fairly basic T-bar spindle type, which used to be common among users of solder paste, as it was the first type of equipment specified by military and federal standards.

The spiral pump type has become very popular. This instrument has acquired a reputation as a more accurate alternative. Both types of equipment are qualified by most international standards.

The more advanced plate/plate equipment requires more skill and a laboratory environment. This type of equipment is able to interpret the torque on the measuring devices with a resolution of 0.01 μm and an angular resolution < 1μrad.

The software-package provides enhanced capabilities for analysis, including smoothing of the raw data, interpolation of data points in a defined range, and calculation of mean values, for ultimately more reliable output.

The use of a plate/plate rheometer offers distinctive benefits: The measuring of a thin layer of solder paste more closely simulates the conditions when the paste is exposed to high and low shear forces respectively during and after deposit by the printing process. The equipment generally offers more accuracy due to the sophistication in micro mechanics and electronics. Their modular design usually enables expansion in terms of monitoring different rheological parameters, some of them exclusively belonging to the field of oscillation rheometry.

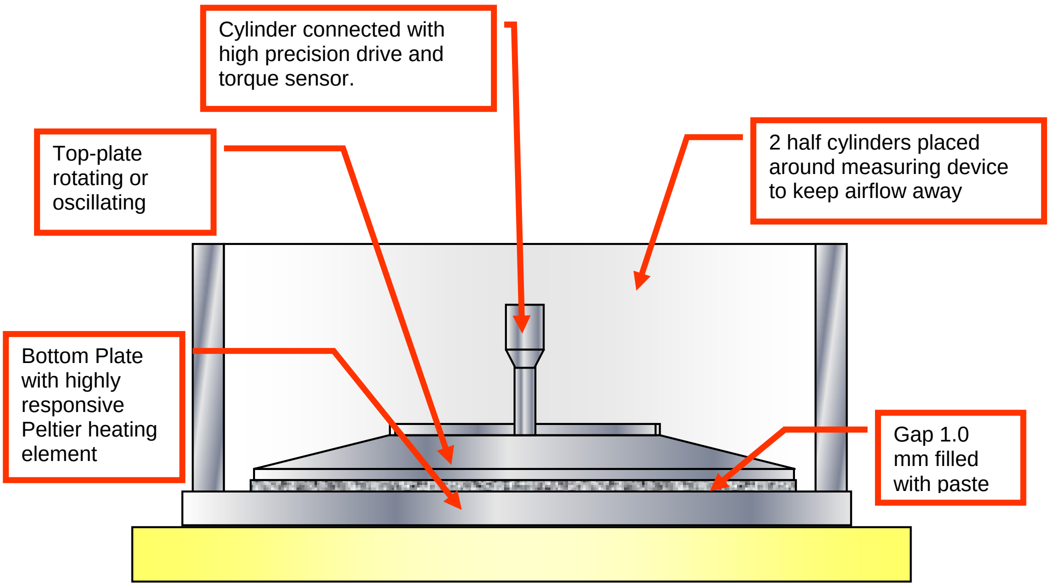

Figure1 - this is a simplified set-up of the measuring device of a plate/plate rheometer. The test sample is between the 2 plates. The bottom plate controls the temperature very accurately. The top-plate rotates or oscillates, depending on the measuring mode. The top-plate can also exercise a precisely controlled downward force to assure a constant contact force with the test sample even at a higher rotational speed.

Characterizing Viscoelastic properties

In terms of rheology, solder paste can be classified as a viscoelastic fluid. This means that solder paste has both viscous and elastic properties. The viscous properties are identified as the Loss Modulus (G”) and the elastic properties as the Storage Modulus (G’). The ratio between both properties is very important. It is expressed as the quotient of G” and G’ and it is identified as the Damping Factor (tan δ).
During storage, transport and after printing, the elastic properties in the solder paste (Storage Modulus) should dominate. Therefore tan δ should be < 1 and, more specifically, within certain maximum and minimum values.

The accurate determination of the elastic fraction of a solder paste can only be carried out by sophisticated rheometry equipment according the principle of oscillation.

A high G’-value generally is an indication of a high resistance towards separation and slumping. The downside of a high G’, however, may be paste hang-up on squeegees, limited print-speeds, ski-sloping and dog-ears.

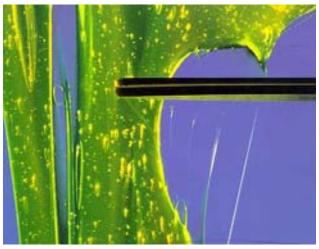

Figure 2 - A jelly film slowly draining from a spatula can even be cut. This experiment shows the interesting viscoelastic properties of a substance.

Defining Solder Paste Properties into Rheometric Concepts

Separation and slumping occur and are measured at low to ultra-low shear forces. The stirred consistency of solder pastes generally relates to the medium shear stress range. The printing of solder paste, in particular the cutting of the wet deposit by the squeegee, occurs in the high shear stress-range. The metal particles, resin system, solvents and some property modifying additives primarily affect the high-shear rate viscosity of a solder paste and thus its printing properties. Generally, the high-shear rate viscosity will increase if the metal content or the molecular weight of the resin system increases. When the particle size of the metal powder or the strength of the solvent system decrease, the high-shear rate viscosity of the solder paste will increase.

Measuring Separation and Slump

When opening a new jar, the user should be looking at a juicy solder paste. The surface should be slightly wet and shiny. There should be no sign of separation of the flux vehicle.

Solder paste is a dispersion of metal particles in a flux vehicle. Over a longer period of rest (wet deposit after printing and storage and transportation), many dispersions tend to separate, quite often identified as sedimentation. In the case of solder paste, this means that flux will tend to rise to the top of the dispersion and the more heavy solder particles will concentrate in the bottom.

The definition of the slumping phenomenon into a rheometric concept already has been described by van Tiggelen[4].

The stability towards separation is a significant parameter of a solder paste. Long-term shelf life covering several months in storage as well as closed-circuit stability in a closed print head for several weeks are a prerequisite for a modern solder paste.

Storage should be defined as a period of rest of the material at a certain temperature. The stress on the material is atmospheric.

The process of separation can be modeled with following equation:

$$V\,[\mathrm{m/s}] = \frac{d^2.g}{18.\eta_{fl}}.\,(\rho_p.\rho_{fl})$$

in which

particle diameter	d [m]
acceleration due to earth’s gravity	$g = 9.81$ m/s^2
viscosity of dispersion medium	η_{fl} [Pa.S]
particle density	ρ_p [kg/m^3]
liquid density	ρ_{fl} [kg/m^3]

Depending of the flux chemistry and the density of the solder powder, the speed of separation is in the order of 3-5 10^{-4} m/s. Storage temperatures, boundary layers and interactions are neglected. They slow down the separation process significantly. The storage temperature parameter can be introduced in the separation test.

So far, 3 different concepts for the determination of long-term stability of solder paste have been defined.

Measuring Separation through a Yield Point with a Flow Curve

The first concept is known as Yield Point. The yield value or yield point is the highest shear stress value in a flow curve at which the solder paste still does not flow. It is the point where the external forces (gravity, squeegee) applied are greater than the internal forces of the rheological network in the solder paste. Below the yield value the behavior of the solder paste is elastic. It behaves more like a solid substance. It does not deform: It does not separate nor does it slump! The first method of yield point traditionally was determined by rotational rheometry in the controlled shear stress mode (CSS). The higher the yield point, the stronger the rheological network and the lower the tendency for separation of solder particles.

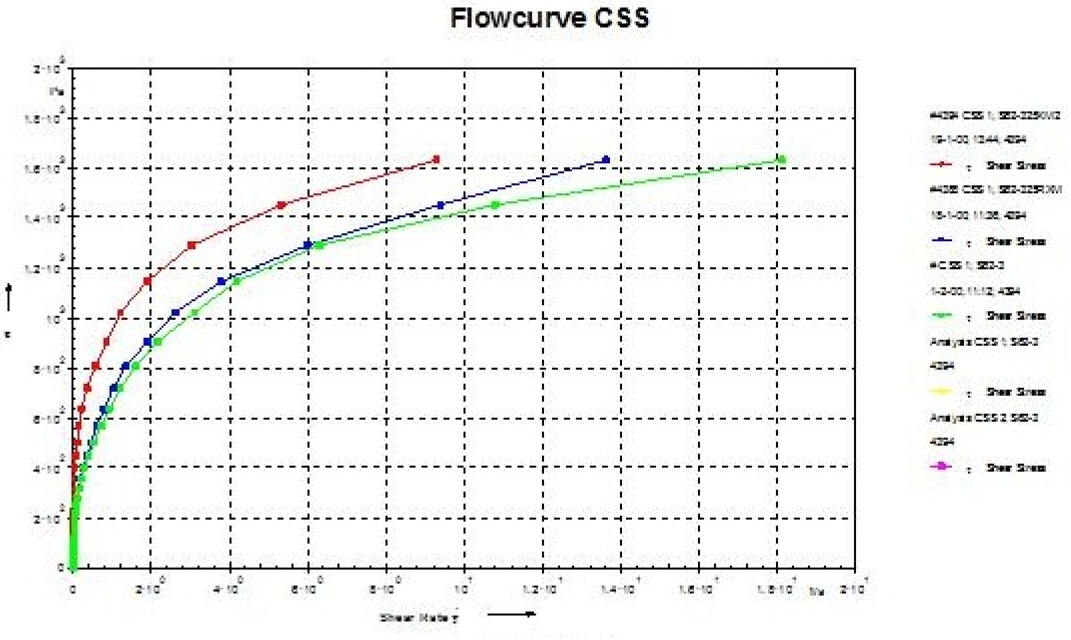

Figure 3 - The solder paste type XM2 has a distinctively higher yield value than RXM and RX, therefore it is less prone to separation.

The more strongly the solder particles have been embedded into the rheological network of the flux, the more stable the solder paste will be. The resolution of the measuring device has been found to be the critical factor with this method. For all practical purposes, one could claim that the higher the resolution of the rheometer, the lower the yield point.

Measuring Separation through the Storage Modulus (G’)

With a rheometer in oscillation mode, it is possible to perform a so-called amplitude sweep test. With a constant frequency, in the order of 1 Hz, the sample is loaded with a ramping amplitude. In the low-end amplitude area, the diagram shows a linear viscoelastic range. The linearity is an indication that the rheological network in the solder paste has sufficient structural strength to withstand the minimum load (strain, deformation) in this range.

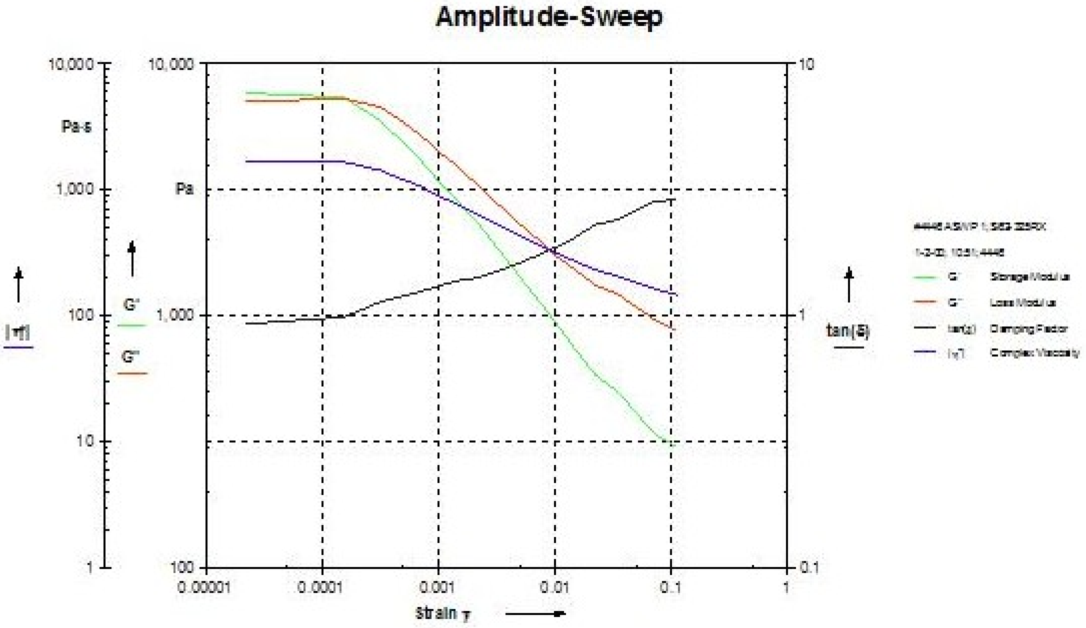

Figure 4 - This test provides more information on the strength of the rheological network. The breakdown of the elastic portion (G’) past the area of 0.0001 Strain (δ), provides an indication of the yield point.

So the substance does not flow, it is at rest. The higher the G’-values in this range and the longer the linear range, the stronger the rheological network. In this case also, the rule applies that there is a maximum resistance against sedimentation and slumping. With advanced software packages, quantitative determination of the yield point can be calculated, using this method.

Measuring Separation through ‘Zero Viscosity’

With a rheometer in oscillation mode performing a frequency sweep test with a constant small amplitude and a frequency in the very low end range, one can determine the complex viscosity[5] (η*) at rest. The higher the zero-viscosity, the higher the resistance against separation.

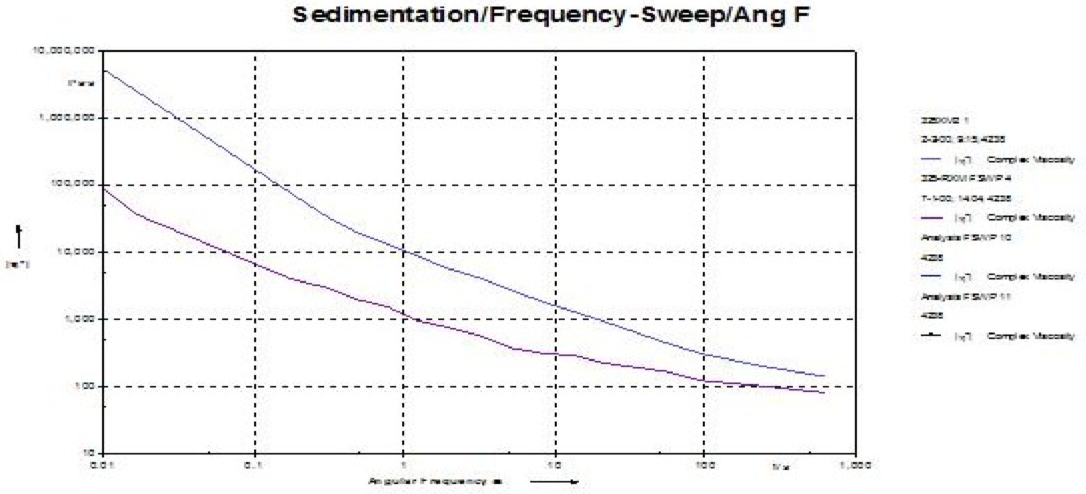

Figure 5 - The solder paste type XM2 has a distinctively higher zero-viscosity than RXM, therefore it is less prone to sedimentation and slumping.

Measuring Printing properties

In an ideal scenario the wet deposit of solder paste, left by the printing operation, has a sharp definition, be it rectangular, ellipsoid, or circular. Normally, the squeegee shears off the solder paste at the top side of the stencil, leaving a wet deposit on the assembly in a clean cut with a relatively flat surface and smooth contours.

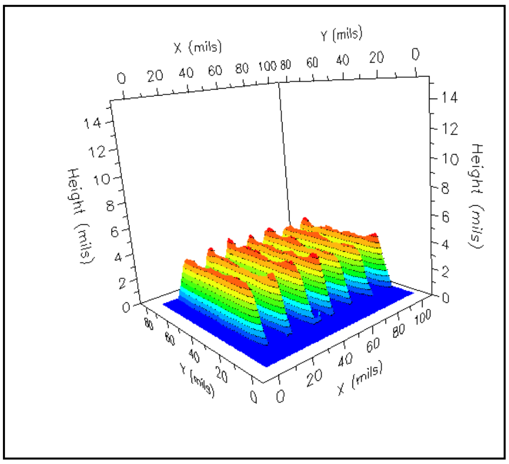

Figure 6 - Print deposit of 0.4 mm QFP pads with a 3-D Measurement System. The different colors indicate the different heights of the deposit.

Viscosity currently is measured at arbitrary low shear rates. Even most international standards on solder paste only use the term viscosity to characterize its printing properties.

Whereas fine-pitch printing and the demand for printing at certain speeds in conjunction with the introduction of closed print heads have moved to center stage in the application of solder paste, it seems necessary to take a more fundamental approach toward the shear forces affecting the paste during the printing process. In the printing process, the phenomena of wiping the stencil clean, smooth filling of the aperture and the fast recovery of the rheological network of the wet deposit on the printed circuit assembly are the point of focus. The most common defects in printing nowadays are inadequate print definition, ski sloping, and dog-ears. Therefore, these phenomena should be considered in rheometric terms. The most critical aperture filling is a QFP-configuration in 0.4 mm pitch and smaller, perpendicular to the print stroke at speeds beyond 30 mm/second. In mobile telephone production, print speeds of 100 mm/second and higher have become quite common.

