

Rheology Testing of Solder Pastes and Conductive Adhesives used in Stencil Printing

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ABSTRACT

A novel method using video sequences to indirectly measure shear strain rate, during the printing process, is utilised to measure the viscosity of paste extracts and conductive adhesives at predetermined shear strain rates. Oscillatory tests were conducted to assess the linear visco-elastic region of solder paste, to characterise material responses at various frequencies. A better understanding of the rheological properties and the ideal parameter values will lead to the widening of the process window during stencil printing. Optimising the rheological properties and maintaining these over a wide range of operational conditions will be key to designing new printing media. The rheology of printing materials are complex and as illustrated in this report are not amenable to single viscosity measurements of the complete media. Hence, simple measurements by the user on media are unlikely to provide valuable information. Full characterisation may be possible but would be only cost effective to a few.

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
Head, Materials Centre

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1. INTRODUCTION

Solder paste is an isotropic visco-elastic fluid with time dependent behaviour. Rheologically it is highly loaded solid dispersion in a medium viscosity continuous creamy phase. The relatively large metal particles are supported against phase separation by the viscous suspending phase. The choice of solder paste for a particular application depends on several properties, including deposition technique, tack capability for components during pick and place, soldering performance and the reliability of the solder joint. The flow and deformation during printing correlate with the number of print defects, and post print behaviour of the solder paste, such as bridging and slump resistance.

The viscosity of solder paste is very dependent on:

- Metal particle content, which is typically 88-91% by weight.
- Size distribution and shape of solder particles, and the compounds that are added to make the paste thixotropic.
- Temperature and humidity are important, and at temperatures above 30°C viscosity rapidly decreases. Therefore application of solder paste should be not carried out at the temperatures above 27 °C.
- Ageing effects. The viscosity of these media does suffer from ageing effects and therefore should be stored in a temperature controlled store, i.e. in a fridge or freezer. In case of conductive adhesive the material should be stored at -40°C.

In Table 1 there is a list of materials used in this work, which consist of three solder pastes and one conductive adhesive. For rheometry tests the control stress/strain rate Bohlin CVO rheometer was used with Ø20 mm parallel plate geometry at 25°C [3].

Table 1: Materials used in rheology testing

Label	Material	Alloy composition	Metall filling wt%	Particle size [µm]
A	Solder Paste NC resin	SnPbAg	89.5	25-45
B	Solder Paste NC resin	SnPb	90.3	25-45
C	Solder Paste NC resin	SnAgCu	88.3	25-45
D	Conductive adhesive	Ag	85	<10

2. PRINTING TRIALS & VIDEO IMAGING

To describe the printing process rheologically it is important to understand the printing process stages. The stages can be separated into three stages: filling of stencil apertures, release of solder paste from stencil apertures and a transitional period in between these. The stages were studied using an under-stencil camera and printing on a glass substrate as shown in Figure 1. An important part of the optical arrangement is a pinhole in front of the lens allowing a large depth of focus. The additional light source is also required (not drawn in the diagram), to achieve satisfactory illumination for the camera.

An important feature of printing, and a necessary property of the media is that it rolls across the stencil, pushed by a blade. Printing is usually achieved in either of two ways, first by conventional squeegee blade, and secondly by an enclosed printing head. In both cases the medium rolls across the stencil. Paste is filled into apertures only in close proximity to the squeegee. In this experiment a 200 mm long metal squeegee blade was used with nominal contact angle of 60° .

Visual examination of the transport of solder paste particles through the aperture allows the determination of how solder particles and flux media flow. By timing a period starting when solder particles enter the aperture and ending when movement of particles in the aperture cease the **filling zone length** can be estimated as period multiplied by squeegee velocity. The filling zone is indicated in Figure 2.

The filling zone length is an essential parameter in modelling of solder paste flow [1]. The length of filling zone was estimated for solder paste A and listed in Table 2 for three different printing speeds. Video sequences used for the determination of filling zone are shown in Appendix A.

