The characterization of printing properties of solder paste

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Introduction

Many engineers in the electronics industry appreciate the complexity of SMT technology. More and more they realize that there are numerous parameters which define the quality of the solder connections of a circuit assembly. Particularly the quality of the solder paste is an important key to the reliability of the final products. SPC-data show that 65% of the yield is lost before the SMT-assembly arrives to the pick & place operation (Figure 1).

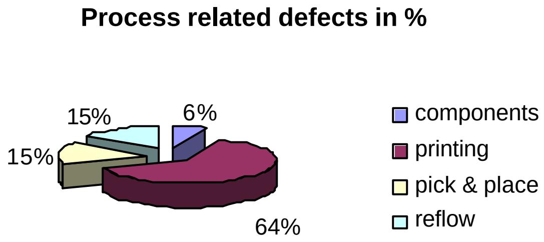

Figure 1. Most of the yield is lost during printing.

This implies that the performance of the solder paste up to and including the printing operation of the assemblies requires more accurate control.
Just to mention a few examples: Separation of the flux vehicle generally causes consistency problems in closed print heads. Poor printing may result in solder beading.

Recent developments, such as the introduction of closed print heads, ultra-fine pitch printing, high-speed printing, zero-defect printing and lead-free solder paste, will require a better understanding of the behavior of solder paste. The behavior of the product should be studied throughout the steps between the manufacture of the solder paste, transport, storage, stencil-life, printing, and wet deposit on the circuit board prior to the pick & place operation.
Phenomena that are relevant throughout these steps are product stability during transport and storage, temperature sensitivity during printing, the printing performance itself at defined speeds, stencil-life (when printed with squeegee systems) and issues such as tackiness.

The printing process by itself is defined by many parameters. Figure 2 illustrates the complexity of this phase in the application of solder pastes. Evidently, the printing properties of solder paste need to be verified in order to assure that this key player in the process provides a consistent and reliable performance at all times. Monitoring properties as viscosity, shear sensitivity and stencil-life are of paramount importance when setting goals for increasing yields.