For a thorough understanding of the printing properties of a solder paste, it should be remembered that the filling of an aperture occurs with a backfill effect. High-speed video recordings clearly show that solder paste does not immediately fill the aperture in a true vertical motion once it has crossed the edge of the aperture. Because of the horizontal motion, which is high relative to the width of the aperture, the solder paste flies in a free, virtually shearless motion only slightly downward in a more horizontal direction, until it bounces against the adjacent wall of the aperture. Subsequently, a part

of the mass of paste falls down and fills up the entire aperture in a backward motion, until the mass of paste in the aperture is cut off by the edge of the squeegee or the wiper of the print head (Figure 7).
The speed with which the aperture in the printing process is filled can be calculated with following equation:

$$V = \frac{\left(A.\frac{(100-R)}{100}\right).\frac{(100-B)}{100}}{V_p}$$

In which:

Print Speed:	V_p [m/sec]
Aperture width:	A [m]
Aperture reduction:	R [%]
Backfill effect:	B [%]

Figure 7 - This picture is taken from an animation in PasteMaster®. The animation is based on a study with high-speed video recordings of aperture filling. It clearly shows the backfill effect when the paste flows into the aperture.

In the case of 0.4 mm pitch QFP apertures, perpendicular to the direction of the print stroke, moving at 100 mm/second, we arrive at the following result:

$$V = \frac{\left(0.0002.\left(\frac{100-10}{100}\right)\right).\frac{(100-30)}{100}}{0.1} = 0.00126 \text{ m/sec}$$

In terms of shear rate the following equation applies:

$$D = \frac{V}{d}$$

In which d represents the diameter of the largest particle in the solder powder. If we take d at 50 microns, D becomes 25.2 1/s.

According to the aforementioned model, the frequency should be set in the order of 800 Hz. In the process of the developing this test, we have found, that settings beyond 500 Hz do not show significant differences.

Nowadays, in most advanced rheometers, the maximum frequency of oscillation is 100 Hz. One should, however, be cautious when using this high frequency, as the mass of the spindle may cause some interference. With a technique known as temperature superposition, it is possible to simulate considerably higher frequencies, in the order occurring during the filling of the aperture in the printing process.

During aperture filling, the viscous properties of the solder paste should be dominating strongly. The viscosity should drop instantly to the lowest possible values. This means that both the G' and G"-values should drop. G" should become higher than G'. Therefore, the damping factor (tan δ) should be > 1 and the complex viscosity (η*) should drop as low as possible.

After the filling of the aperture, instant recovery of a significant part of the rheological network should occur. This means that both the G' and G"-values should increase instantly. G' should become higher than G" as fast as possible. Therefore, the damping factor (tan δ) should return to its original value, below 1, as quickly as possible and the complex viscosity (η*) should increase as steeply as possible.

The simulation of these events is done in a creep test, also known as a thixotropy or recovery test.

In the first phase, the solder paste is loaded with high shear forces, so the rheological network is completely destroyed. This phase is set at 3 seconds. That is much longer than the time needed to fill the aperture in the printing process. The time of 3 seconds is necessary to allow the device to collect some measuring points. The recovery phase is set at 2.5 minutes. Also this phase is longer than the pause after a print cycle, when the printer is operating in full production. However, in order to get a good resolution of the differences in the structure recovery of solder paste with only minimal differences in their formulation, it is advisable set to the recovery phase this long.

Experiments in our laboratories have shown that repeated load-phases, followed by as many recovery phases, do not show a significant difference.

In rotation mode, in the first phase, the solder paste is loaded with a high shear rate. A recovery test in rotational mode only provides information about the viscosity.

A recovery test in oscillation mode provides information about the changes in G', G" and –optionally- the tan δ and complex viscosity. In the first phase, the paste is loaded with the highest consistent frequency and amplitude Combined with temperature superposition, this will ensure complete breakdown of the rheological network, similar to the destruction of the structure taking place during the aperture filling in the printing operation, During the second phase, the paste has the chance to recover while the temperature is moved back up to 25 °C within seconds and the aforementioned values are recorded whilst the solder paste is submitted to the lowest possible amplitude and frequency.

Solder pastes showing quick recovery in the second phase have a lower tendency towards slump and smearing. Conversely, paste with a relatively high G’ in the load phase may tend to produce irregular deposits, ski sloping and dog-ears. In the course of the work in our laboratories, it has become evident that the right viscoelastic balance in a solder paste is of paramount importance.

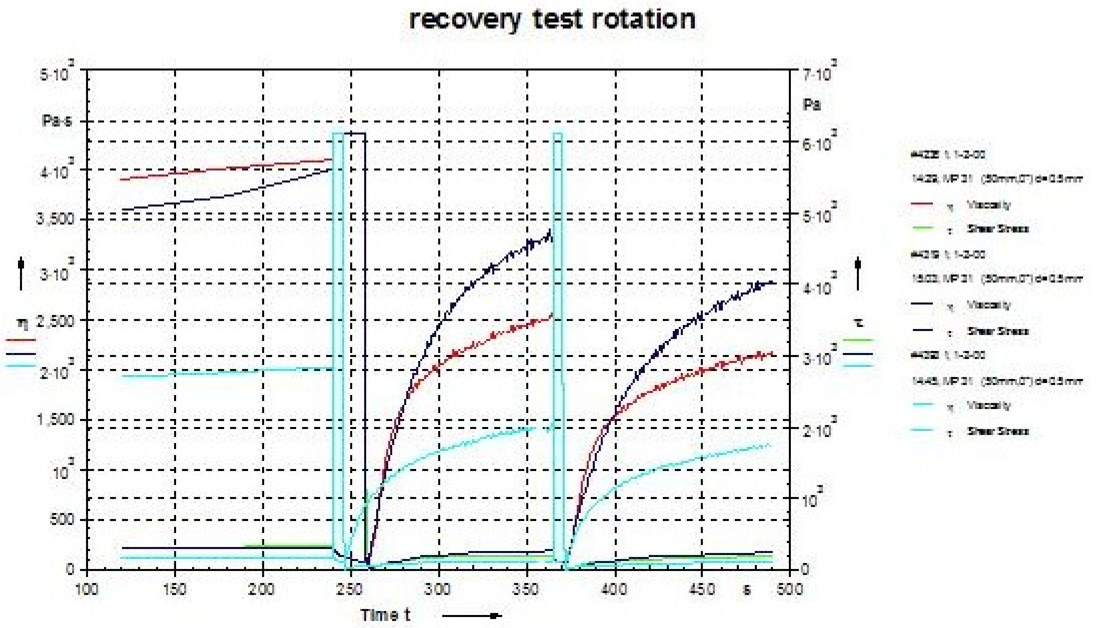

Figure 8 - This is a recovery test entirely in rotation mode. In the first phase, the solder paste is measured in “a state of rest”, under an ultra-low shear rate. The second phase is a load phase for 3 seconds. It simulates a print stroke at high speed. The viscosity of the paste drops down. The third phase is the first recovery phase. It simulates a pause after a print stroke. The pause during this test however, is longer than during printing (2.5 minutes). This allows the rheometer to record the recovery of the paste. The phases 4 and 5 are a load phase and recovery phase again. Experiments with more of these phases did not yield any further significant data. Evidently the recovery of none of the pastes tested brought the rheological parameters back to their values like those in “a state of rest”. Solder paste XM2 (red) recovers faster with a steeper curve to the values necessary for smooth filling of the aperture. Solder paste RXM (light blue) does not recover fast enough, and the structure does not get strong enough for closed print heads. Solder paste RX (dark blue) has limited printing speed. Its viscosity becomes too high in the recovery phase.

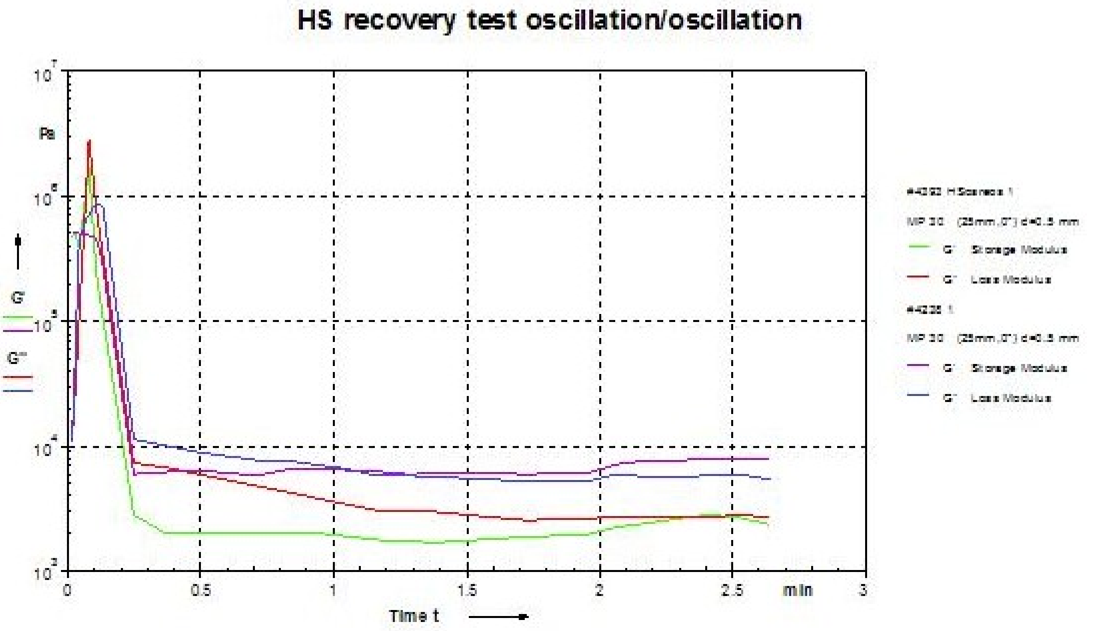

Figure 9 - The first phase of this test in oscillation mode simulates a print stroke at high speed. The high frequency (>500 Hz) is realized with temperature superposition. The duration of this phase is 3 seconds. Through the powerful Peltier-element of the rheometer, the temperature is brought back up again to 25 °C within a few seconds. In the recovery phase (2.5 minutes), the elastic and viscous portion (G”) are monitored. This diagram clearly shows that XM2 (purple: G’; blue G”) flows easier during the print stroke. Both its G’ and G” values remain lower as with RXM (green: G’; red: G”). Moreover G” (the viscous portion) dominates clearly, so the flow properties during printing are in command. With RXM the G’ and G” are both higher when sheared to high-speed in the first phase, so the resistance to flow is significantly higher. In the recovery phase it takes a long time before G’ dominates G”. With solder paste XM2 the recovery of both values is much faster and G’ dominates G” significantly quicker. Therefore this paste is less sensitive to shear thinning and slumping.

Parameters affecting the Repeatability & Reproducibility

The following is a listing of parameters that can affect the repeatability and reproducibility of rheometric measurements[1].

1. Production tolerances of solder paste
   - 1.1 Quality & quantity of raw materials
   - 1.2 Equipment settings, process times, etc.
2. Elapsed time between moment of measurement & date and time of manufacture
3. Temperature during measurement
4. History of paste
   - 4.1. Temperatures in transportation & storage
   - 4.2. Has paste already been used before?
   - 4.3. The delay between measurement and the time the paste stirred or agitated in any other way
   - 4.4. The shear-stress applied and the duration of the agitation as mentioned under 4.3
5. Measuring equipment
   - 5.1. Measuring principle
   - 5.2. Equipment settings
   - 5.3. Calibration
   - 5.4. Workmanship

Many of these parameters can be controlled in a straightforward manner. The parameters 2 up to and including 4 are related to the sample preparation.

Controlled Shear Stress versus Controlled Shear Rate

As controlled shear stress is the most direct and independently controlled input parameter in a rheometric experiment, measuring in controlled shear stress mode generally provides more reliable results than measuring in controlled shear-rate mode[1,2,3]. In order to simulate the flow properties of solder paste during storage and printing, a more fundamental approach is necessary and an index calculated of measurements under measured under different levels of controlled shear stress.

The influence of temperature

Whereas most facilities for printing solder paste by now have climatic control with temperatures set at 20°C, most standards still specify the viscosity of a solder paste to be declared as a single point measurement at 25°C. Even a temperature variation of 1 degree Centigrade makes a significant difference in the viscosity of a solder paste.

Accurate control over the temperature of the sample is a prerequisite for reproducible rheometric results. Plate/plate rheometers control the temperature of a sample more directly through close contact with the heating in the base plate. Temperature control is achieved via a Peltier element, providing a control within 0.1° C. accuracy. The element is also capable of programmable temperature changes within seconds. The temperature can be set at a constant value, or it can vary in intervals or in a continuous ramp as much as 0.8 °C/Sec.

Generally, solder paste vendors provide the user with a recommended operating temperature for their products. The significance of these recommendations can be illustrated with a temperature profile. The profile is based on an oscillation sweep test with constant settings of an ultra-low amplitude and low frequency. The G', G" and tan g are measured. With this test, one can clearly explain that a paste of 18 °C is too cold, as below a temperature of 22 °C G' and G" are too high. Moreover, their balance is wrong (tan δ). Beyond 26 °C these values reach a level that should be avoided.

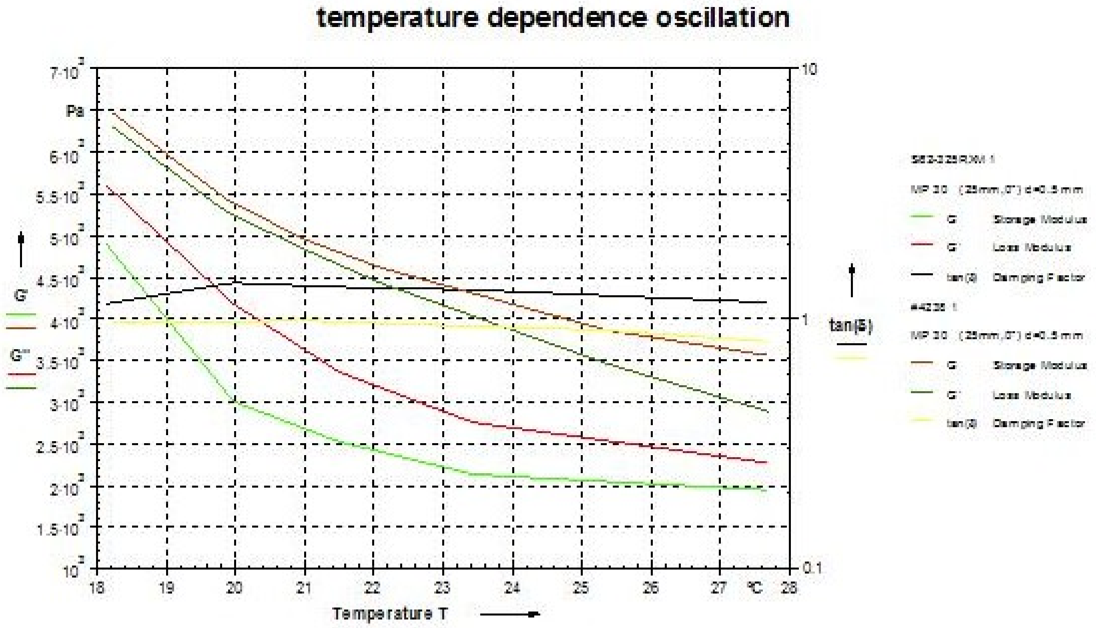

Figure 10 - Measured in "a state of rest", solder paste XM2 features an elastic portion that dominates throughout the entire temperature range. Moreover both G' and G" are higher than those of solder paste RXM. For these solder pastes the temperature window between 22 and 26 °C seems to be optimal.

The sensitivity of a solder paste to temperature variations can best with expressed with the I_t-index[4].

Sample Preparation is Key to Reducing Variation

In our quest for further reduction of the variation in rheometric measuring results, we realized that the rheological history of the test sample most probably would provide a significant contribution to the variation in measuring results. Therefore, controlling the most recent history would most likely yield a further reduction of the variation.

In line with our explanations under the section Pseudoplastic and Thixotropic Properties of this paper, and based on our experience, we developed a procedure to further reduce the variation in the measurement system analysis (MSA) for rheometric parameters of the solder paste:

- We print the pattern with the test sample on a laser shaped ceramic plate. For this purpose, we designed a stencil with a round aperture accommodating the diameter of the top-plate of the rheometer. In order to prevent scooping, we bridged the aperture in the center. The bridge is parallel to the print direction. The stencil thickness is 200 . The pattern is printed at slow speed with a DEK 240 semi-automatic printer, equipped with a stainless steel squeegee. This is to minimize the variation in definition of the paste deposit. For QC, all patterns are printed directly following the production of the solder paste batches concerned.
- The samples are stored in a dessicator to minimize variations potentially caused by drying of the samples or absorption of humidity.
- After 60 minutes in the dessicator, the sample is placed in a holding device that locks it tightly in position in the center on the bottom plate of the rheometer. By leaving the test sample in a resting state for 60 minutes, we are able to smooth the effect of the most recent rheological history. On the other hand, by keeping the sample off-line on a ceramic coupon, we are able to contribute to the most efficient use of the rheometer.
- The top plate comes down on the sample and leaves a gap of 150 , thus assuring a firm contact with the paste deposit and thereby squirting out the diameter of the paste deposit, always to the same extent and in the same way.

- The start of the measurement program has been set at a specific threshold torque for each paste. This extra condition contributes to the reduction of the variation in rheometric measurement system analysis (MSAs).