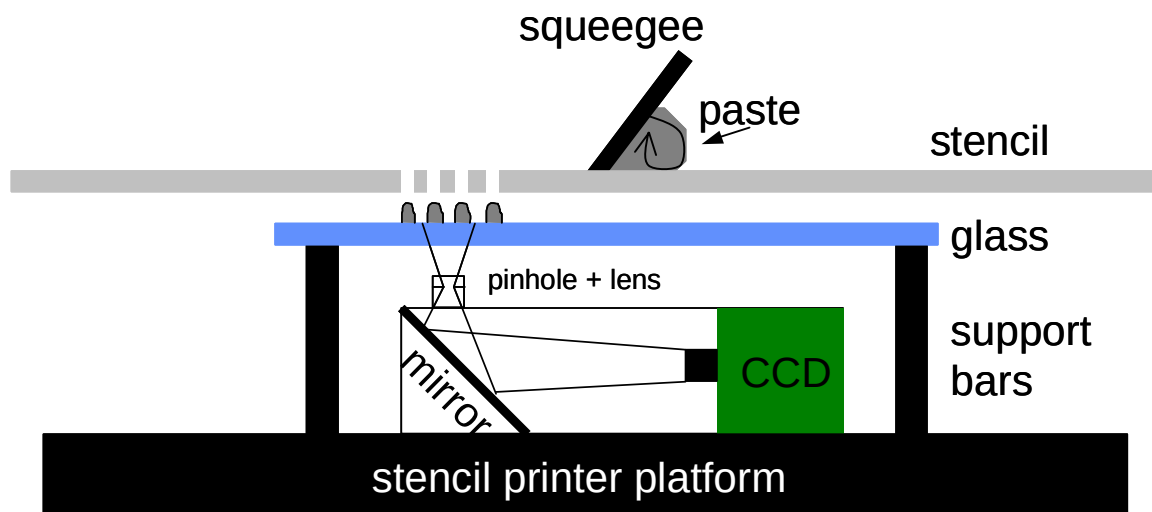


Figure 1: Schematic of under-stencil camera arrangement recording printing

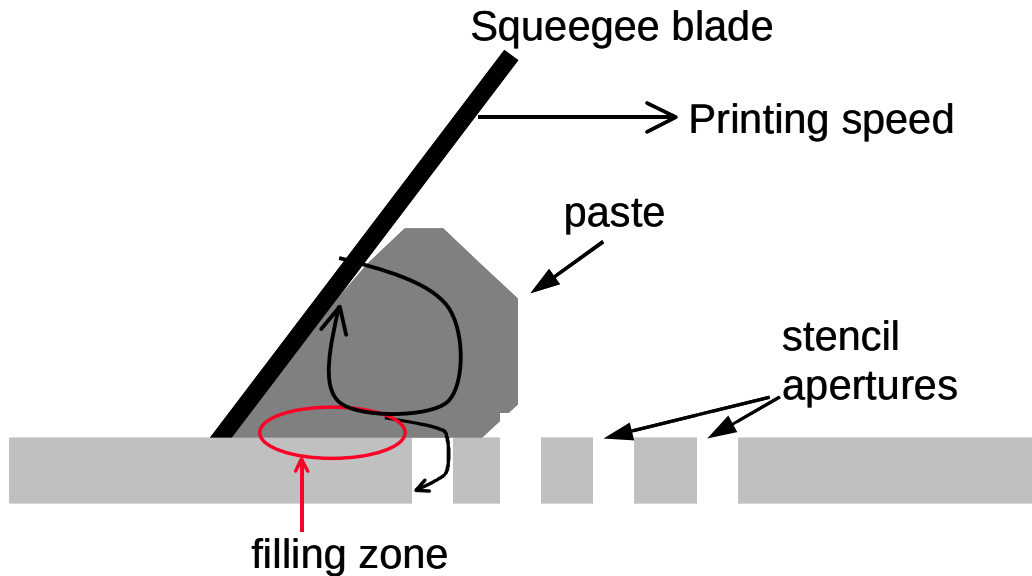


Figure 2: Identification of filling zone in front of squeegee blade

Table 2:
Estimate of filling zone length for paste A at 5kg/m blade pressure

Printing speed	Filling zone length
[mm/s]	[mm]
10	> 6.4
20	~ 6.4
30	< 4.8

One of the main tasks in characterising material rheology is to identify **the shear strain rate** of the printing process. From an examination of the flux media movement under a stencil the shear strain rate of the fluid can be determined since a cavity is formed between the stencil and a substrate surface (glass in this experiment). The size of the cavity is close to the maximum solder particle diameter as visible from trapped particles between the stencil and a substrate after an initial print. The solder paste is type 3 (25-45 μm) hence a maximum cavity of 50 μm is assumed. The material flowing inside this cavity is a solder paste liquid vehicle (solder paste liquid extract) propagating from one aperture towards other apertures. The average propagation velocity is obtained from the movement of the liquid vehicle front between individual video frames, and knowing the frame speed of the video sequence. Distance travelled by the extract wave depends on the pressure applied to a squeegee blade and on printed material. An example is shown for paste A in Figure 3. The movement of extract wave from stencil apertures is sometimes called “flux bleeding”. Using the average propagation velocity the shear strain rate can be measured. Table 3 lists propagation velocity measurements for two solder pastes differing in metal content.