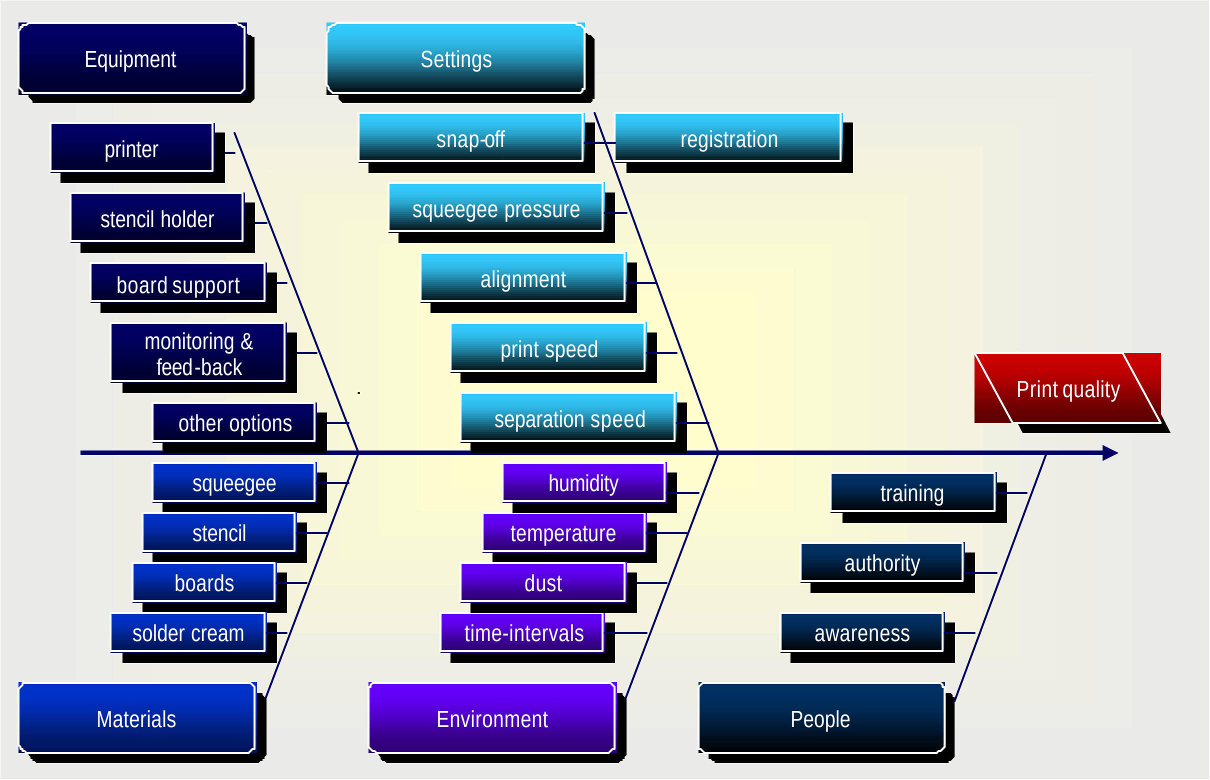

Figure 2. The control parameters printing process solder pastes.

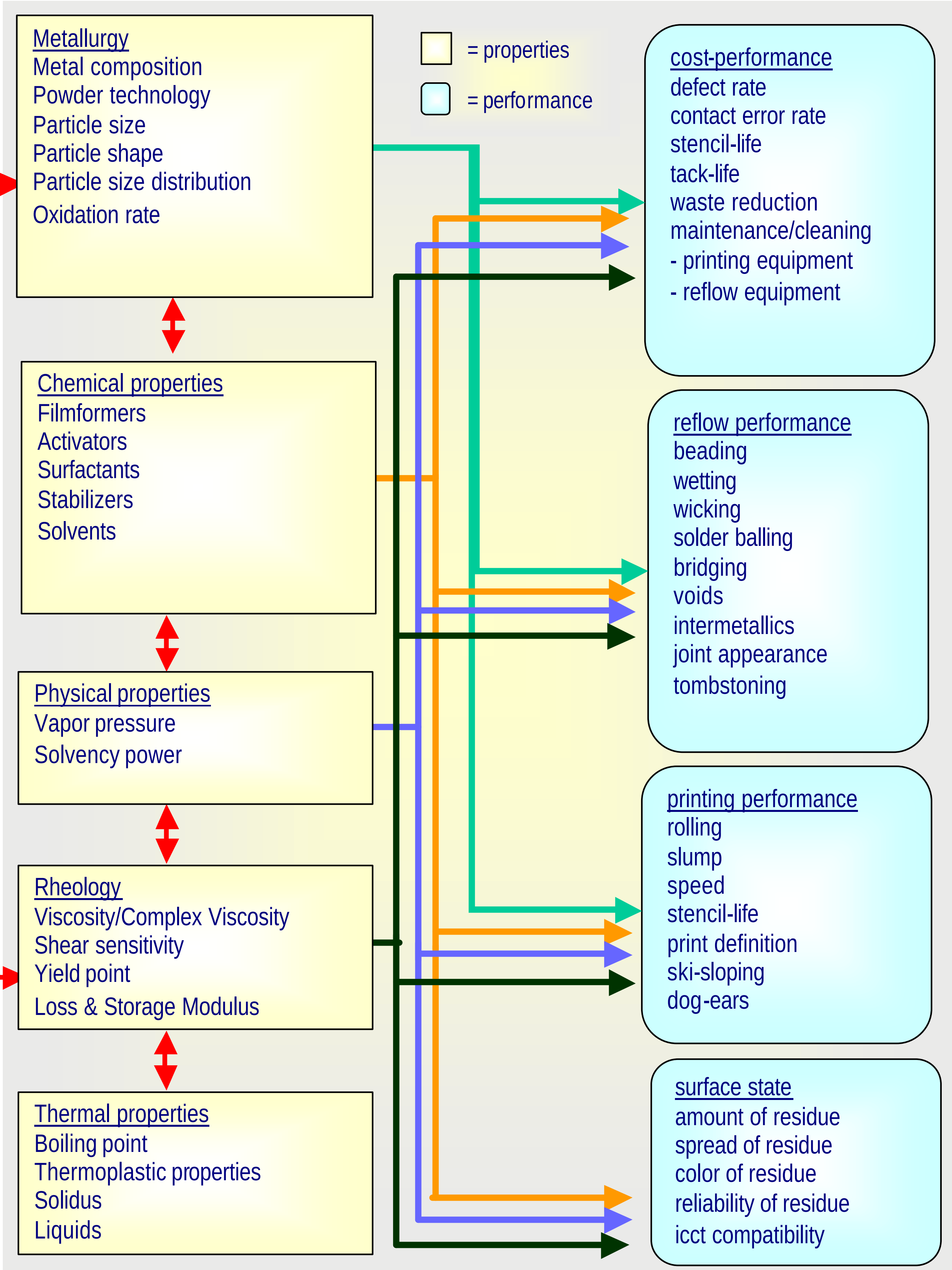

Figure 3. A simplified model representing the main functional constituents in a solder paste and its related performance.