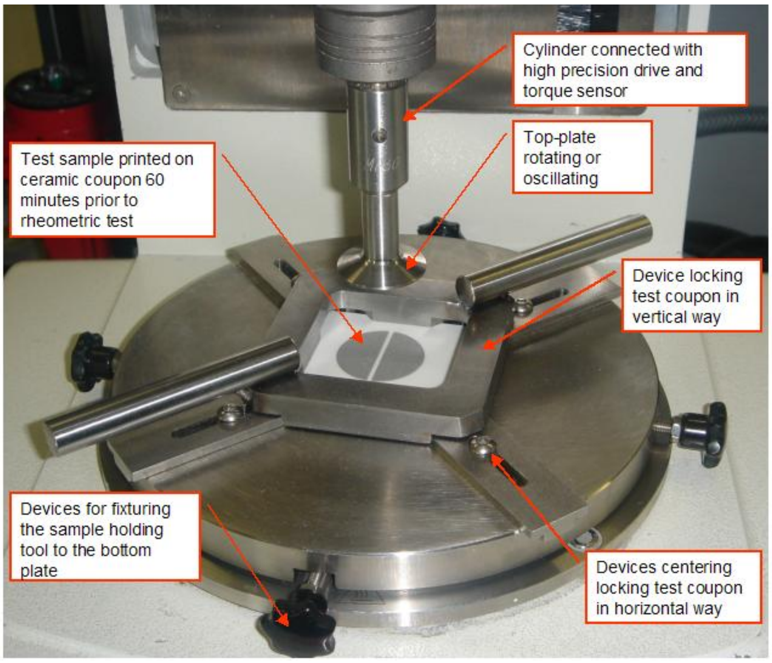

Figure 11 - The rheometer equipped with the fixturing device for the off-line printed ceramic test coupon, part of the new sample preparation procedure reducing MSA variation in solder paste rheometry. Also see Figure 1 f

Conclusion

The aforementioned sample preparation method in conjunction with the use of rheometric indexes that have been proposed before[4], yields significantly more accurate and reproducible results, and also saves time and money. The procedure requires approximately 5 to 10 minutes for the lab technician to set it up. The rheometer phase requires no more than 16 minutes to produce the final numbers. As proposed before, we are able to determine rheometric slump and tackiness as well as index for speed and temperature sensitivity. All output data is measured, smoothed, interpolated and calculated automatically. With the sample preparation routine we can even determine rheometric tackiness of the solder paste after time intervals like 1,2,4,8,16 hours as we print the test coupons and leave them in the dessicator for the duration as required by the test specification.

Whereas the ISO-TS 16949 Instruction Manual for the Parts Production Approval Process (PPAP), Fourth Edition, March 2006, Section F9[6], page 46, acknowledges the larger measurement variability for properties (such as viscosity) in the process industry, accounting in some cases for 50% or more of the total variation, we are able to certify variations of maximum 5% with the recent enhancements to our rheometric techniques as described in this paper.

A new industry standard based on indexes such as i_t,i_v, i_{vt} and other rheological parameters including slump and tackiness would finally put an end to confusion and discussions about all kinds of test conditions regarding viscosity. It would also end the hassle associated with control items such as slump stencils, tackiness probe alignment and other issues. Moreover, this test provides much more useful and reliable information about the printing properties, under varying operating conditions, of a solder paste to the user.

Initially, one might be concerned with the apparent higher initial investment in instrumentation, which also requires a well-trained lab technician to operate and correctly interpret the results. However, many users never measure viscosity and other rheological properties, and rely on certification by the vendor, which may not always be reliable. The abovementioned procedure provides a solid level of assurance to the user.

It is therefore important for the user to demand a certificate of compliance from the paste vendor regarding the testing of aforementioned rheological parameters.
In modern business practice, transparency is a key word. Therefore, paste vendors should allow customers to audit their SPC data under certain conditions.

1. A Simpler Approach to Cost-Effective Solder Paste Testing, Ineke van Tiggelen-Aarden, Proceedings APEX-2003 Conference
2. Ein kostengünstiger Methode für Qualitätsicherung, Ineke van Tiggelen-Aarden, Productronic, October & November 2003

3. Correlation of Malcom Spiral Viscometer vs. Brookfield T–bar Spindle Viscometer, Kantesh Dos, Austin American Technology
4. A Fast, Precise and Reproducible QC-Rheometry Routine for Solder Paste, Ineke van Tiggelen-Aarden, Proceedings APEX-2004 Conference
5. The Complex Viscosity is determined by sinusoidal shear loads through oscillatory testing and therefore noted with an asterisk to indicate the complex form, and thus distinguish it from a viscosity value that has been established by rotational testing.
6. Chrysler, Ford & GM: “Parts Production Approval Process – PPAP”, Reference Manual AIAG, Troy, Michigan 2006

Thixotropy of Solder Paste Impacts Repeatability & Reproducibility of Rheometric Results

Ineke van Tiggelen-Aarden
Technical Director

Eli Westerlaken
President

APEX 2007

Cobar®

Pb-Free Process Window

- Window is smaller
- Process Variation will be Reduced
- Also for Soldering Materials
- Quality Management becomes More Important

Quality of Solder Paste

- Key Parameter: Flow Properties
- Most Critical to Measure in a Repeatable & Reproducible way

Quality of Solder Paste

- Key Parameter: Flow Properties
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F.9 Measurement System Analysis (MSA) Studies (see 2.2.8)

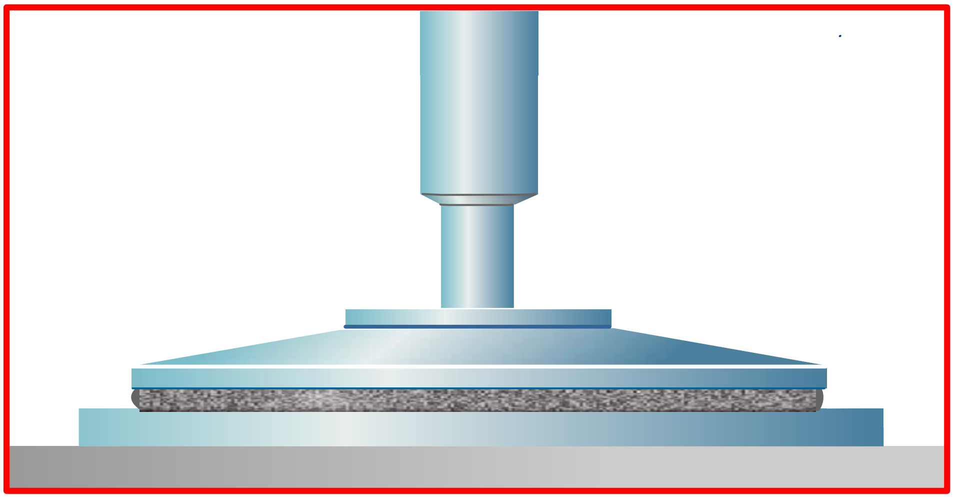
Bulk material often require further processing after sampling in order to make a measurement.

Measurements are often destructive in nature and this prevents retesting the same sample.

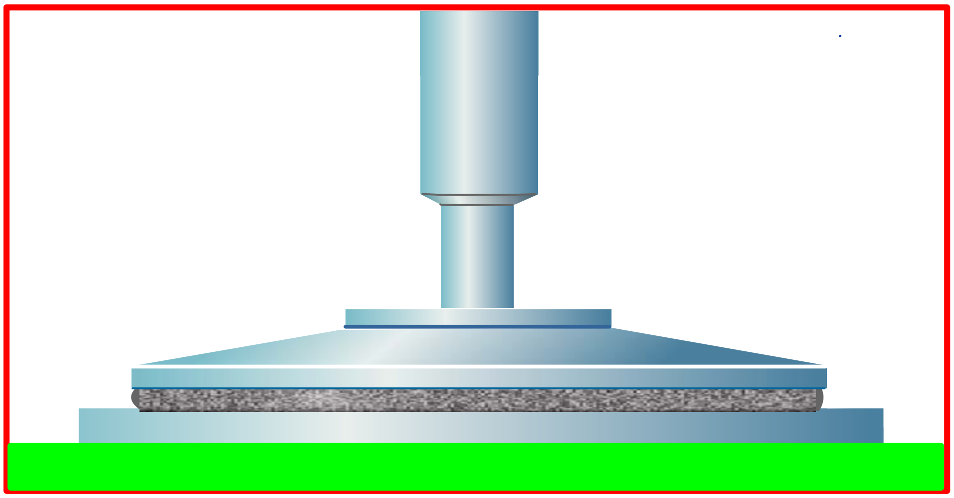
Measurements variability is often much larger for properties important in the process industries (e.g., viscosity and purity) than it is for properties measured in mechanical industries (e.g., dimensions).
Measurement may account for 50% or more of the total observed variation.

Setup of a Rheometer

Setup of a Rheometer

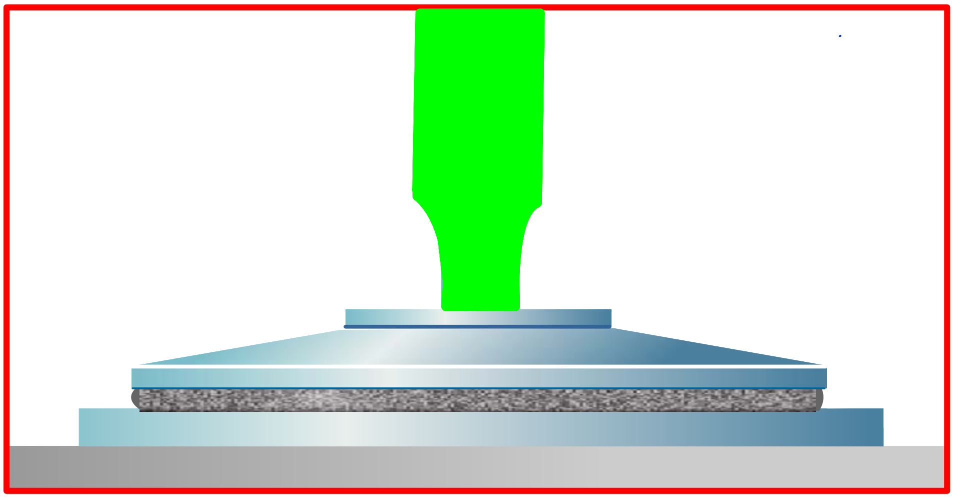


Setup of a Rheometer



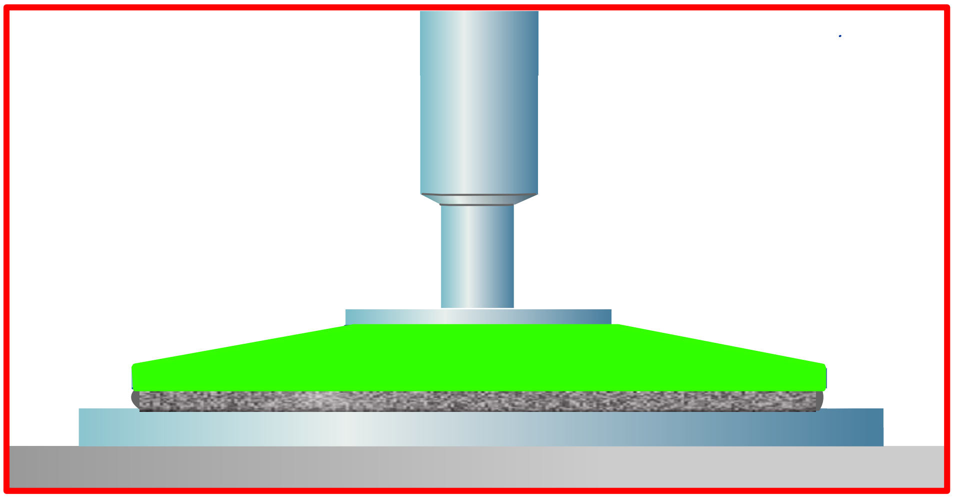
Vibration-proof base

Setup of a Rheometer



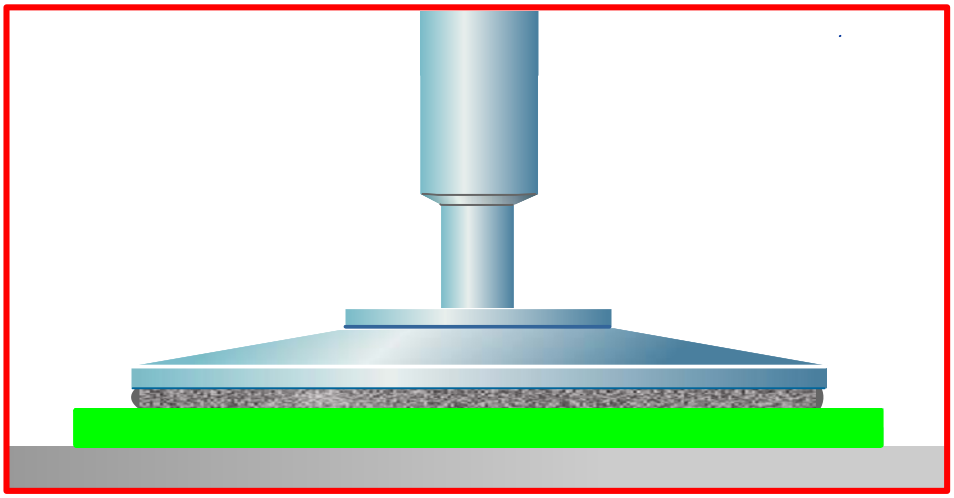
Cylinder connected with high precision drive and torque sensor

Setup of a Rheometer



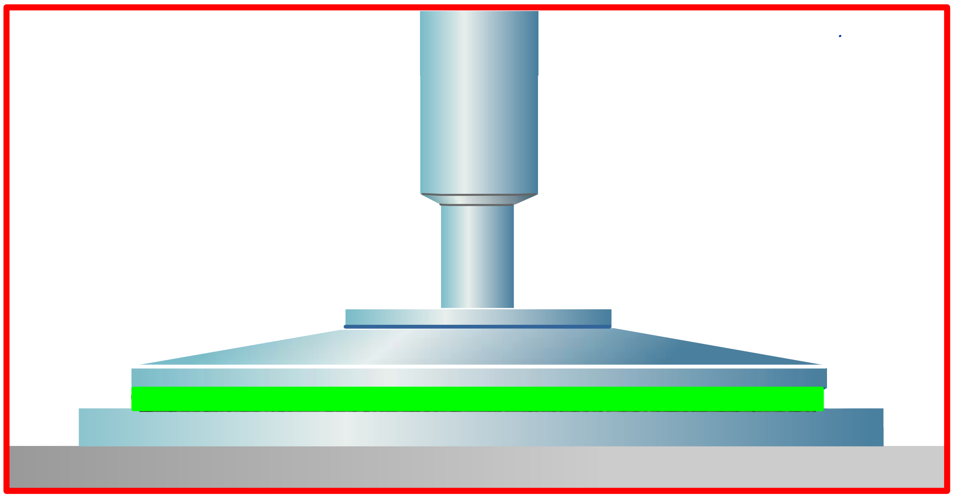
Top plate rotating or oscillating

Setup of a Rheometer



Bottom Plate with highly responsive Peltier heating element

Setup of a Rheometer



Gap 1.0 mm filled with paste

Capabilities of a Rheometer

Possible Measurements for Solder Paste:

- Viscosity
- Tackiness
- Slump
- Temperature Sensitivity
- Range Determination of Print Speed

To Repeat & Compare Results

We Need Identical...

- Measuring Principle
- Instrument Capabilities
- Tooling
- Working Conditions:
  - Vibration
  - Temperature
  - Air flow

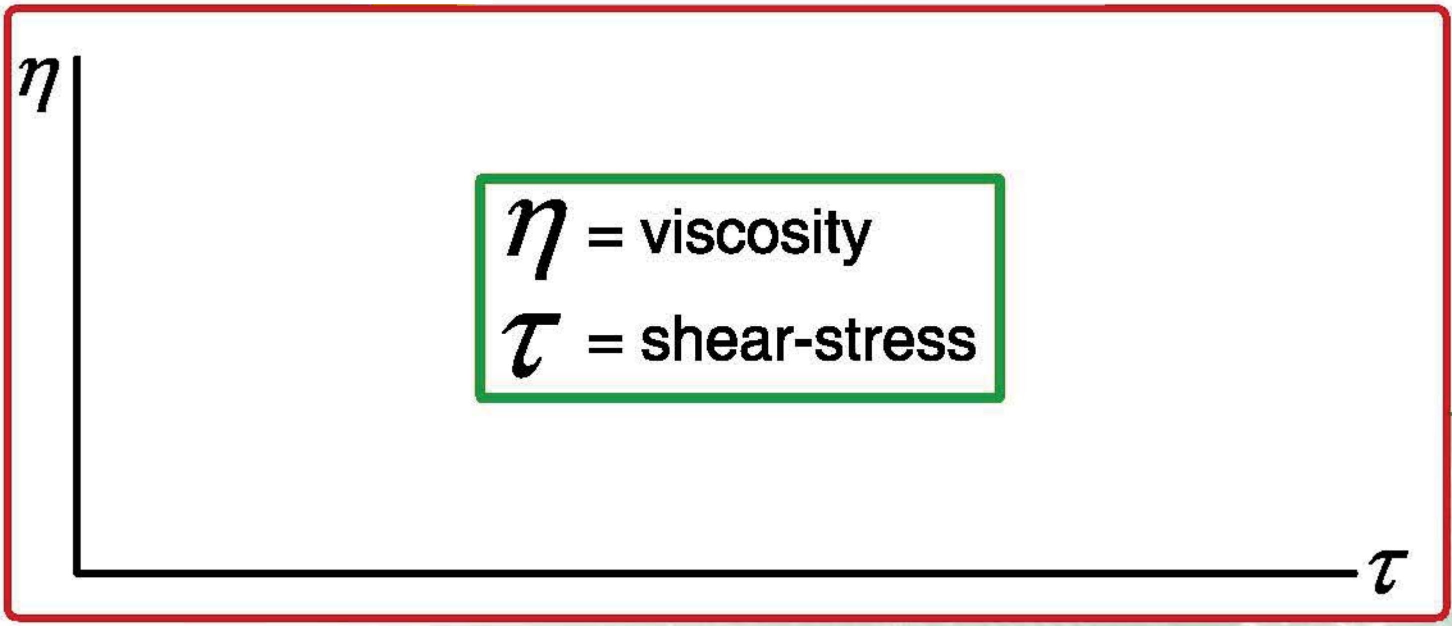
To Repeat & Compare Results

We Need Identical...