Table 3:
Shear strain rate observed for two solder pastes liquid vehicles

Paste (metal loading)	Propagation velocity	Gap	Shear strain rate
	[$\mu\text{m/s}$]	[μm]	rad/s
A (89.5%)	52	50	1.04
B (90.3%)	625	50	12.5

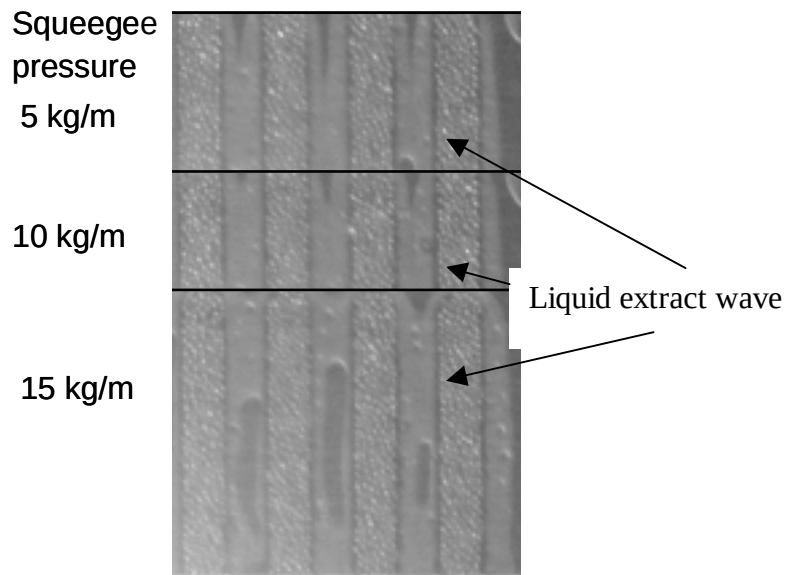


Figure 3: Flux bleeding, Paste A at 20 mm/s

If the gap between the bottom surface of stencil and printing substrate is large (as caused for example by misalignment with printing pads) solder paste will easily fill this gap and causes severe bridging.

Another defect occurs when wet solder paste bridges form in the last stage of printing process. This is effected by the solder paste release, and dominated by the quality of stencil apertures i.e. trapezoidal shape and surface roughness of the aperture inner walls. During solder paste release the substrate travels away from the stencil surface, requiring the paste to release from the aperture walls. During this process phase separation occurs and the flux vehicle separates from solder paste volume and forms an anulus around the deposit. During the printing process there is a opportunity for this anulus to be disturbed and spread, which would then cause a defect such as bridging. For example if the aperture is partly filled, then the anulus only forms on one side of the print and during the stencil separation, the remanent flux vehicle appears to readily transport a block of particles between the apertures creating a wet bridge, as seen in Figure 4 and video sequences in Appendix B. The initial cause of a partly filled aperture could be an insufficient volume of solder paste in a printing roll and/or problems with the roll sliding on the top side of stencil.

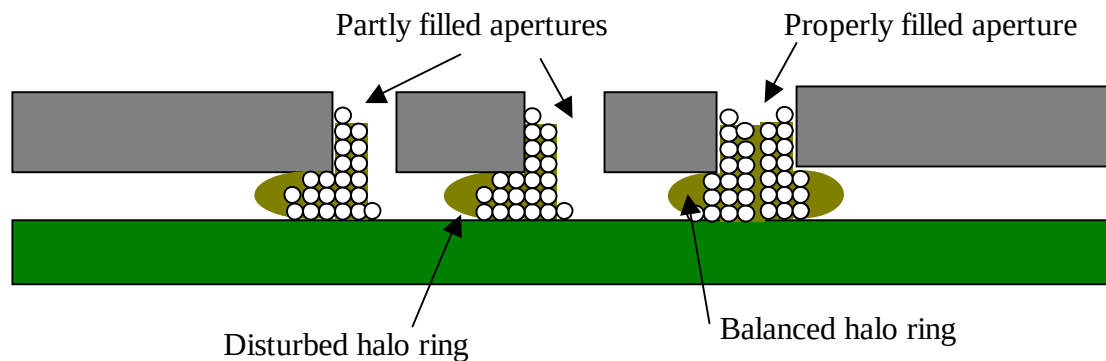


Figure 4: Formation of the halo rings

Having established the shear strain rates acting on the pastes, the appropriate rheology tests can be performed.