It is not just the combination of solder, flux and the rheology additives that constitute a good solder paste. Of equal importance is the complex chemistry and physical properties of these materials. Thus, a small variation in its composition, environmental changes (e.g. temperature, humidity) and manufacturing techniques can have dramatic effects on the behavior of the solder paste.

Figure 3 illustrates the main functional constituents of a solder paste affecting the properties of the product, and the related performance. In fact, it represents a simplified model showing just a few of the interactions, as within each category of properties also interactions take place. For instance: the oxidation rate of powder strongly correlates with the size and shape of the particles.

The aforementioned phenomena related to product stability temperature sensitivity, the printing performance itself at defined speeds, stencil-life and issues such as tackiness, all can be explained in terms of flow and deformation of the solder paste.

The rheology of solder paste

Rheology is the science that studies the flow behavior and deformation of matter. For solder pastes 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 rate and shear stress. Apart from the shear forces, the deformation and flow of a solder paste – but also its recovery – are time and temperature dependent.

So far, the study of the flow behavior of solder paste generally 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 by users of solder paste, as it was the first type of equipment specified by military and federal standards.

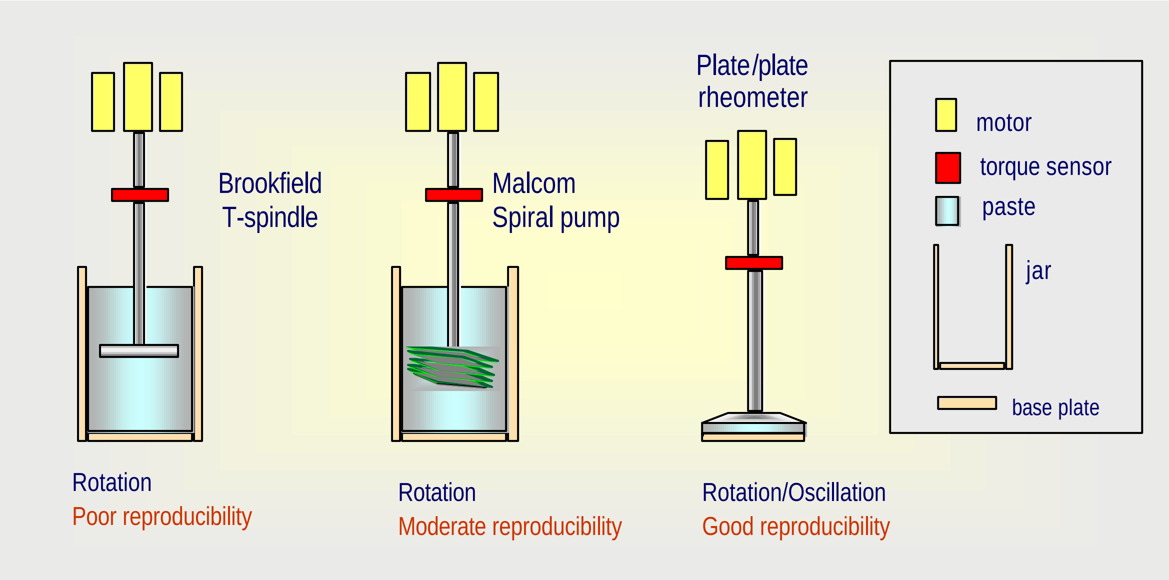

Figure 4. A Brookfield spindle device only has an extremely small surface. This is one of the reasons why the reproducibility of measuring data is limited. The Malcom spiral pump instrument is a measuring device with moderate reproducibility. The plate-plate rheometer, is significantly more accurate and has more possibilities for advanced rheometry, such as oscillation, temperature superposition etc.

The spiral pump type recently has become very popular. This type of equipment has made its 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. They enable a precise characterization of the viscous behavior of a solder paste. Their modular design usually enables expansion in terms of monitoring different rheological parameters, some of them exclusively belonging to the field of oscillation rheometry.