- Software for Measuring, Smoothing & Analysis
- Programming of Measuring/Analysis procedure, including temperature settings
- Calibration Procedures, Standards, Planning
- Level of Workmanship

Pseudoplastic Flow

- AKA: Shear-Thinning
- Viscosity ⇩ when Shear-Stress ⇧
- It's a non linear function



Pseudop stic Flow

- AKA: She Thinning
- Viscosity ↓ when Shear-Stress ↑
- It's a non-linear function

Pseudoplastic Flow

- AKA: Shear-Thinning
- Viscosity ⇩ when Shear-Stress ⇧
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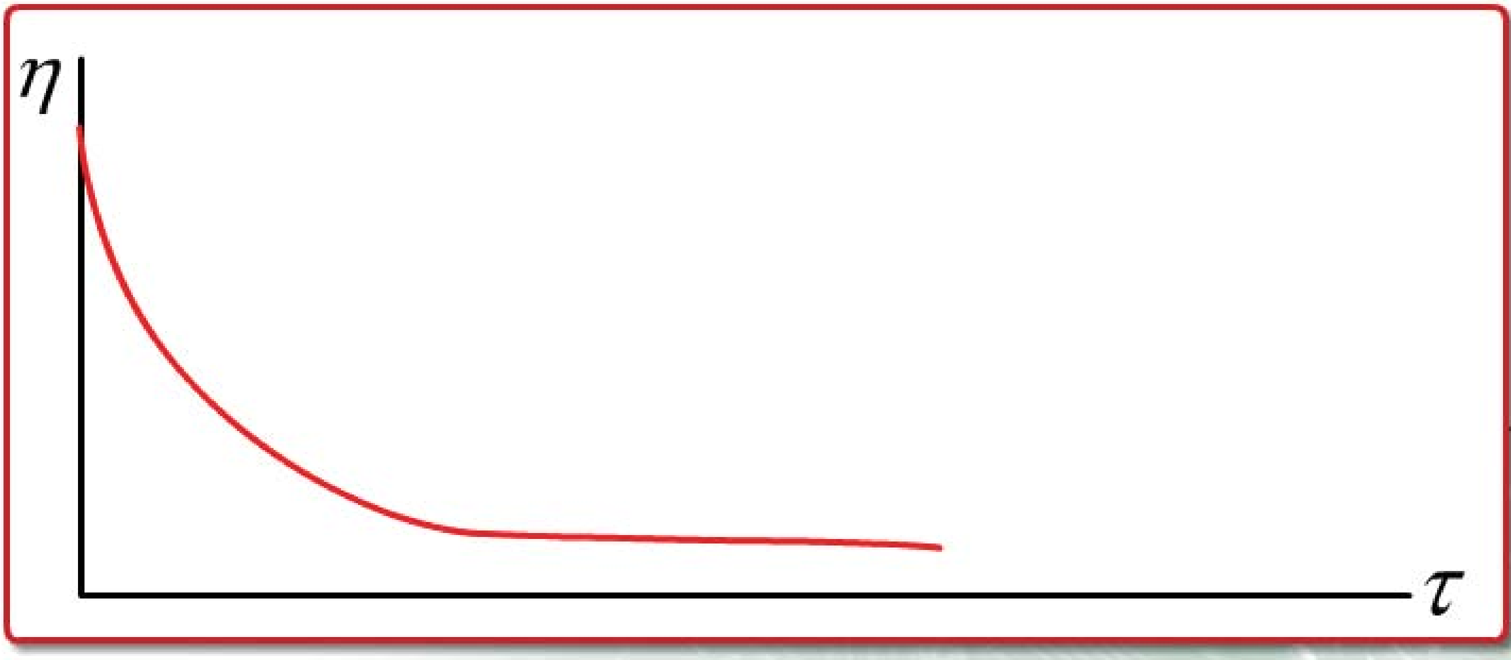
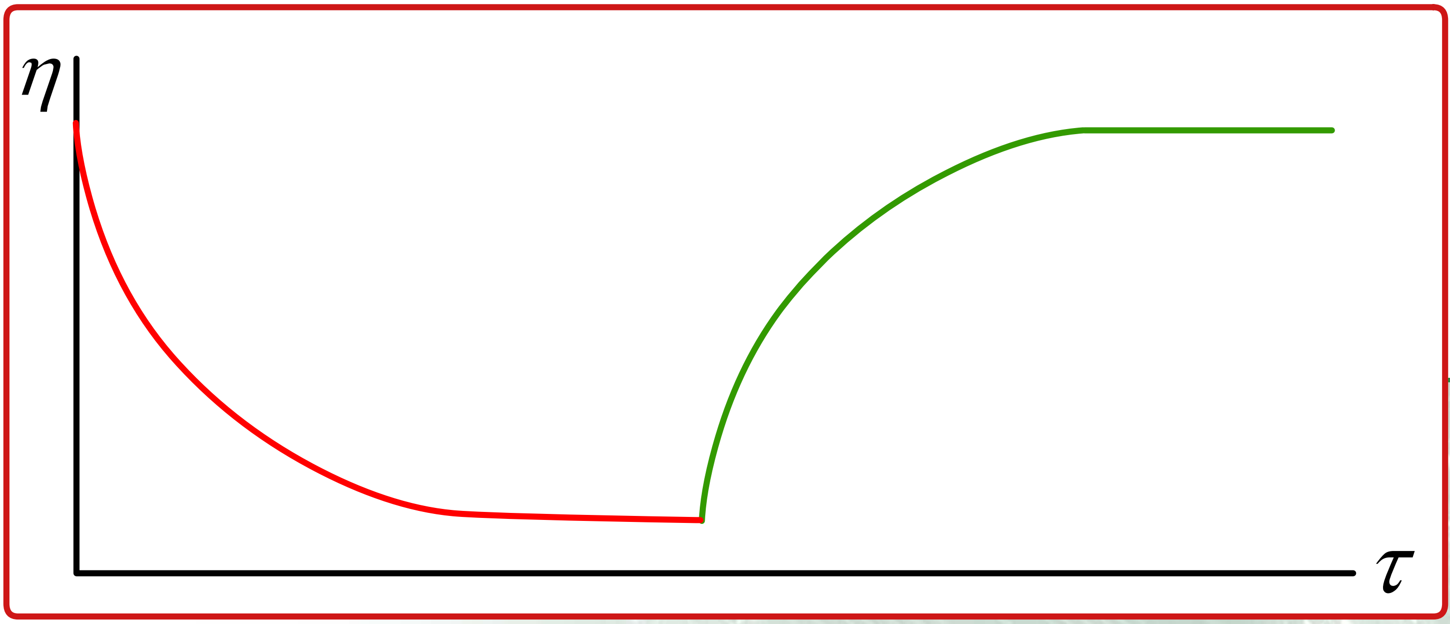


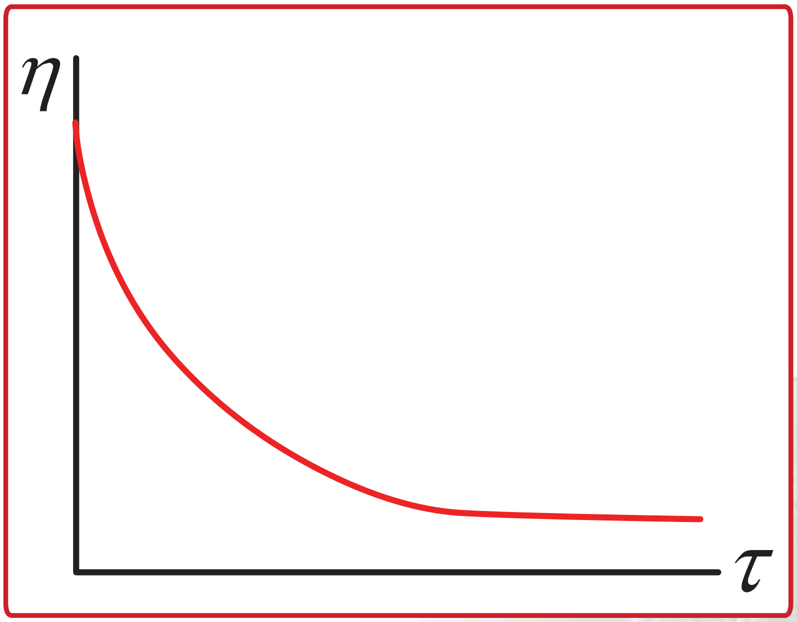
Thixotropy

- AKA: Time-Dependent Recovery
- Recovery of the Structure is a Function of Time. It follows a logarithmic pattern.

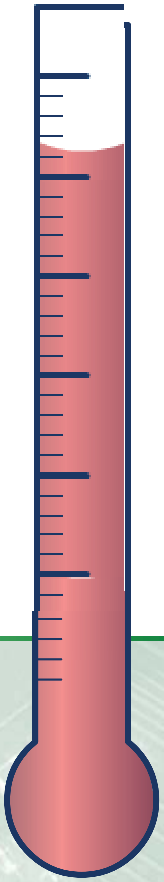


Roots of Shear-Stress

- Gravity (Storage)
- Vibration (Transport & Handling)
- Shock (Transport & Handling)
- Stirring
- Spinning
- Printing



Temperature has Significant Impact on Pseudoplastic Flow



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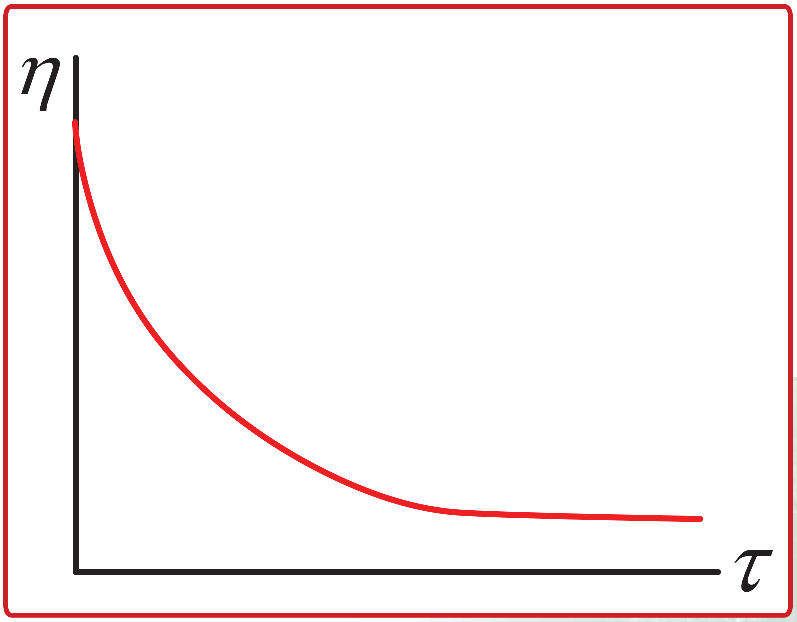

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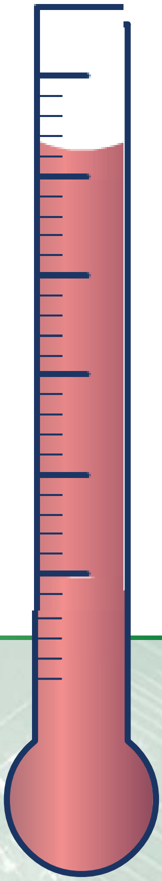
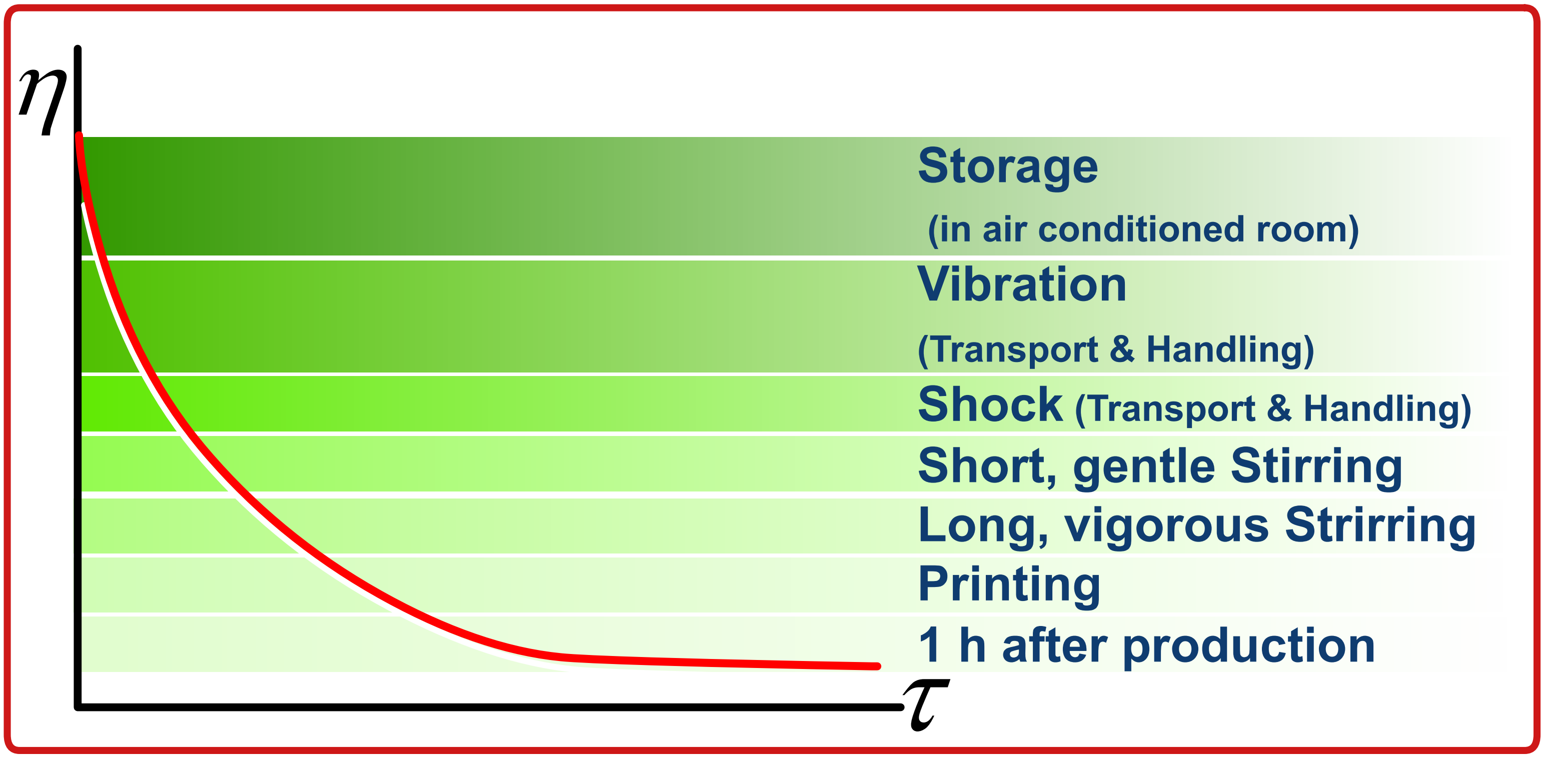


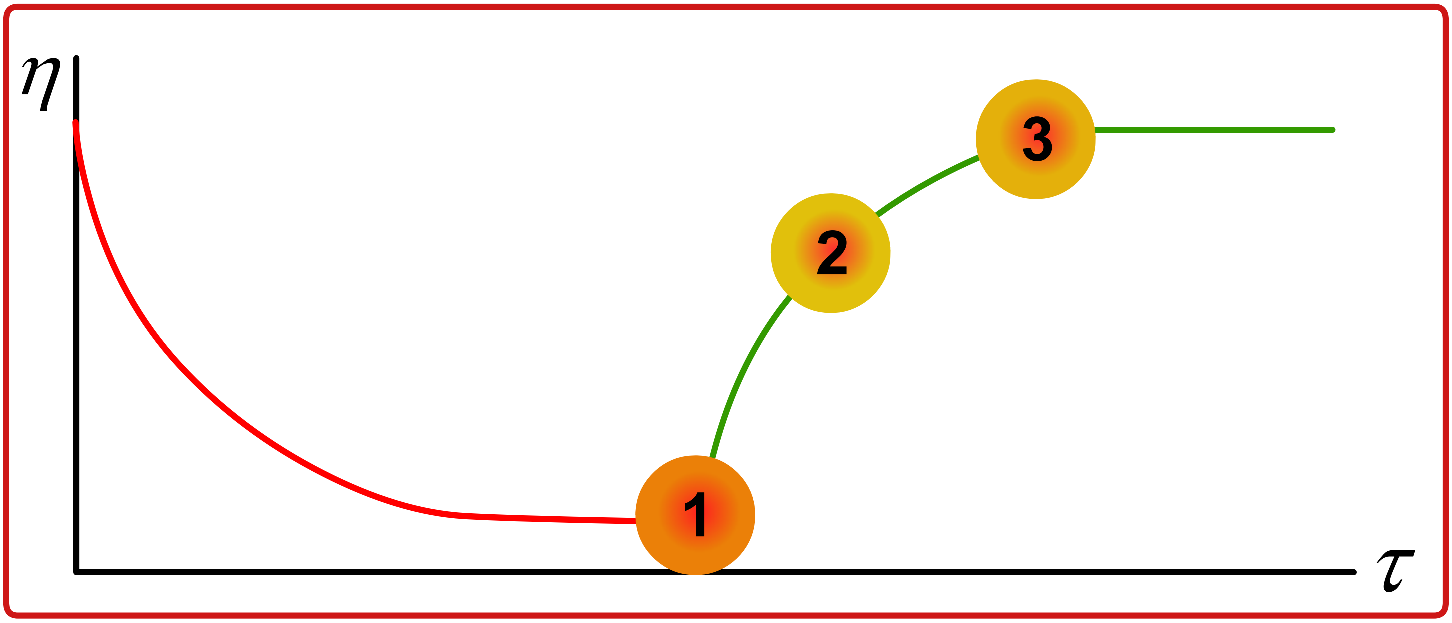
How much was it Stressed?