3. RHEOLOGICAL TESTS

3.1 Viscometry of Solder Paste

The viscometry test is a destructive test, assessing the materials response to resist deformation, when measured at controlled deformation rates. Measurement of apparent (synonym of instantaneous or dynamic) viscosity of solder paste has been performed by solder paste manufacturers as a SPC tool for evaluating product quality, typically measured on a Brookfield or Malcolm viscometer. Unfortunately apparent viscosity of solder paste does not characterize the material sufficiently. The value of viscosity is very dependent on metal loading and hence creates problems when comparing pastes. The disadvantage of these simple techniques is that solder paste and conductive adhesive products are characterised by one static number i.e. apparent viscosity at 5-6 rad/s of shear strain rate. An advantage of the parallel plate rheometer is in applying variable shear strain rate or stress and has found favour recently for more demanding applications.

A further modification to the standard approach is to look at the flux vehicle following extraction from the solder paste. The advantage is that the properties of the material, that actually fills the gap and flows between stencil and substrate, are measured directly. Another advantage is that the measurement is independent of metal loading and particle size of the solder paste.

The flux extract was removed in a centrifuge (6000 rev/min for 1 min) and measured directly. The measurement gap between the parallel plates was set to 50 μm to reflect the typical gap between the stencil and board once particles have been trapped there. The measurement was taken at 25°C. In Figure 5 there is a comparison of apparent viscosities from two paste extracts. As revealed from video sequences, the liquid front propagates in the gap at shear strain rate of 1.04 and 12.5 for pastes A and B respectively (Table 2). The apparent viscosities

for these two pastes extracts are 270 Pa.s (paste A) and 35 Pa.s (paste B). Both pastes are no-clean with the same particle sizes (Type 3, 25-45 μ m). Paste A is 89.5 % metal filled and mixed with **thicker** liquid vehicle than Paste B with 90.3% metal loaded, to compensate for lower metal loading.

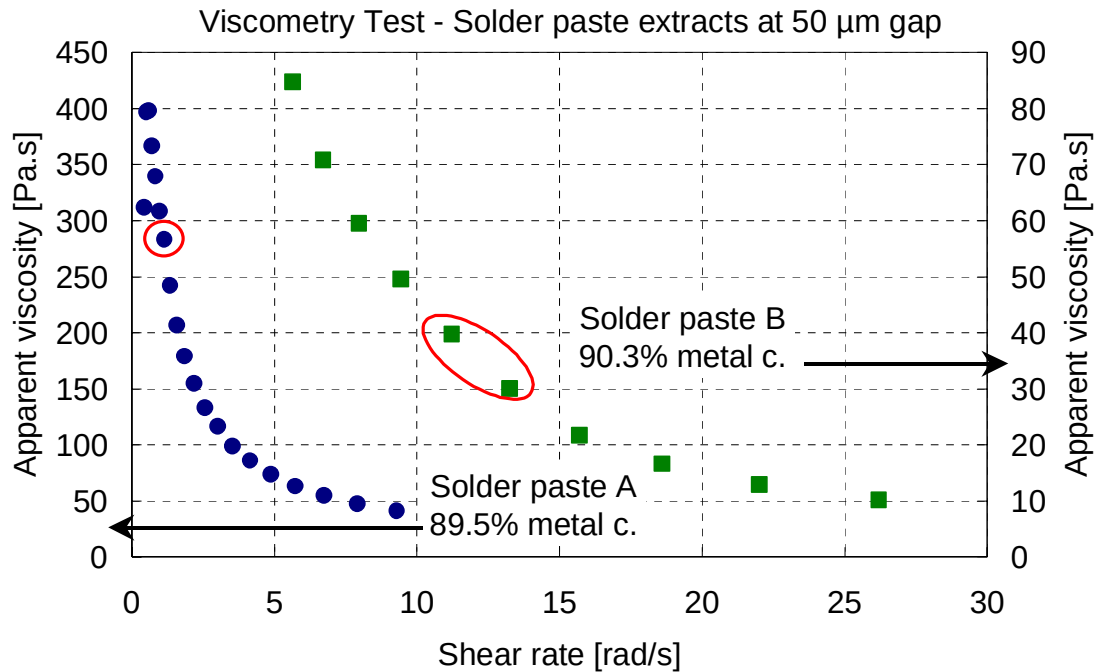


Figure 5: Viscometry test for Paste A and B extracts, with the working point of the extracts for both pastes identified in red

The viscosity dependency of paste extract C is similarly dependent on shear rate, as presented in Figure 6. This confirms that each paste should be inspected separately, since pastes with different metal-loadings work in different shear strain rate ranges. Paste C is lead-free, but this has no particular impact on viscosity.