Viscosity of solder paste in Pa.S:

System	**M**	**P**
325-RXM	177	188
325-RX	225	177
325-XM2	231	254

M = Malcom, controlled shear rate at 6 1/s

P = Paar-Physica UDS-200, controlled shear stress, data taken at 6 1/s

Figure 5. Single point viscosity values compared. The table shows that it is virtually impossible to compare data measured with different types of equipment

An interesting parameter belonging to the latter field of rheometry is the determination of the viscous and elastic fraction of a substance. The latter property will be discussed under the section 'Visco-elastic properties'.

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. In order to simulate the flow properties of solder paste during storage and printing, a more fundamental approach is necessary.

A viscosity profile is the plot of viscosity versus shear rate. The equation for the so-called thixotropic index is as follows:

$$TI = \log \frac{\eta(D=1.85\ s^{-1})}{\eta(D=18.5\ s^{-1})}$$

in which:
η = viscosity (Pa.S)
D = shear rate

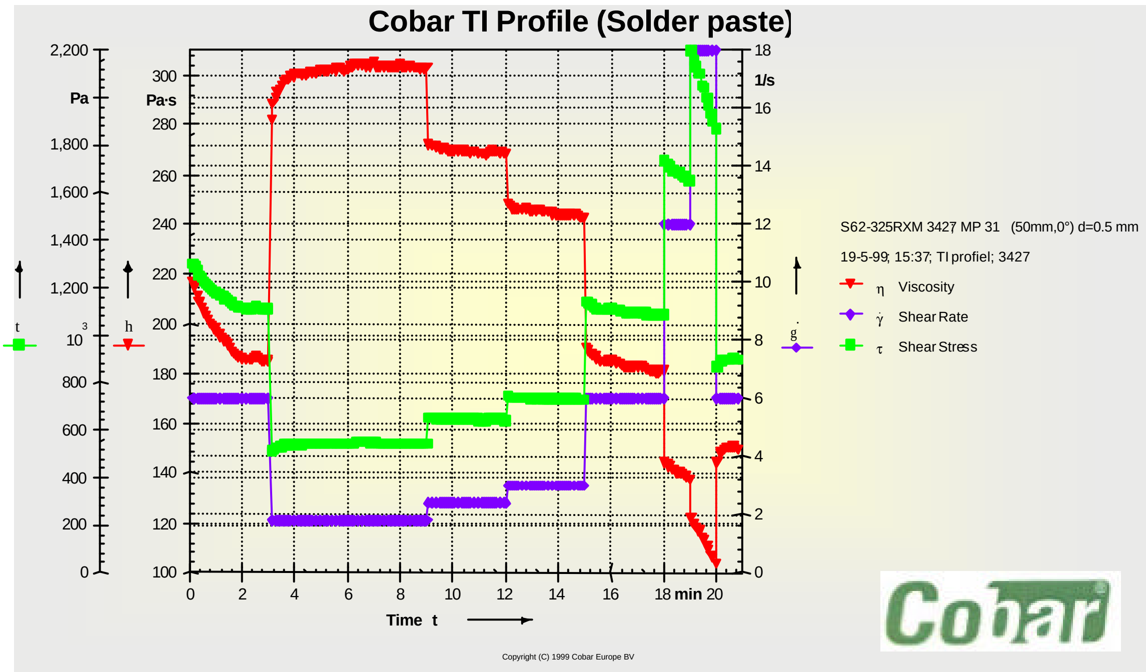

Figure 6. A so-called TI-Profile of a solder paste established with a plate-plate rheometer. Although this test provides more information than a TI-measurement with a spiral pump viscometer, its resolution is still limited.

The influence of temperature

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 a 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.