In Theory we could determine the point.

In Practice we don’t know.

Did it Recover?

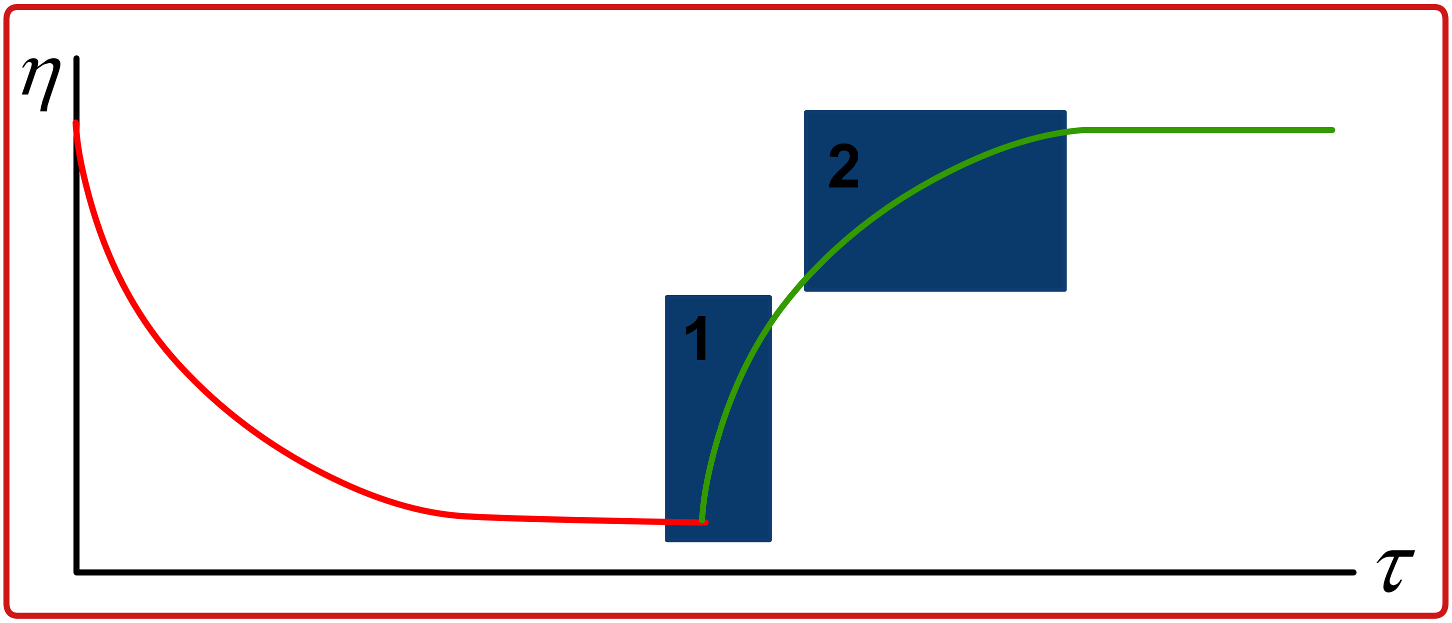


1 1 hour after production?

2 Directly after stirring/spinning/agitation/printing?

3 1 hour after stirring/spinning/agitation/printing?

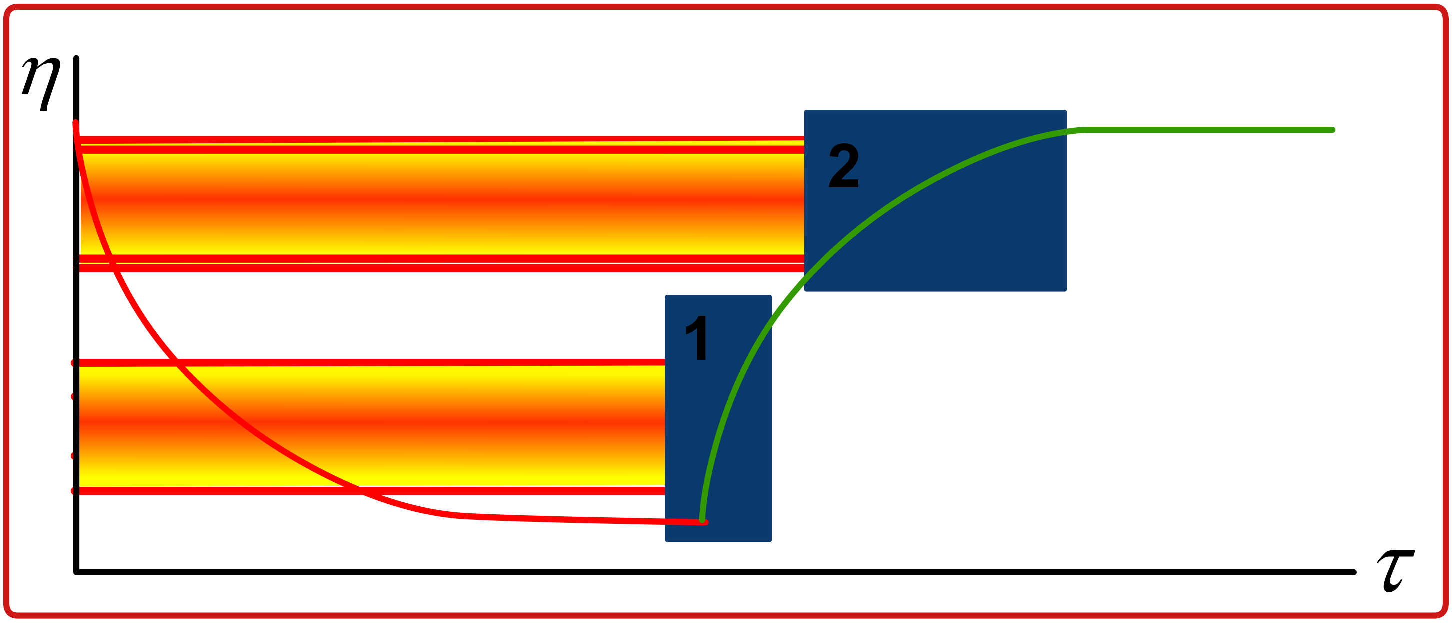
Which Recovery Do We Need?



1 **Instant Recovery to avoid Bridging, Smearing & Slumping**

2 **Recovery to achieve Reproducible Viscosity Values**

What is an Acceptable Window?



1 **Instant Recovery**
2 **“Full” Recovery**

The Variation in the samples is Too Large!

The History of the Paste

- The Elapsed Time between Moment of Measurement & Date/Time of finishing the Blending Process.

- The Elapsed Time between Last Moment of Significant Shear Stress (stirring, spinning, scooping, printing) & Date/Time of Measurement.

When We don’t know, We Need to Compensate....

We Compensate for Thixotropy!

Reduction of Measurement Variations

- Follow the Checklist we provided before:
- Prepare the sample in a more accurate way

We Need Identical...

- Measuring Principle
- Instrument Capabilities
- Tooling
- Working Conditions:
  - Vibrations
  - Temperature
  - Air flow
- Software for Measuring, Smoothing & Analysis
- Programming of Measuring/Analysis procedure, including temperature settings
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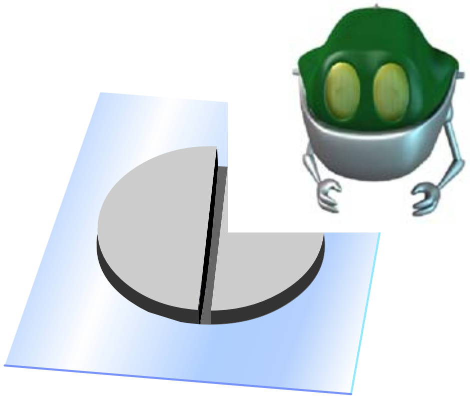

The History of the Paste

- The Elapsed Time between Moment of Measurement & Date/Time of finishing the Blending Process.

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- ► Follow the Checklist we provided before:
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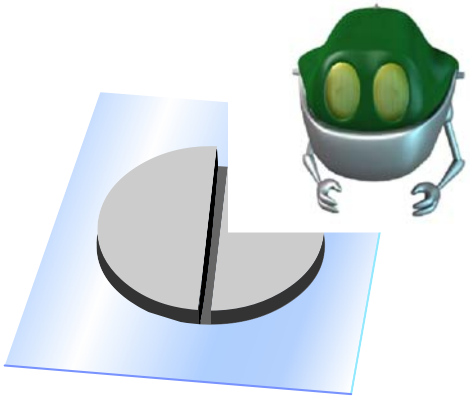


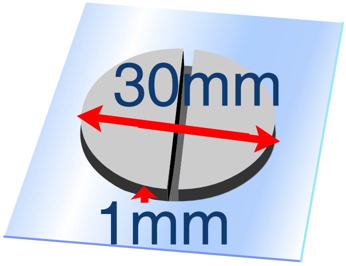
We Compensate for Thixotropy!

Viscosity Comparison by Customer/vendor

- Follow the Checklist we provided before
- Prepare the sample in a more accurate way
- We correct the viscosity in retrospect

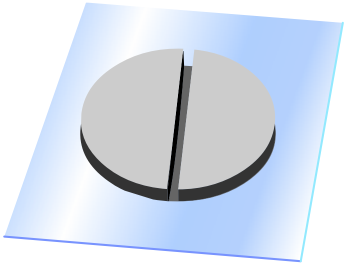
$$IV = V\,I - {}^{d}\log x + (c - (({}^{10}\log x + {}^{10}\log (x-1)) \,.\, c))$$

Sample Preparation



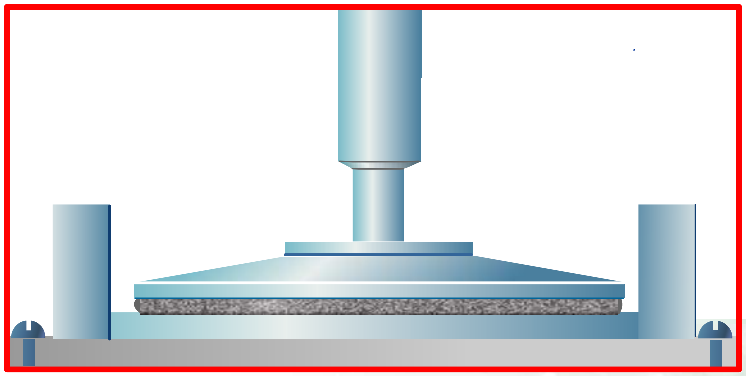
Test sample (dia 30 mm, h 1mm) printed on ceramic coupon with semi-automatic printer, 60 minutes prior to rheometric test.

Sample Preparation



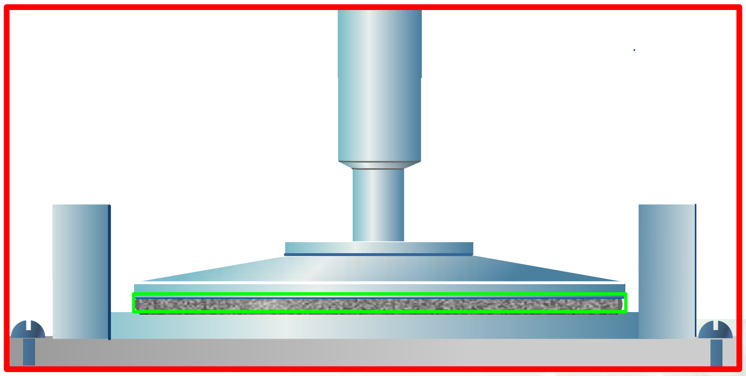
Test sample (dia 30 mm, h 1mm) printed on ceramic coupon with semi-automatic printer, 60 minutes prior to rheometric test.

Sample Preparation



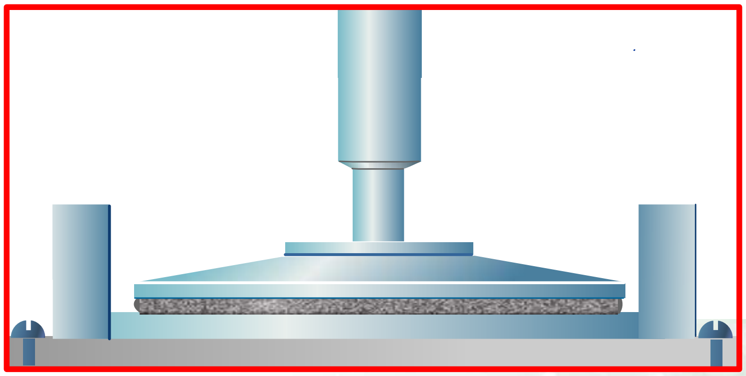
Sample Preparation

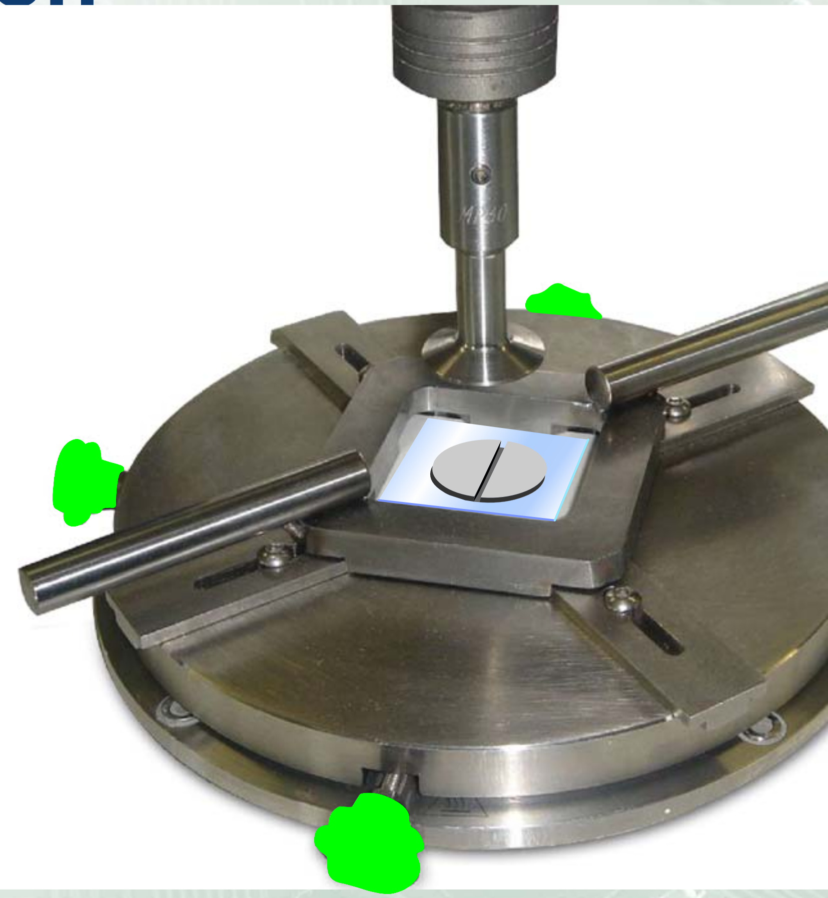
Place the Sample
in the Instrument



Sample Preparation

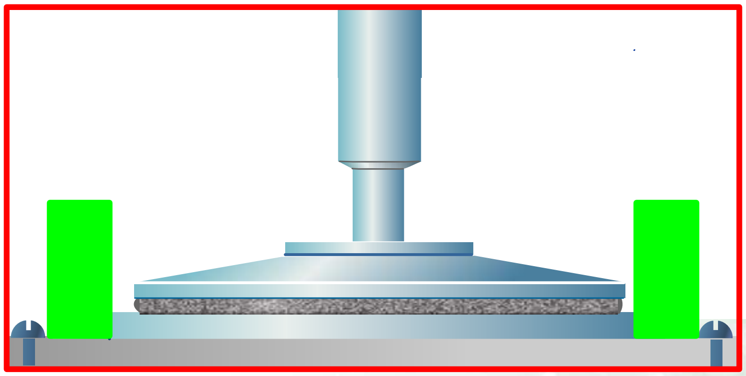
Devices for fixturing the sample holding tool to the bottom plate