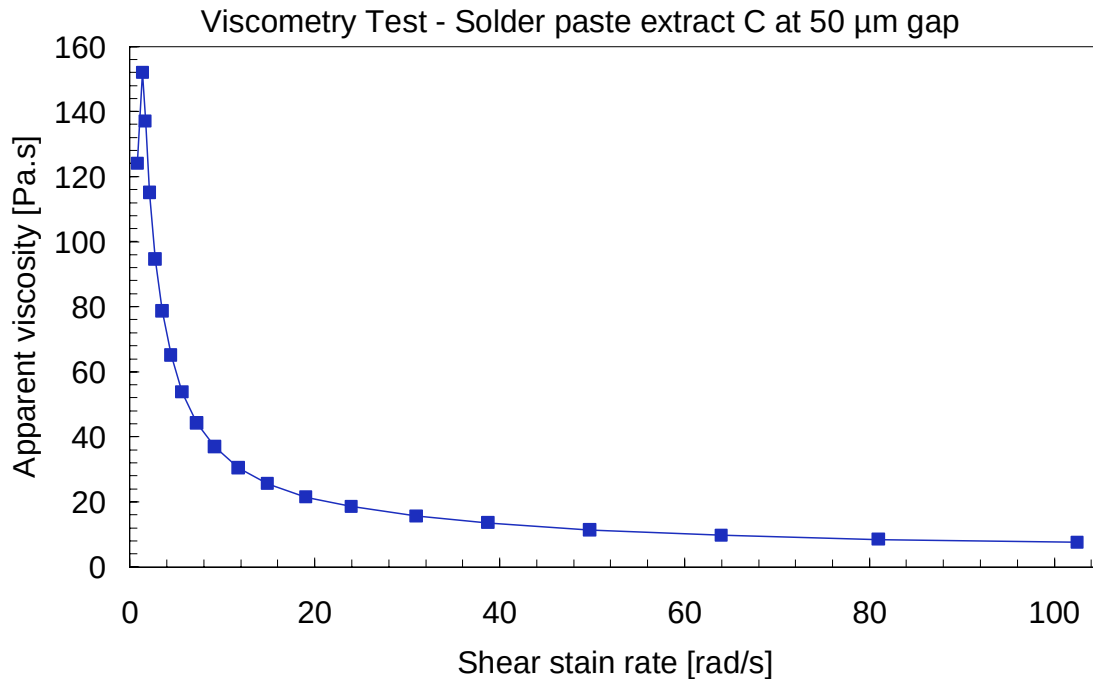


Figure 6: Illustration of viscosity for the extract of solder paste C

3.2 Viscometry of Conductive Adhesive

To evaluate viscosity of conductive adhesive the size of solid particles must be considered. As the particle size is below 1 μm in diameter, particles do not separate from the liquid vehicle and the whole system is more compact. Additionally it is very difficult, in adhesive systems, to separate resin from metal particles and filler by centrifuging. The viscosity response of a conductive adhesive is shown in Figure 7. Although the viscosity of a conductive adhesive is similar to that of solder paste extract (Figures 6 and 7), the system behaves differently in the dynamic range as shown later.

The rheology of materials in the dynamic range can be evaluated by the oscillation test.

3.3 Oscillation Test

The oscillation test is a non-destructive test for determining visco-elastic behaviour. This is achieved by modulating the applied shear stress with a sine wave. A parallel plate (spindle) is again used and the shear strain rate response is measured. The response delay, called phase lag, is a measurement of visco-elasticity. During the test the amplitude of the shear stress sine wave or frequency of oscillations, are varied.

To perform the oscillation test the appropriate shear stress must be determined. The flow curve for Paste A is presented in Figure 8, and the working point is shown by the red ellipse, which is drawn based on the data from Table 3. From the known shear strain rate, the relevant shear stress is identified; i.e. 1.04 rad/s is equivalent to the shear stress of 80-100 Pa.