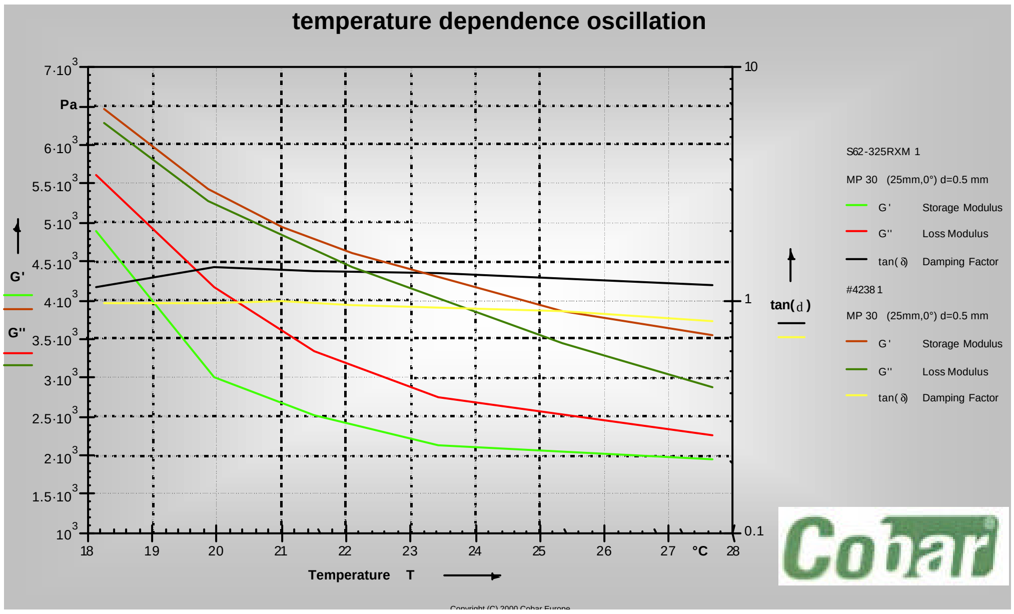

Figure 7. Measured in "a state of rest", solder paste 325-XM2 features an elastic portion that dominates throughout the entire temperature range. Moreover both G' and G" are higher than those of solder paste 325-RXM. For these solder pastes the temperature window between 22 and 26 °C seems to be optimal.

Visco-elastic properties

In terms of rheology, solder paste can be classified as a visco-elastic 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.

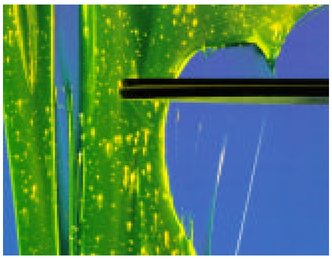

Figure 8. A gelly film slowly draining from a spatula can even be cut. This experiment shows the fascinating visco-elastic properties of a substance.

By this time it may have become clear to the reader, that the determination of a single parameter such as the viscosity of a solder paste by a simple rotational device, no longer matches the requirements of today's SMT-process.

The rheological network

The flux vehicle of a solder paste consists of functional groups such as resins, rheological and other property modifying additives. 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 the so-called rheological network (also identified as the superstructure).

The short-chained fractions in the network are only physically and relatively weakly entangled. 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 in well-formulated solder pastes.
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.

The solvent system

The stencil-life and tack time of 8 hours and longer require the selection of a solvent system with extremely low volatility at ambient temperatures. Even without this prerequisite the solder paste formulator has to tackle many problems to select the right solvent system. That is, because - as with most other functionalities in chemistry - there is no such thing as the ideal universal solvent, when it comes to solubility power for the considerable number of different species of organic materials that may form the flux vehicle.

In order to assure maximum consistency and efficiency, regardless of the usual tolerances of physical and chemical properties of the raw materials, the loss of traces of the solvent during production and application of the solder paste, the window for solubility power should be adequately large. This is important when one has to deal with all aforementioned tolerances and still provide consistent printing properties.

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 visco-elastic behavior of the solder paste.

Shear rate versus rheological properties of solder pastes

Separation and slumping occur and are measured at low to ultra-low shear rates.
The stirred consistency of solder pastes generally relates to the medium shear rate range. The printing of solder paste, in particular the cutting of the wet deposit by the squeegee, occurs in the high shear rate-range. Solder pastes are 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 have their contribution to the flow properties of a product. 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. Also 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.

Stability during storage, transport and in the print head.

After opening a new jar or other type of packaging, 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 sedimentation stability 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 sedimentation can be modeled with following equitation:

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

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 sedimentation is in the order of 3-5 10^{-4} m/s. Storage temperatures, boundary layers and interactions are neglected. They slow down the sedimentation process significantly. The storage temperature parameter can be introduced in the sedimentation test.
So far, 3 different concepts for the determination of long term stability of solder paste have been defined.

Yield Point
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 sedimentation of solder particles. The stronger the solder particles have been embedded into the rheological network of the flux, the more stable the solder paste. 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.