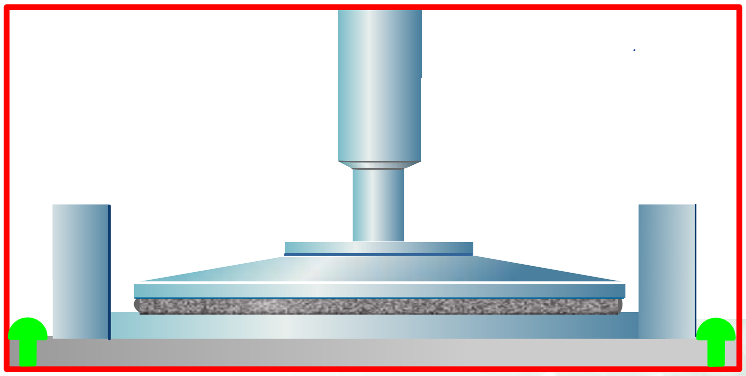
Sample Preparation

Device locking test coupon in vertical way



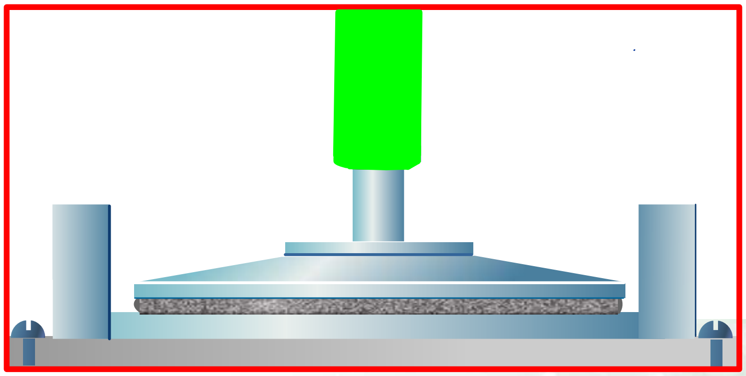
Sample Preparation

Devices centering locking test coupon in horizontal way



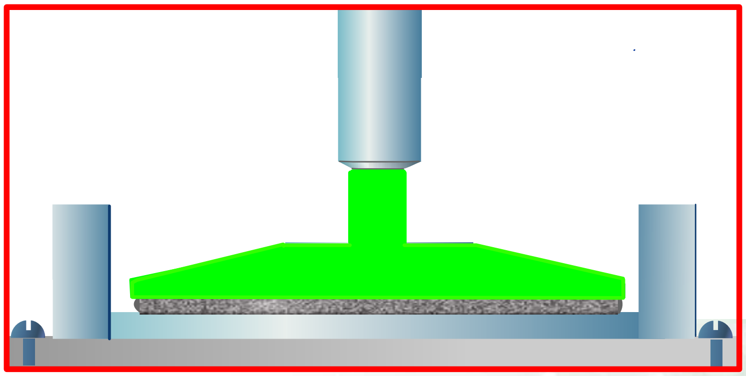
Sample Preparation

Cylinder connected with high precision drive and torque sensor



Sample Preparation

Top-plate rotating
or oscillating



Predicting Thixotropy

- Logarithmic Pattern
- Every Paste is different in...
  - Initial Recovery
  - Full Recovery

Predicting Thixotropy

$$\boxed{VT = IV + {}^{a}\log x + (c - (({}^{10}\log x + {}^{10}\log (x-1)) \cdot c))}$$

In which:

VT = Viscosity after Full Development/Recovery

IV = Initial Viscosity

a = Differs per paste from 1.05 (Strong Slope) until 1.35 (Moderate Slope).

x = Elapsed time (hours) between Moment of Measurement & Date/Time of finishing the Blending Process.

c = Differs per paste from 1 (Moderate) to 10 (Strong Slope).

Retrospective Correction

With the Inverse Function we can correct the measured Viscosity in Retrospect

$$\boxed{IV = VT - {}^{a}\log x + (c - (({}^{10}\log x + {}^{10}\log (x-1)) . c))}$$

In which:

IV = Initial Viscosity

VT = Viscosity after Full Development/Recovery

a = Differs per paste from 1.05 (Strong Slope) to 1.35 (Moderate Slope).

x = Elapsed time (hours) between Moment of Measurement & Date/Time of finishing the Blending Process.

c = Differs per paste from 1 (Moderate) till 10 (Strong Slope).

MENU PREV

Example of Correction

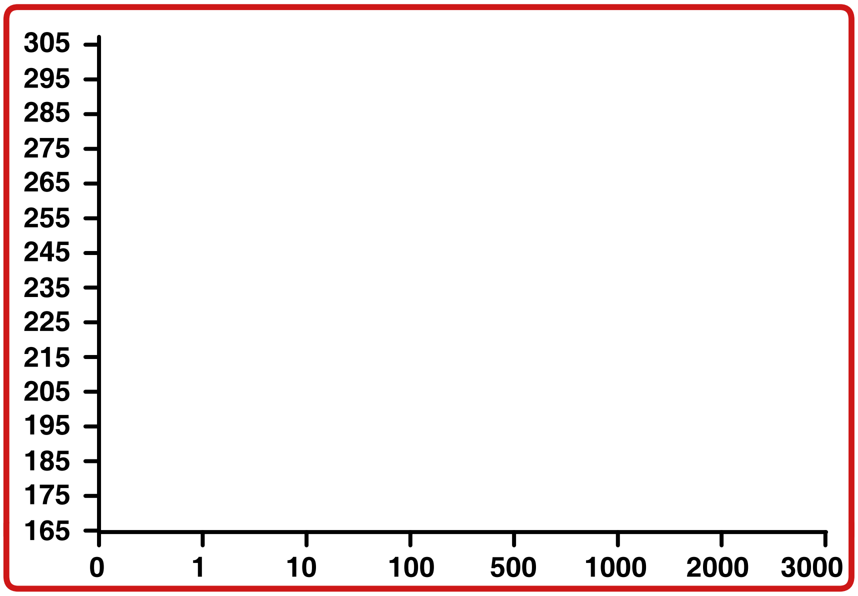
Finish Blending

4-7-2006 9:00

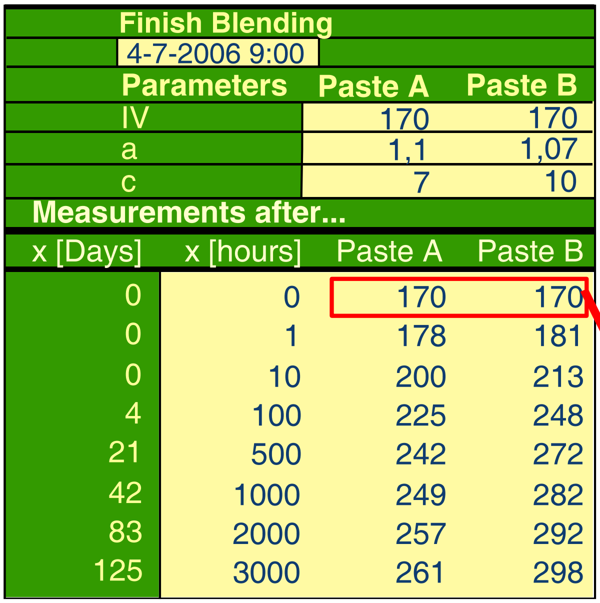
Parameters	Paste A	Paste B
IV	170	170
a	1,1	1,07
c	7	10

Measurements after...

x [Days]	x [hours]	Paste A	Paste B
0	0	170	170
0	1	178	181
0	10	200	213
4	100	225	248
21	500	242	272
42	1000	249	282
83	2000	257	292
125	3000	261	298



Example of Correction



Finish Blending			
4-7-2006 9:00			
Parameters		Paste A	Paste B
IV		170	170
a		1,1	1,07
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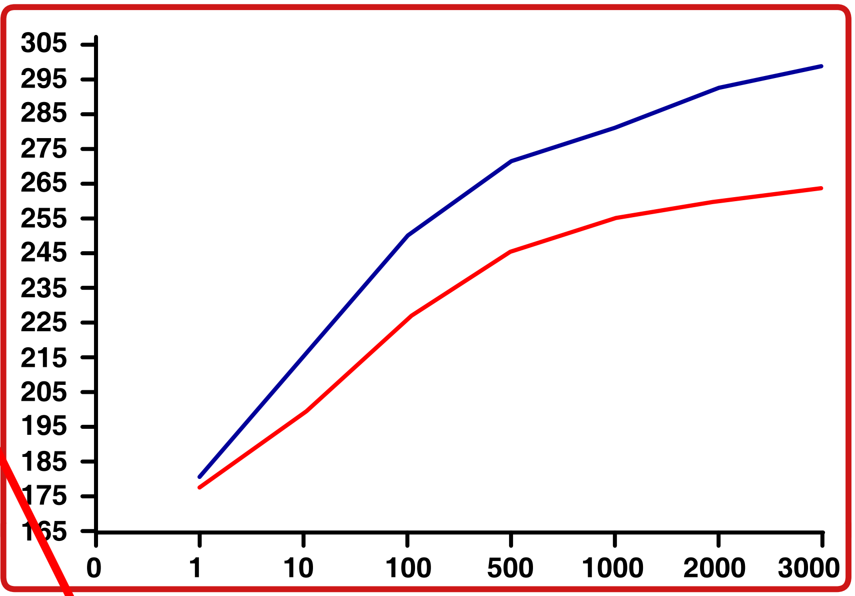

IV Initial Viscocity

Example of Correction

Finish Blending

4-7-2006 9:00

Parameters	Paste A	Paste B
IV	170	170
a	1,1	1,07
c	7	10

Measurements after...

x [Days]	x [hours]	Paste A	Paste B
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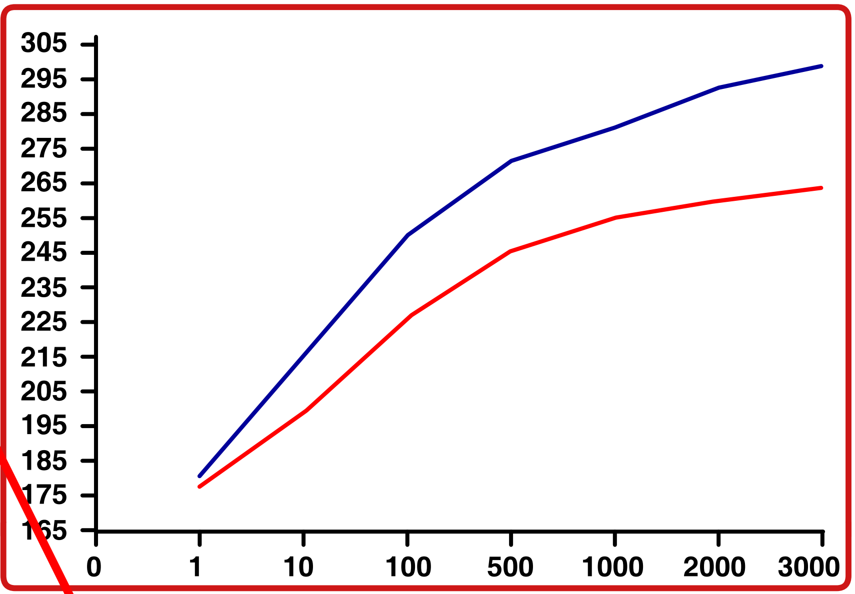

IV Initial Viscocity

Example of Correction

Finish Blending

4-7-2006 9:00

Parameters	Paste A	Paste B
IV	170	170
a	1,1	1,07
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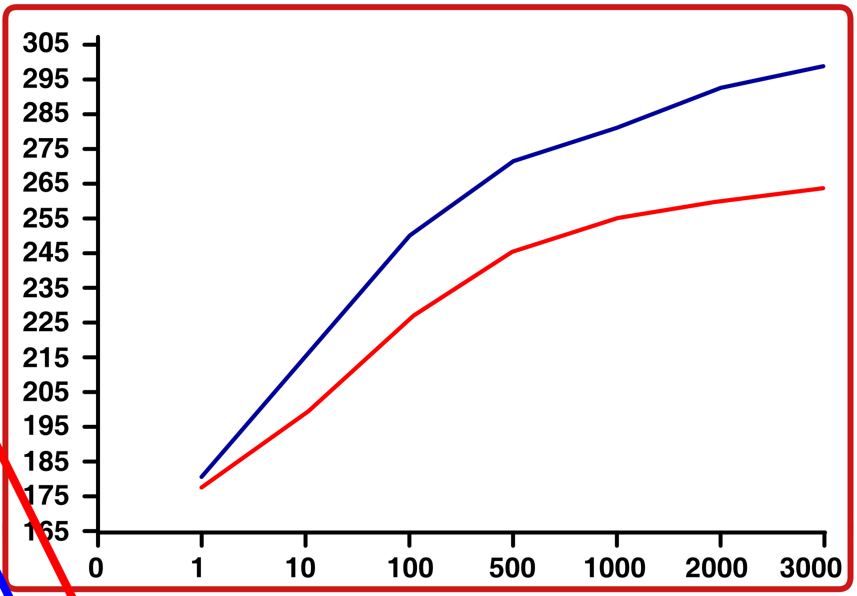

IV Initial Viscocity

Specified Viscosity

Example of Correction

Finish Blending

4-7-2006 9:00

Parameters	Paste A	Paste B
IV	170	170
a	1,1	1,07
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Measurements after...

x [Days]	x [hours]	Paste A	Paste B
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0	1	178	181
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4	100	225	248
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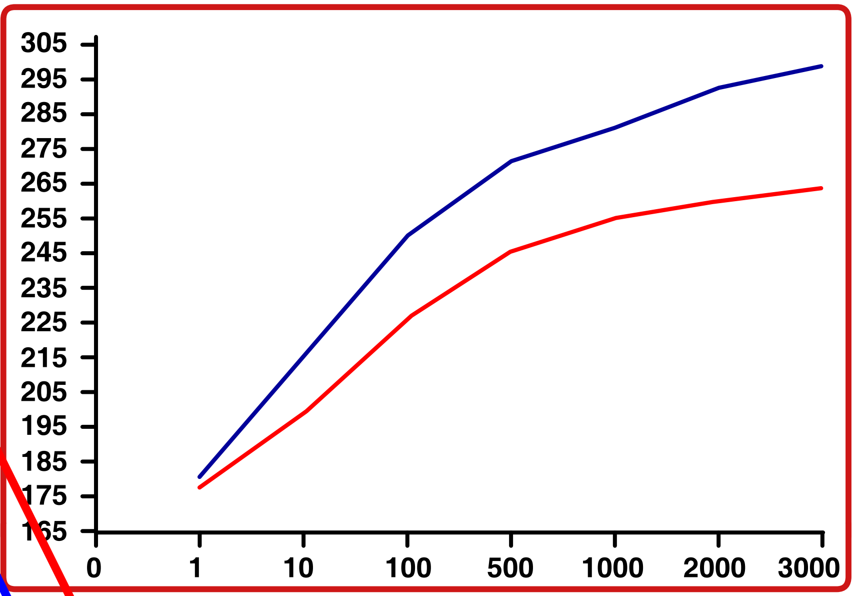

IV Initial Viscocity

Specified Viscosity

Example of Correction

Finish Blending

4-7-2006 9:00

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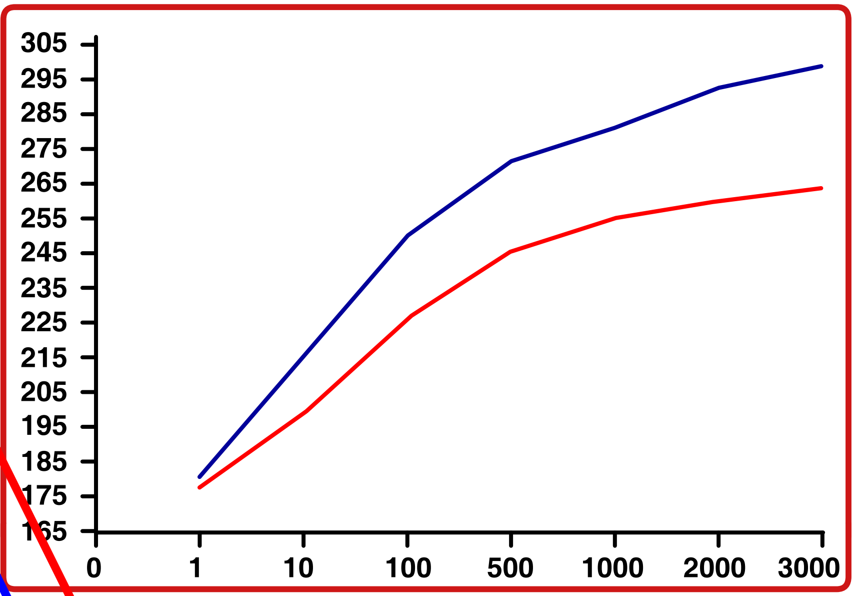
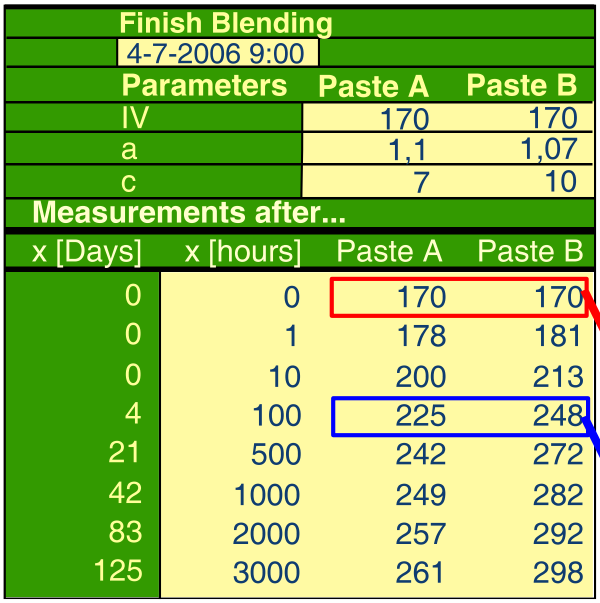