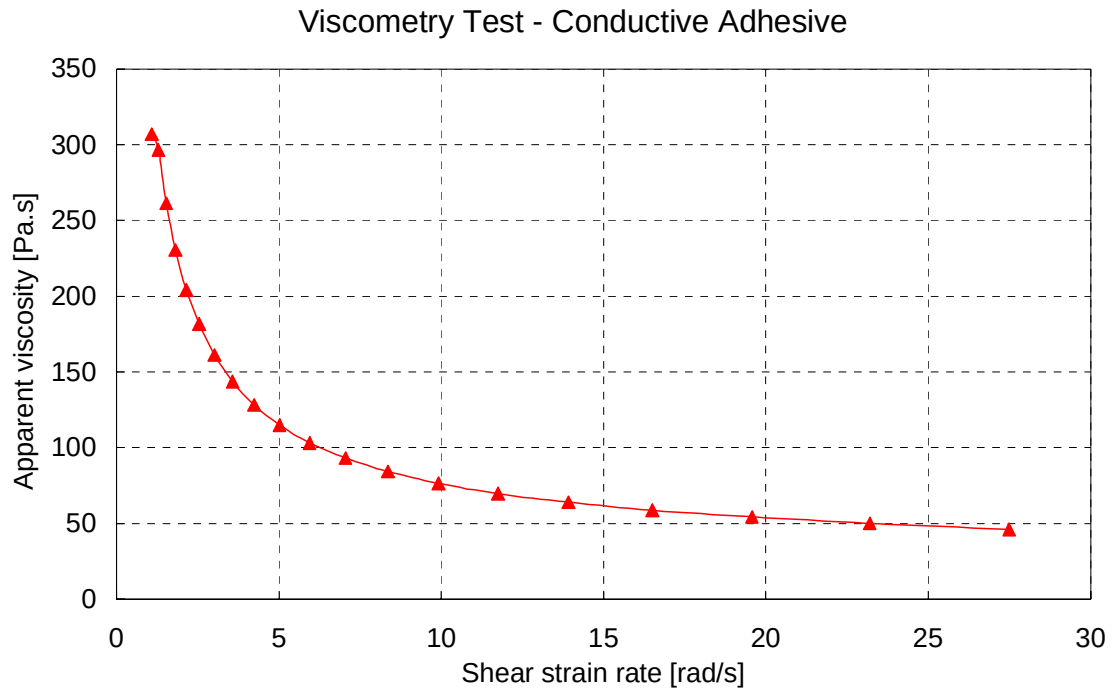


Figure 7: Viscosity of conductive adhesive as complete system of metal and filler particles mixed in resin

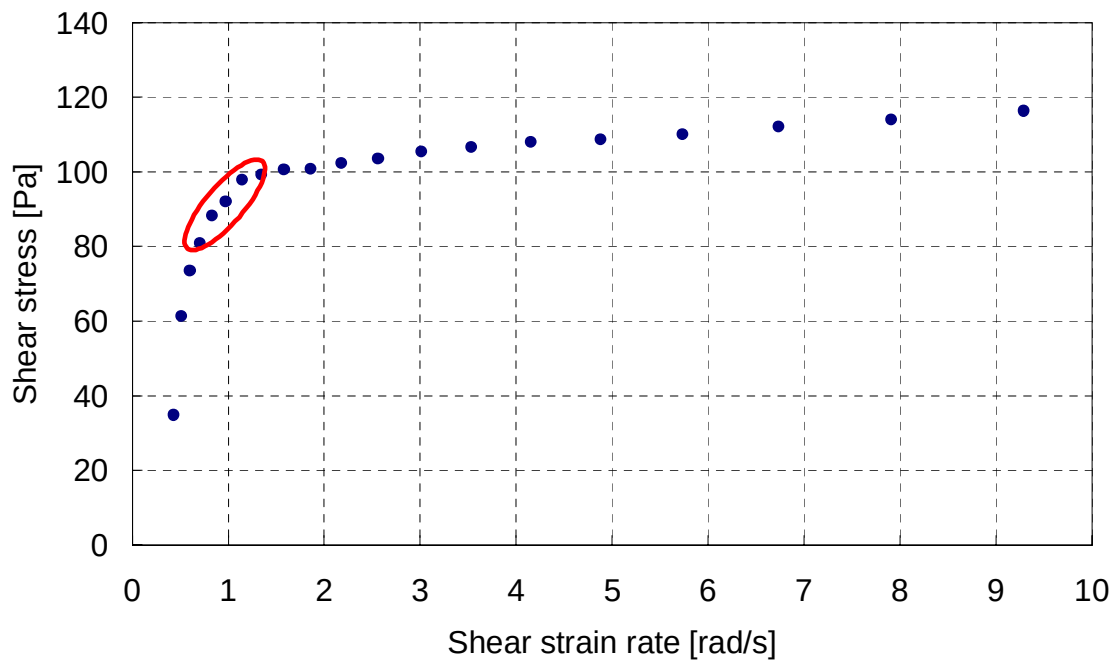


Figure 8: Flow curve, red ellipse indicates working point of shear strain rate and related stress for solder paste extract A

The effect of varying the shear stress in the oscillation test at 1Hz is shown in Figure 9. The relevant range for the paste is again highlighted, with a blue ellipse. In this range the phase lag is typically 60°, revealing the pastes are responding with a more viscous behaviour than elastic.