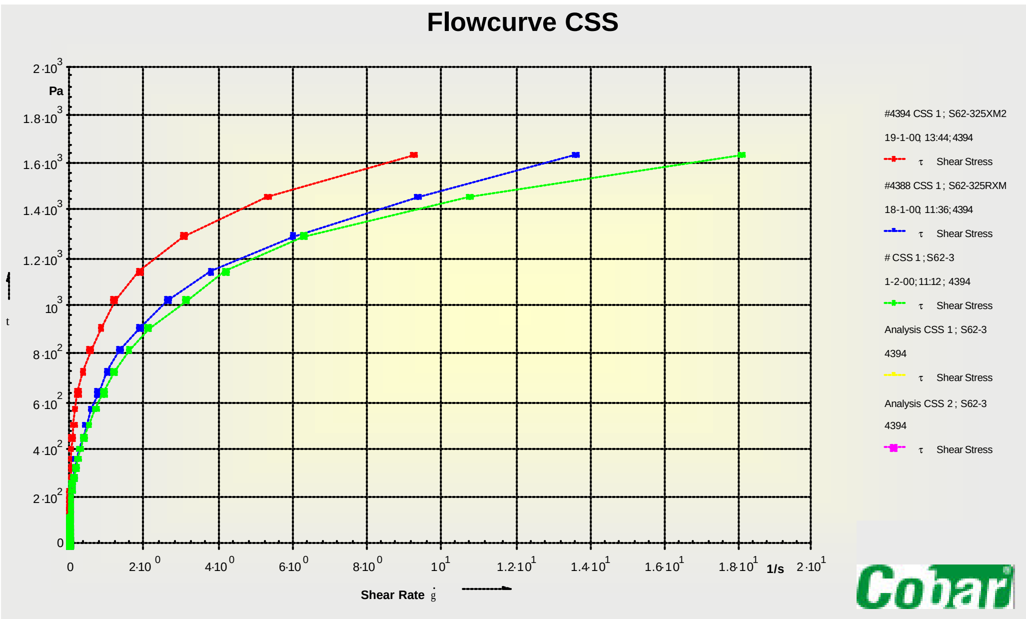

Figure 9. The solder paste type 325-XM2 has a distinctively higher yield value than 325-RXM and 325-RX, therefore it is less prone to sedimentation.

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 visco-elastic 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. 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.

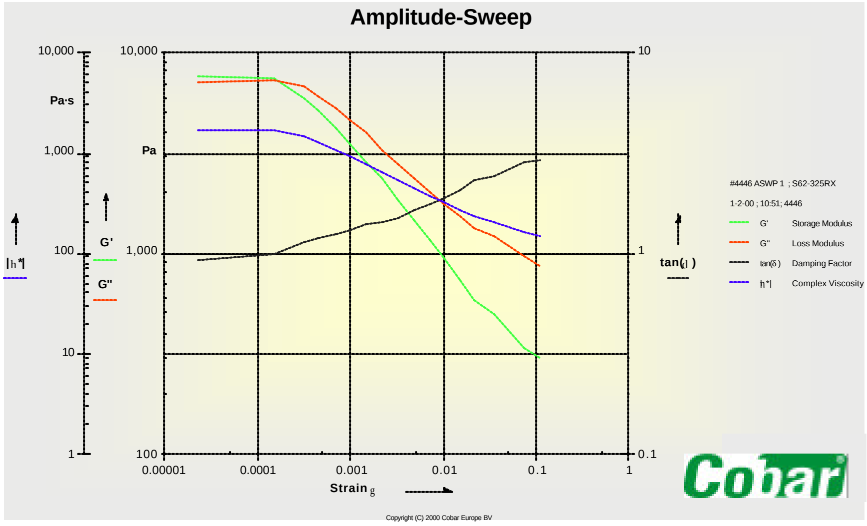

Figure 10. This test provides more information on the strenght of the rheological network. The breakdown of the elastic portion (G') past the area of 0.0001 Strain (d), provides an indication for the yield point.