IV Initial Viscocity

Specified Viscosity

Example of Correction



Finish Blending

4-7-2006 9:00

Parameters	**Paste A**	**Paste B**
IV	170	170
a	1,1	1,07
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4	100	225	248
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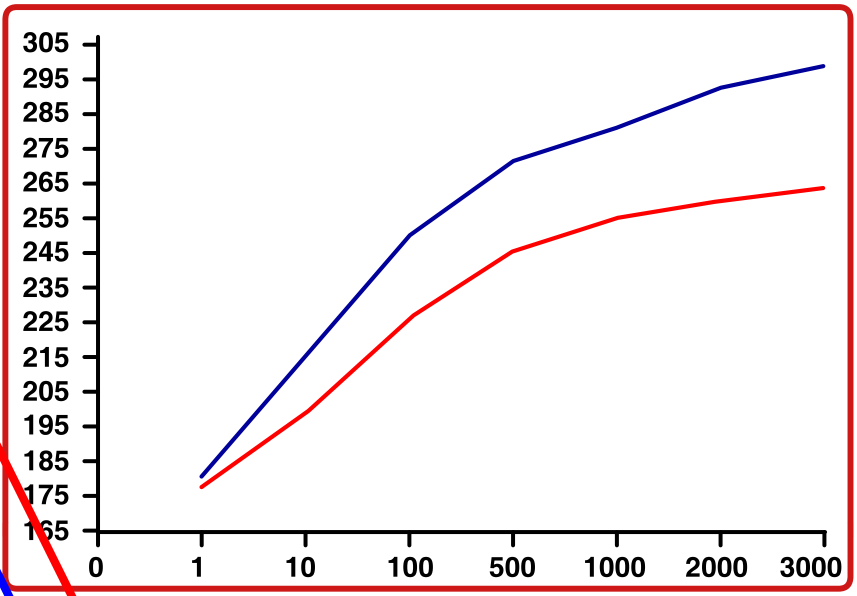
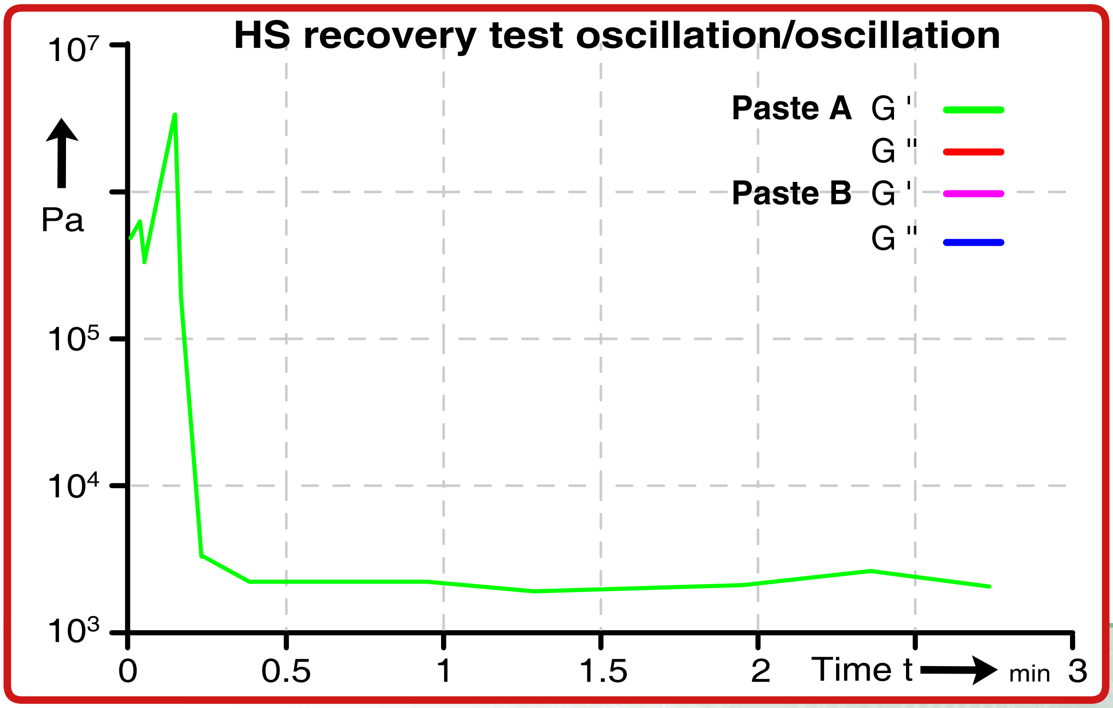


IV Initial Viscocity

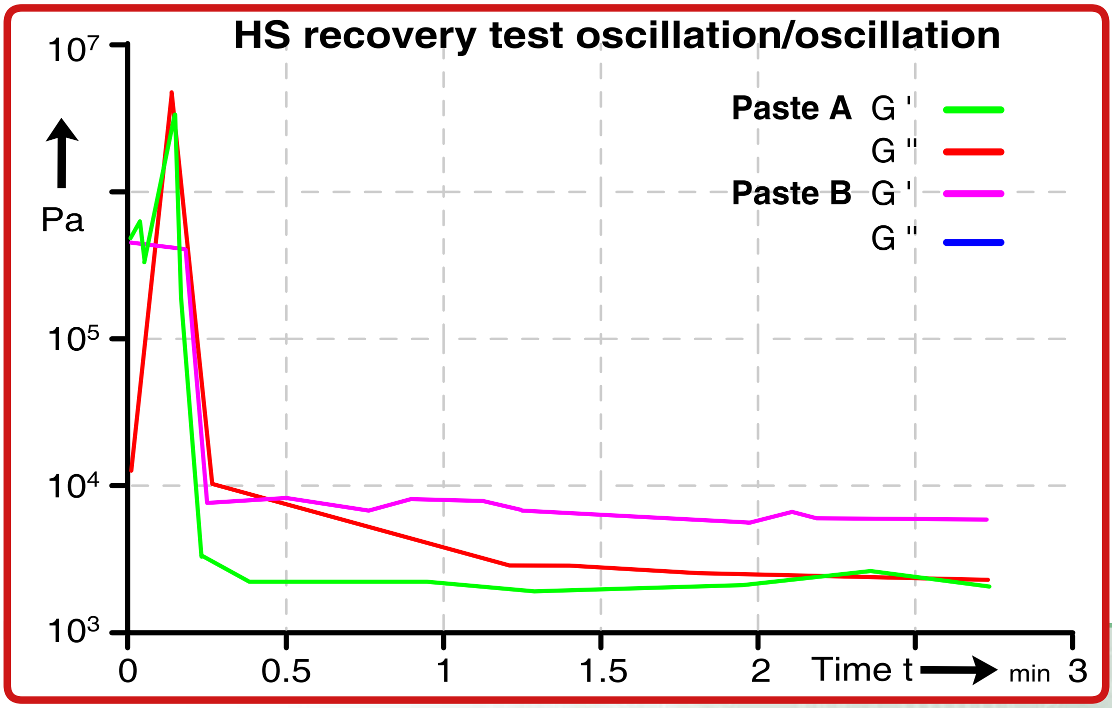
Specified Viscosity

The Measured Values at 125 days (3000 hours, 4 months) can be corrected to the Initital Viscosity

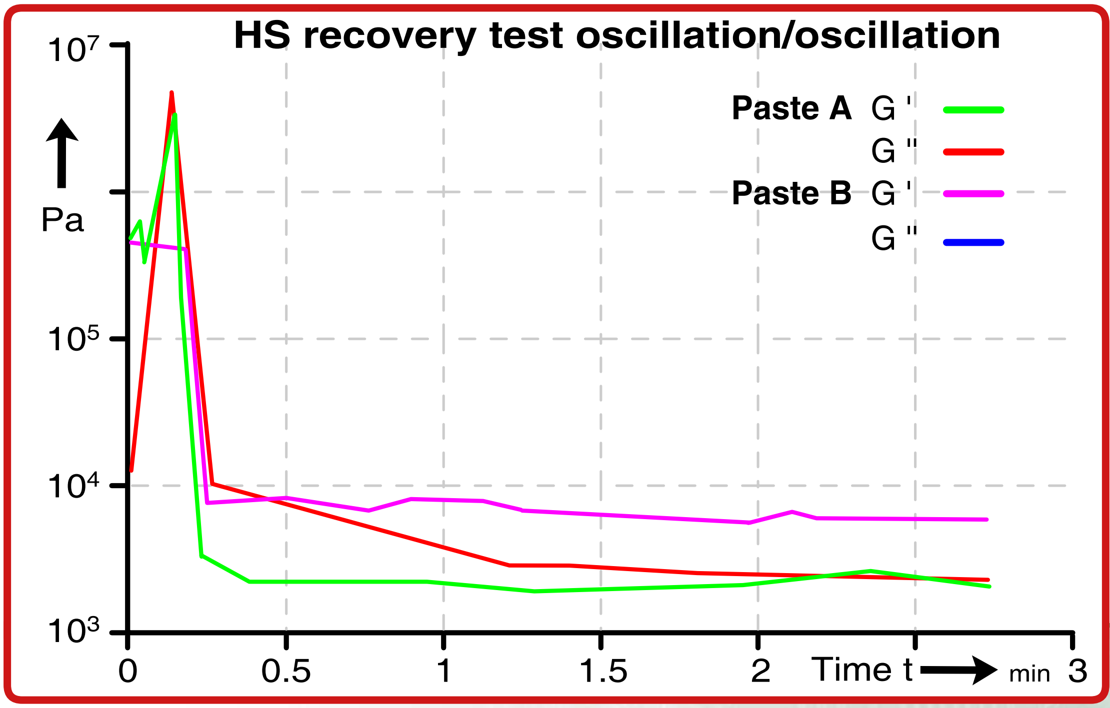
Initial Recovery Measurements



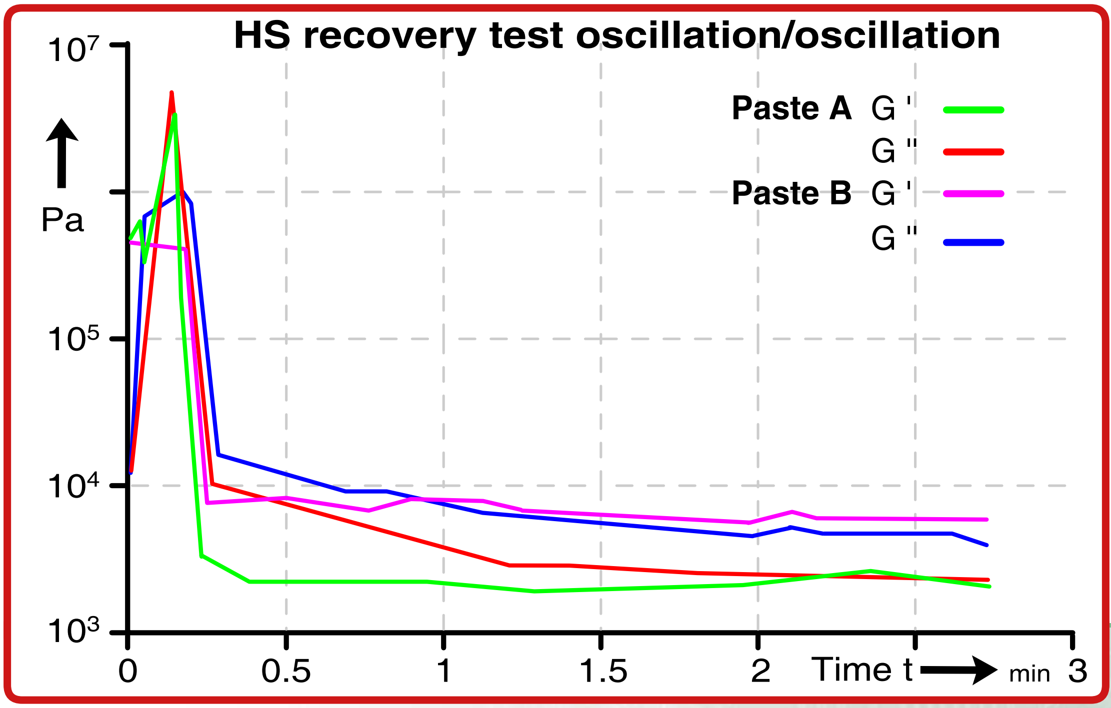
Initial Recovery Measurements



Initial Recovery Measurements



Initial Recovery Measurements



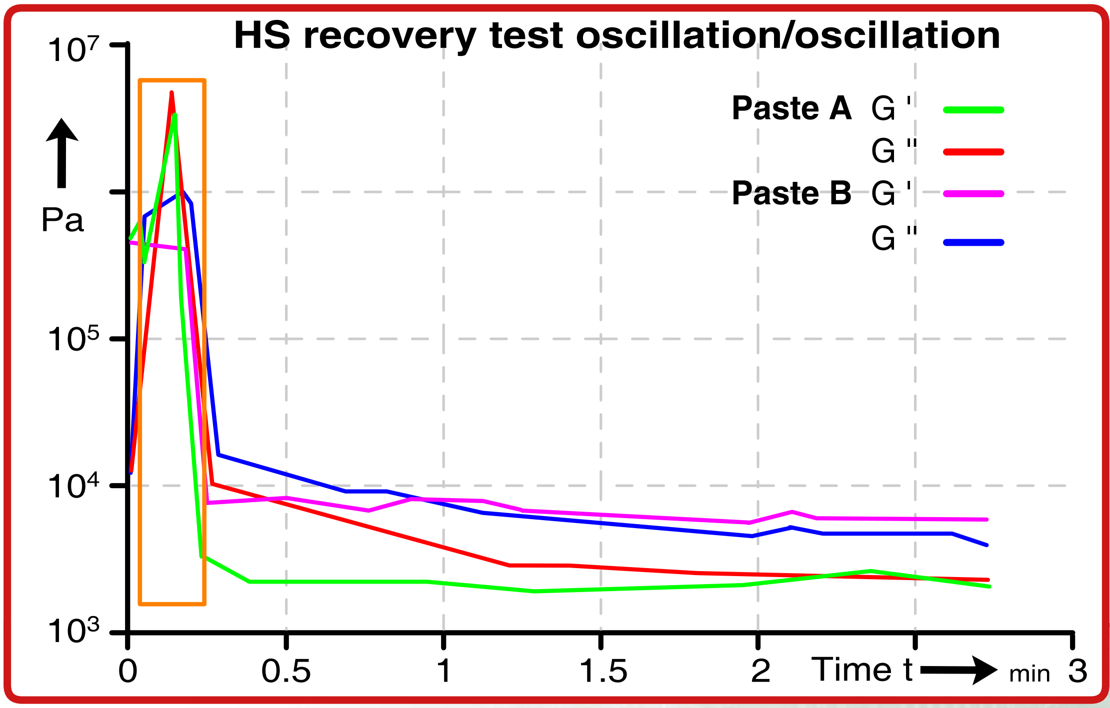
The elastic (G') and viscous portion (G") are monitored.

Observations:

O Prints Faster & is Less Sensitive to Smearing and Bridging.

Initial Recovery Measurements

Print



The elastic (G') and viscous portion (G") are monitored.

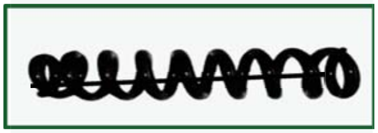
Observations:

O Prints Faster & is Less Sensitive to Smearing and Bridging.

Print/Stress Phase: 3s, >500 Hz by Temperature Superposition. Recovery Phase 2.5 m, t 25 °C.