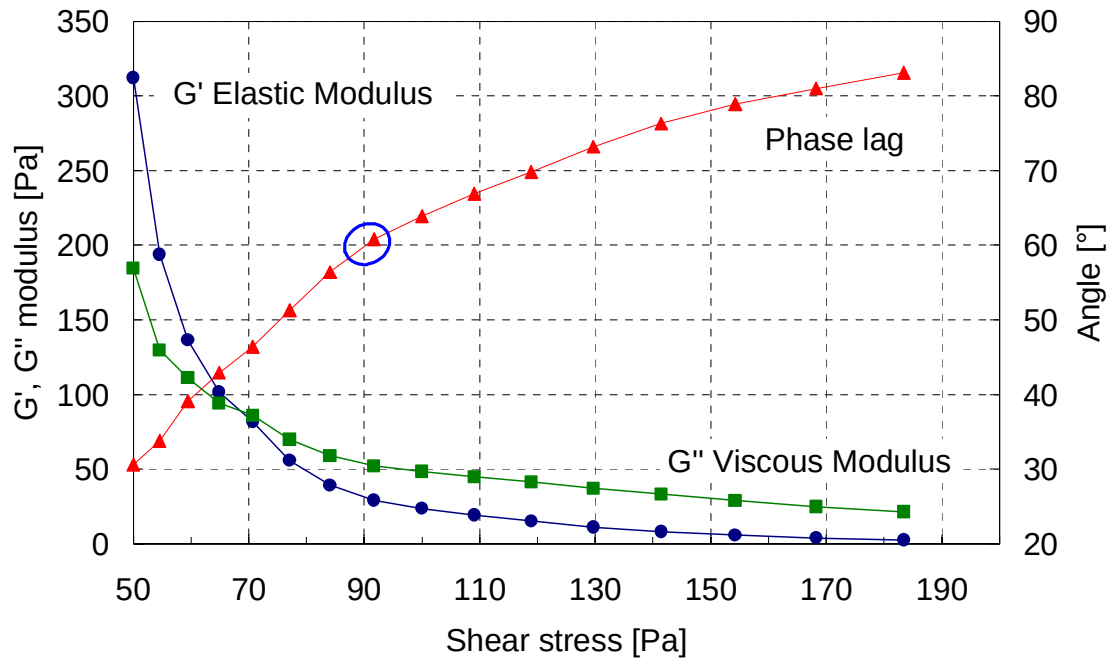


Figure 9: Oscillation test run at 1 Hz for determining the visco-elastic region [3] (paste A)

Selecting an amplitude of 90 Pa the frequency was swept over a range of 0.1-10Hz, and the results are shown in Figure 10.