Zero Viscosity

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

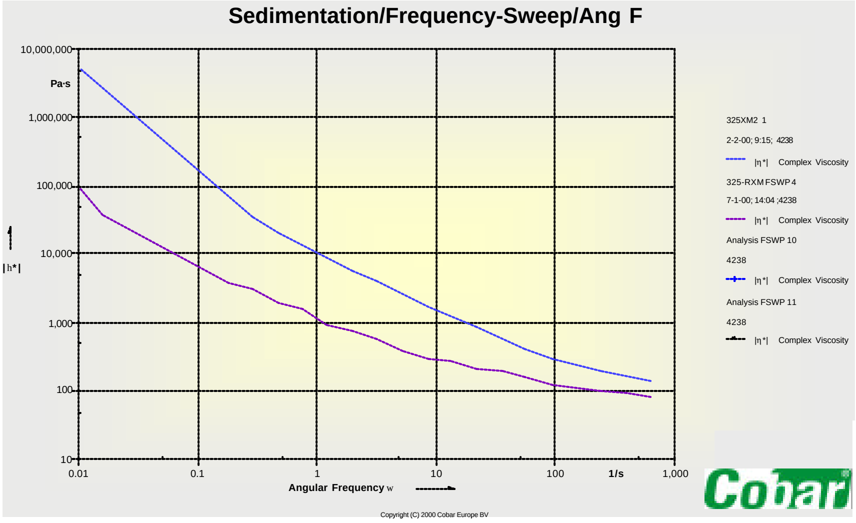

Figure 11. The solder paste type 325-XM2 has a distinctively higher zero-viscosity than 325-RXM, therefore it is less prone to sedimentation and slumping.

Printing properties

In its ideal situation 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 topside of the stencil, leaving a wet deposit on the assembly in a clean cut with a relatively flat surface and smooth contours.
The printing properties of solder pastes are defined by their rheology.

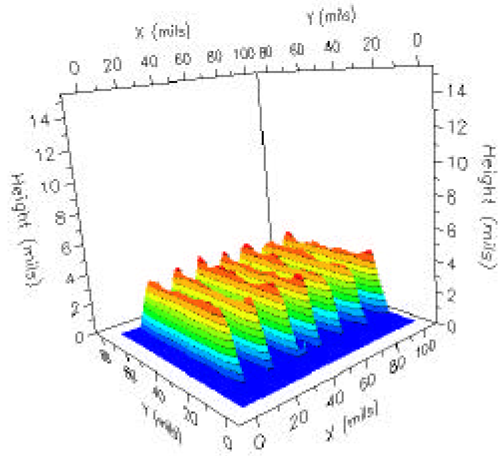

Figure 12. Print deposit of 0.4 mm QFP pads with a 3-D Measurement System. The different colours indicate the different heights of the deposit.

Whereas fine-pitch printing and the demand for printing at certain speeds in conjunction with the introduction of closed print heads have moved center-stage in the application of solder paste, it seems necessary to take a more fundamental approach towards the shear forces exposed on 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 productions print-speeds of 100 mm/second and higher have become quite common.
For thorough understanding of the printing properties of a solder paste, it should not be ignored that the filling of an aperture occurs with a so-called 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 (Fig. 12).
The speed with which the aperture in the printing process is filled, can be calculated with following formula:

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

In which:

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

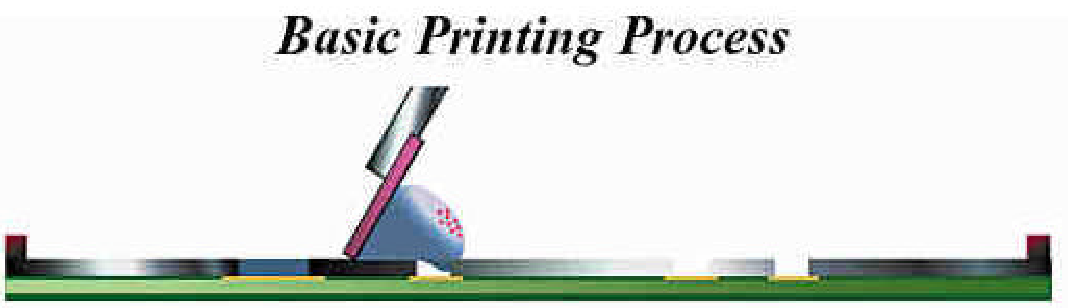

Figure 13. This picture is taken from an animation in PasteMaster®. The animation is based upon a study with high-speed video recordings of aperture filling. It clearly shows the backfill effect when the paste flows into the aperture.

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:

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

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 development of this test we, however, 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 in 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 the 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 the rheological network should occur. This means that both the G' and G''-values should increase instantly. G' should become higher than G'' as fas t 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 so-called, 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 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, 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. On the other hand, paste with a relatively high G' in the load phase may tend to irregular deposits, ski sloping and dog-ears. In the course of the work in our laboratories it has become evident that the right visco-elastic balance in a solder paste is of paramount importance.