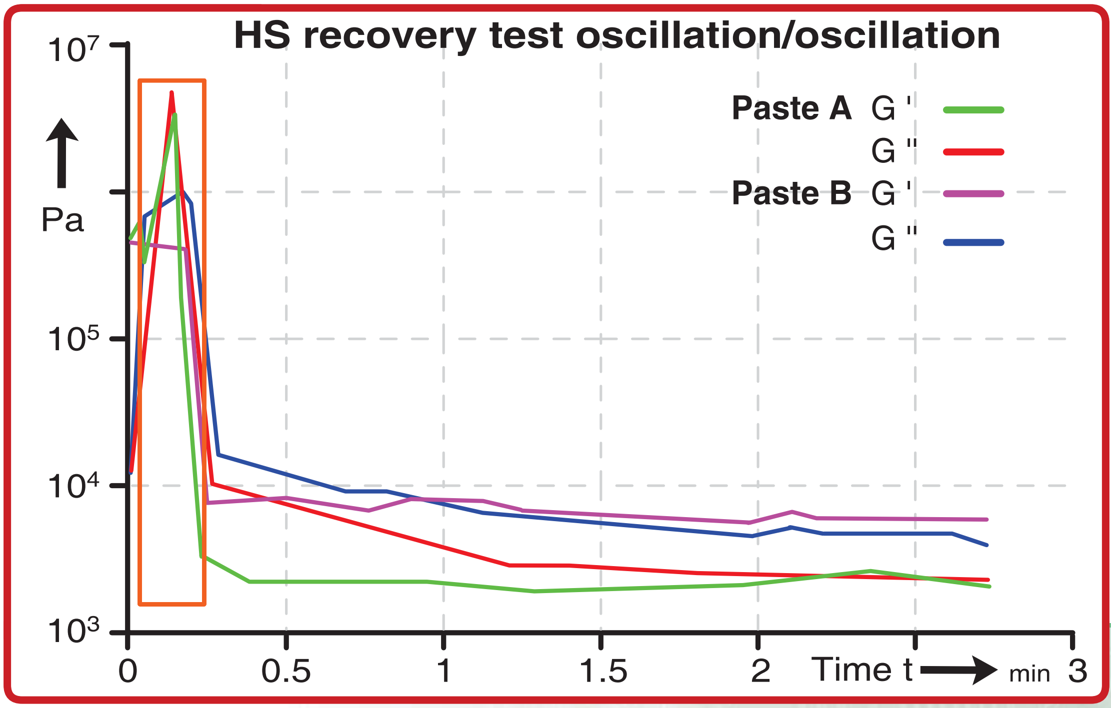
Initial Recovery Measurements

Print



F = High

A = Large



The elastic (G’) and viscous portion (G”) are monitored.

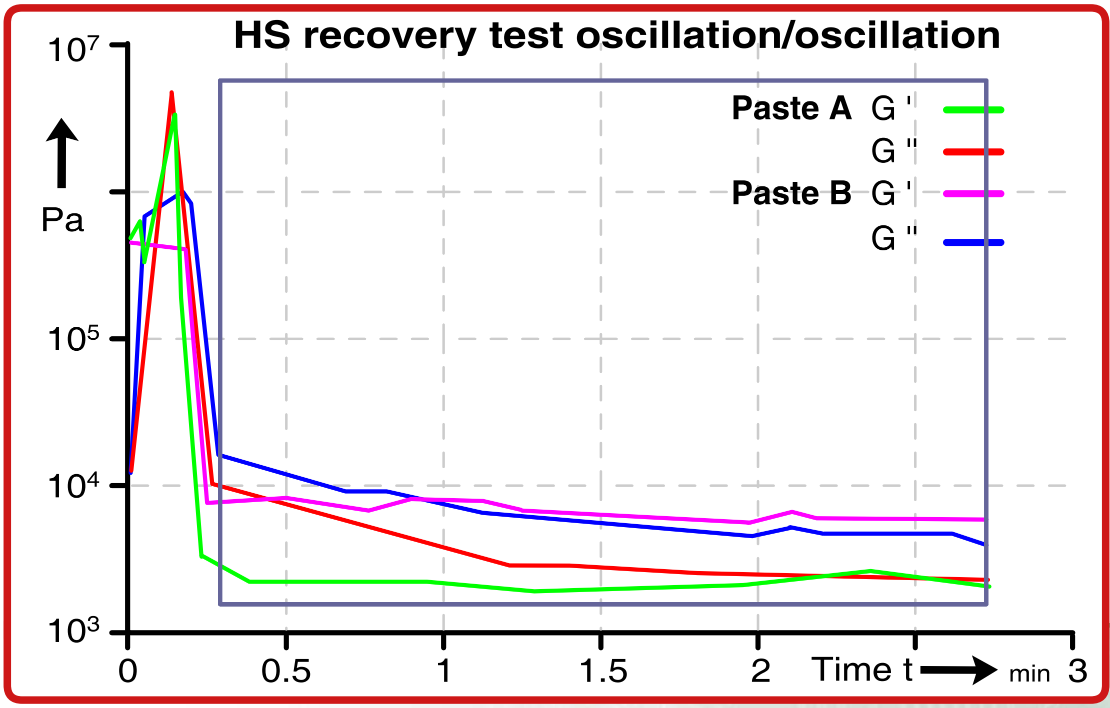
Observations:
O Prints Faster & is Less Sensitive to Smearing and Bridging.

Print/Stress Phase: 3s, >500 Hz by Temperature Superposition. Recovery Phase 2.5 m, t 25 °C.

Initial Recovery Measurements

Recovery

F = High
A = Large



The elastic (G’) and viscous portion (G”) are monitored.

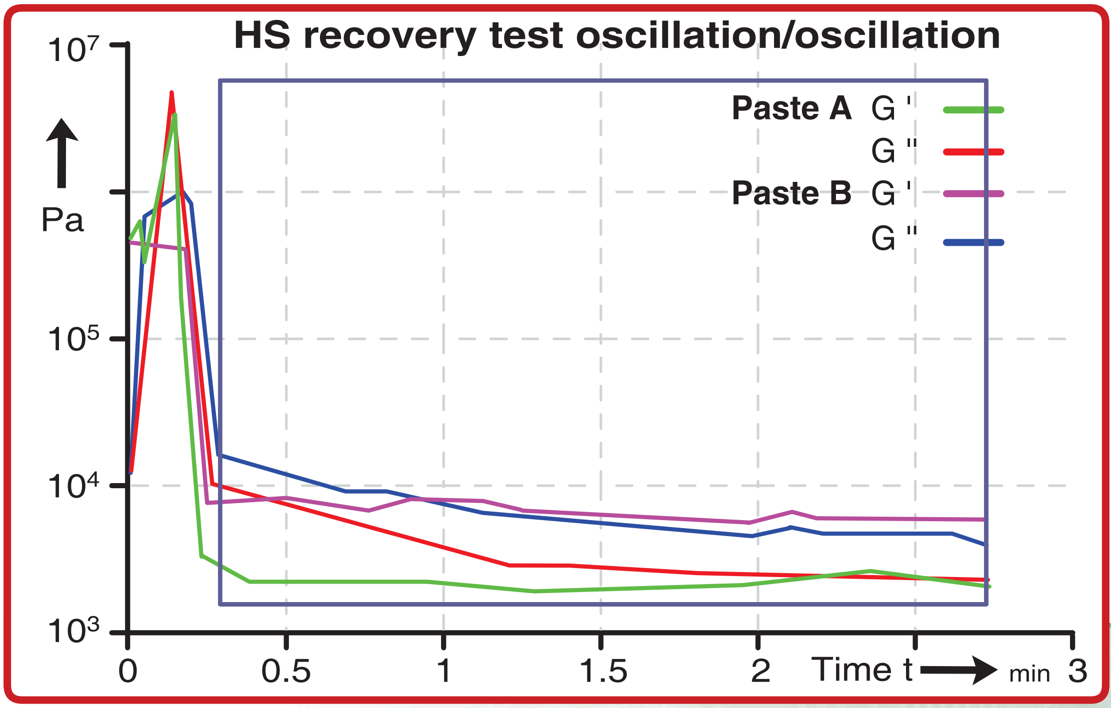
Observations:
O Prints Faster & is Less Sensitive to Smearing and Bridging.

Print/Stress Phase: 3s, >500 Hz by Temperature Superposition. Recovery Phase 2.5 m, t 25 °C.

Initial Recovery Measurements

Recovery

F = High
A = Large

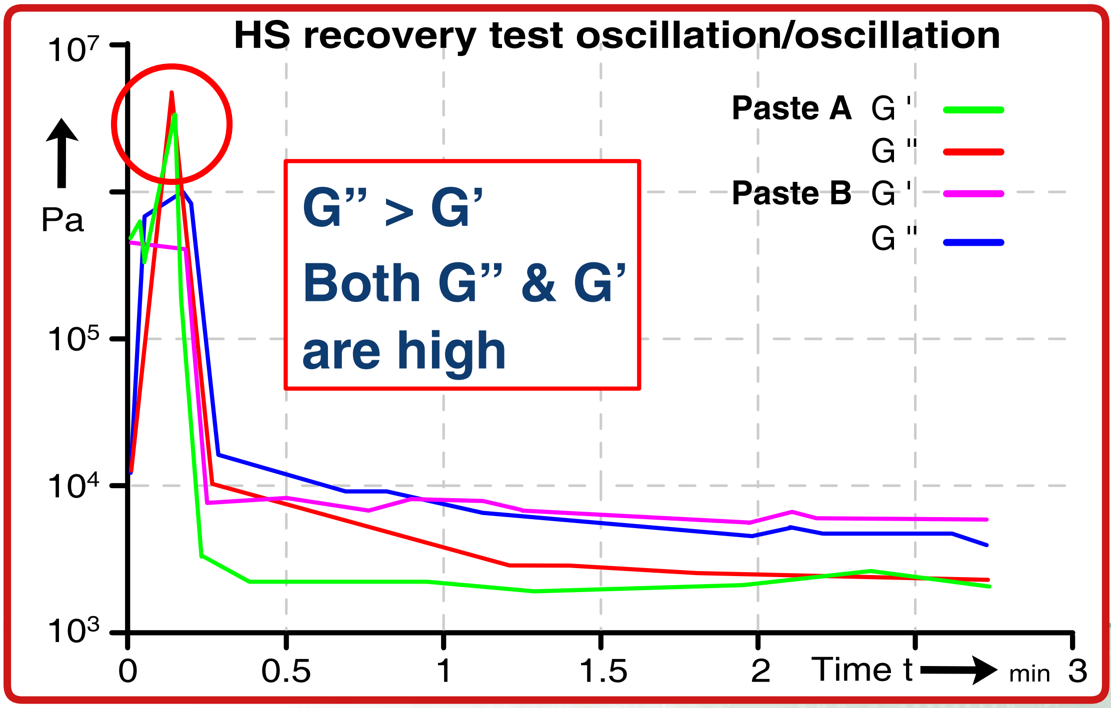


The elastic (G') and viscous portion (G") are monitored.

Observations:
O Prints Faster & is Less Sensitive to Smearing and Bridging.

Print/Stress Phase: 3s, >500 Hz by Temperature Superposition. Recovery Phase 2.5 m, t 25 °C.

Initial Recovery Measurements



G” > G’

Both G” & G’ are high

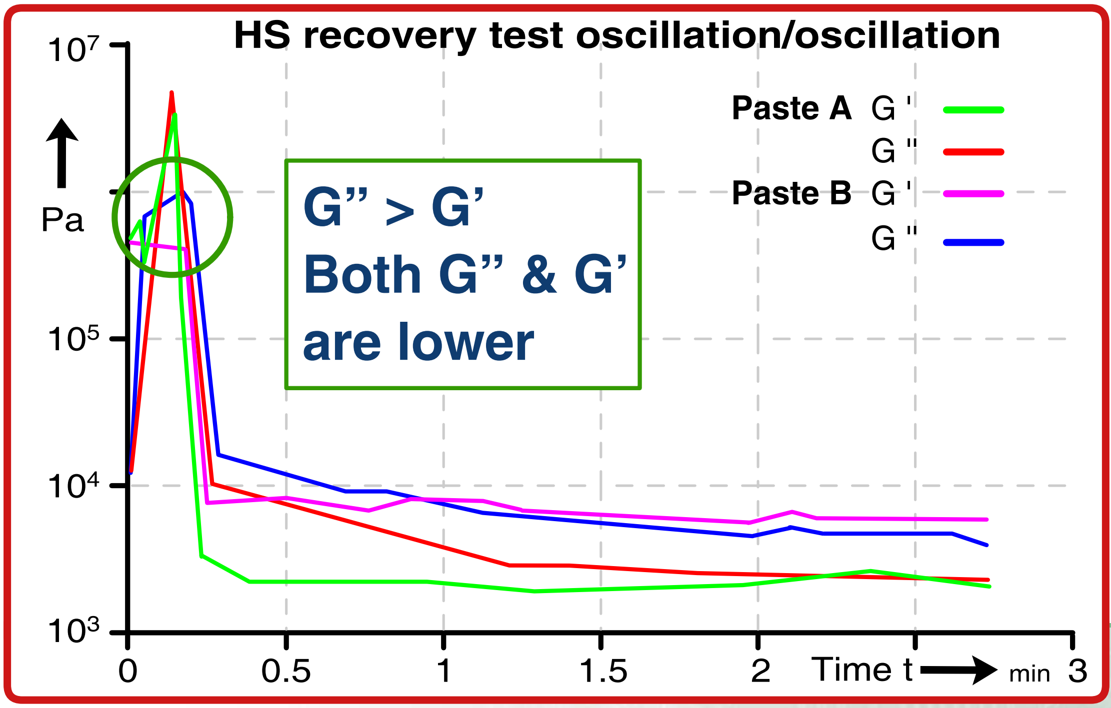
The elastic (G’) and viscous portion (G”) are monitored.

Observations:

O Prints Faster & is Less Sensitive to Smearing and Bridging.

Print/Stress Phase: 3s, >500 Hz by Temperature Superposition. Recovery Phase 2.5 m, t 25 °C.

Initial Recovery Measurements



G” > G’

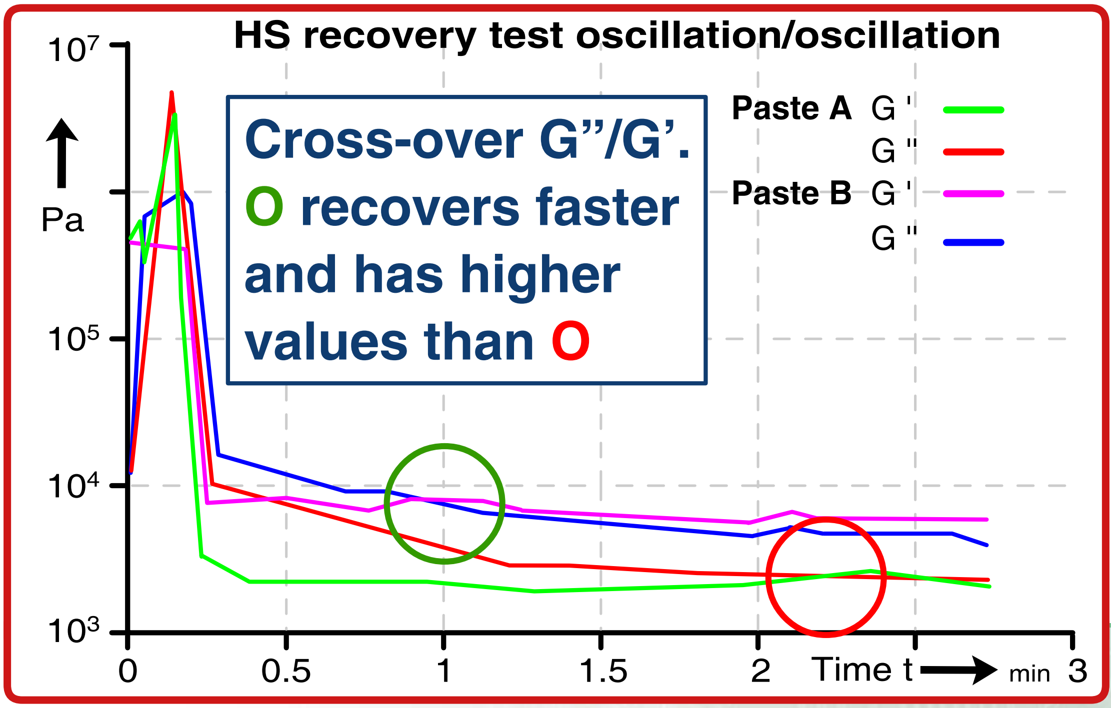
Both G” & G’ are lower

The elastic (G’) and viscous portion (G”) are monitored.

Observations:
O Prints Faster & is Less Sensitive to Smearing and Bridging.

Print/Stress Phase: 3s, >500 Hz by Temperature Superposition. Recovery Phase 2.5 m, t 25 °C.

Initial Recovery Measurements



Cross-over G''/G'. O recovers faster and has higher values than O

The elastic (G') and viscous portion (G'') are monitored.

Observations:
O Prints Faster & is Less Sensitive to Smearing and Bridging.

Print/Stress Phase: 3s, >500 Hz by Temperature Superposition. Recovery Phase 2.5 m, t 25 °C.

Conclusions

The complexity of Repeatable & Reproducible Viscosity Measurements is widely Underestimated and Misunderstood.

- ☑ The complexity of Repeatable & Reproducible Viscosity Measurements is widely Underestimated and Misunderstood.
- ☑ Industry Standards such as ISO TS-16949 Do Recognize these Significant Measurement Variations.
- ☑ Our Industry Now Needs to Reduce Variations in Soldering Materials, Implying Improved Measurement Techniques.
- ☑ Many Improvements can be made to Improve Viscosity Measurements.
- ☑ This will Provide a Technique with Acceptable R&R results

Thank You

for Your Attention!

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