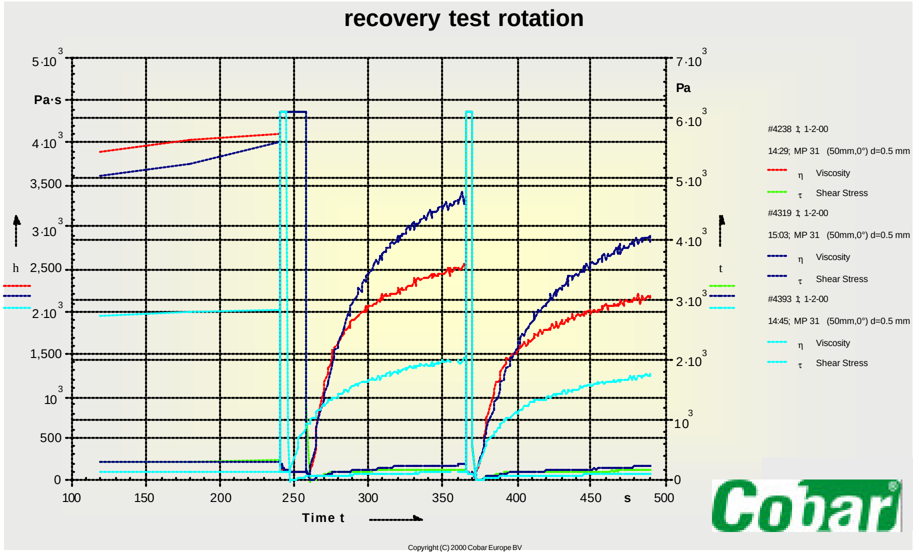

Figure 14. This is a recovery test entirely in rotation mode. In the first phase, the solder paste is measured in "a state of rest", under an ultra-low shear rate. The second phase is a load phase for 3 seconds. It simulates a print stroke at high speed. The viscosity of the paste drops down. The third 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 325-XM2 (red) recovers faster with a steeper curve to the values necessary for smooth filling of the aperture. Solder paste 325-RXM (light blue) does not recover fast enough, and the structure does not get strong enough for closed print heads. Solder paste 325-RX (dark blue) has limited printing speed. Its viscosity becomes too high in the recovery phase.

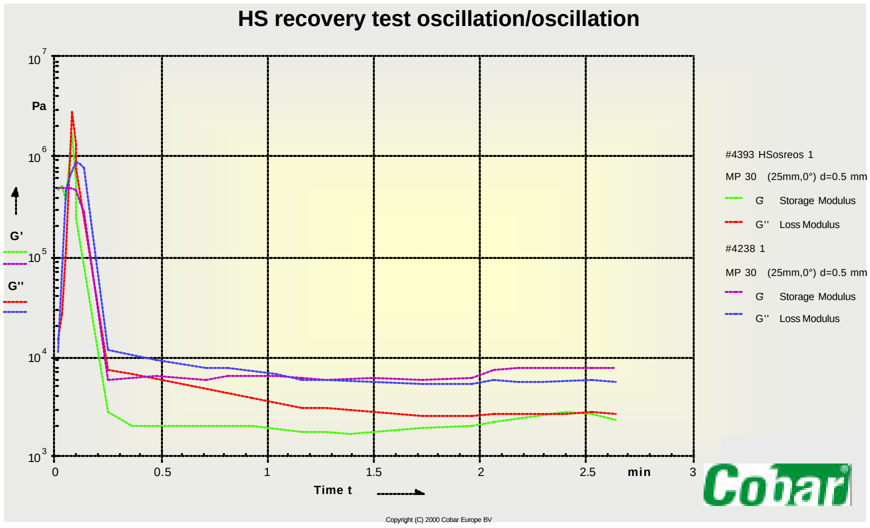

Figure 15. The first phase of this test in oscillation mode simulates a print stroke at high speed. The high frequency (>500 Hz) is realized with temperature superposition. The duration of this phase is 3 seconds. Through the powerful Peltier-element of the rheometer, the temperature is brought back 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 325-XM2 (purple: G'; blue G") flows easier during the print stroke. Both its G' and G" values remain lower as with 325-RXM (green: G'; red: G"). Moreover G" (the viscous portion) dominates clearly, so the flow properties during printing are in command. With 325-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 325-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.

Summary
Yield improvement of the printing process will cause increased attention for more advanced rheometry of solder paste. The present paper contains a number of different methods to characterize the rheology of solder paste. New methods and SPC-data will result in a technique for reliable characterization of a solder paste for future SMT-processes.

References
PasteMasterÒ, an interactive software package, a virtual engineering assistant in working with solder paste (by Cobar Europe BV).