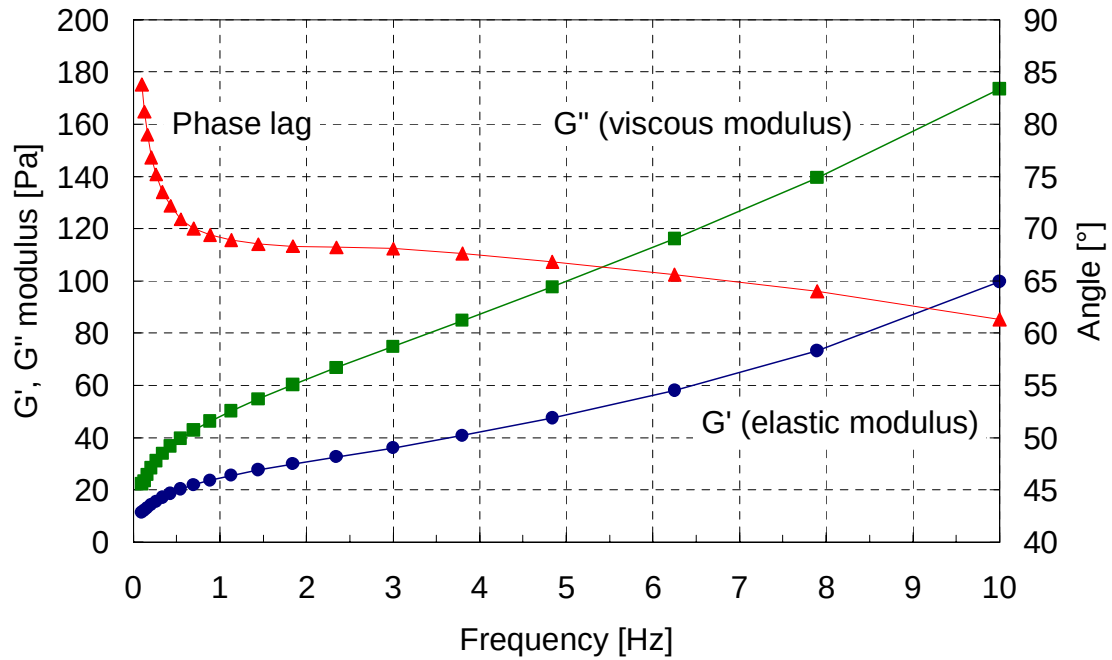


Figure 10: Oscillation test run at 90Pa shear stress of harmonic amplitude for determination of frequency response of solder paste extract (paste A)

Figure 10 reveals the frequency response of the solder paste extract A, and hence the visco-elastic behaviour of liquid vehicle can be predicted. The data show that the liquid extract becomes more elastic as the shear stress frequency is increased. The increase in elasticity as opposed to flow is equivalent to solidification of a material and ability to return input energy in a short time.

The tendency for the paste to become more elastic with frequency is interesting. It is possible to hypothesise that if horizontal vibrations were applied during stencil printing, then theoretically the print quality would improve. Since as the frequency is increased the paste becomes more elastic and the viscous properties responsible for paste retention in the aperture are reduced. Further characterisation and a wider selection of pastes would be needed to confirm this.

Conductive adhesive can be measured by the oscillation technique in a similar way as solder paste liquid extract. The only difference is that sample of conductive adhesive is not centrifuged and is tested complete. Figures 11 and 12 show an illustration of flow curves and oscillation tests for conductive adhesive. Closer analysis was not possible as the gap between stencil and substrate during the printing process is unknown.

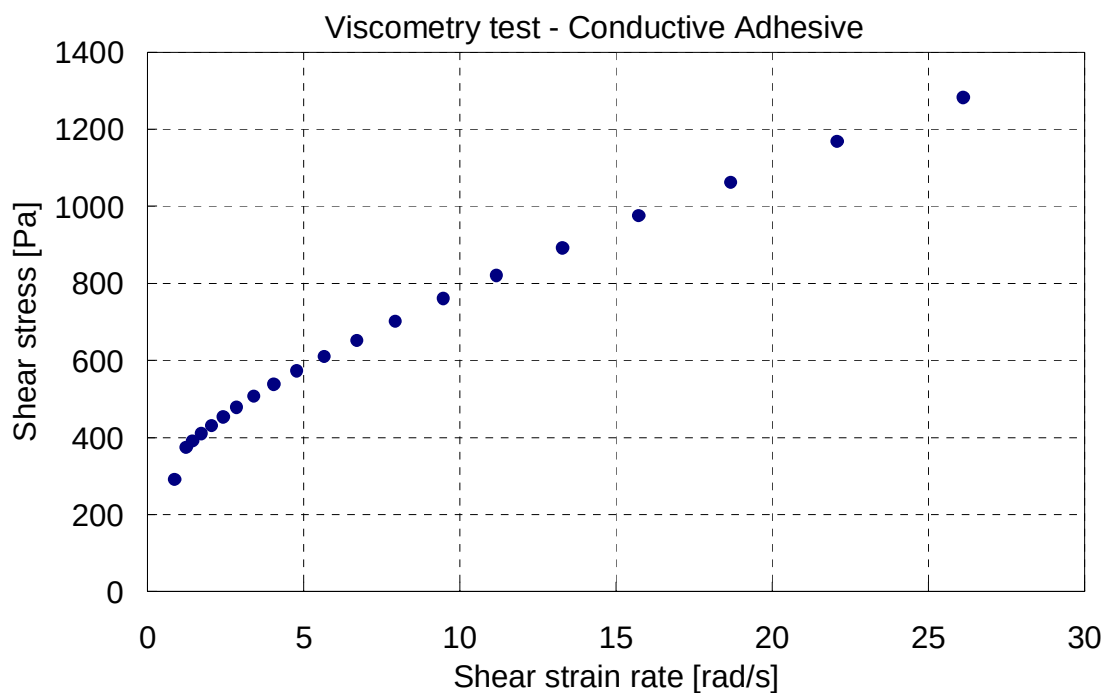


Figure 12 Flow curves for conductive adhesive (3 samples measured)

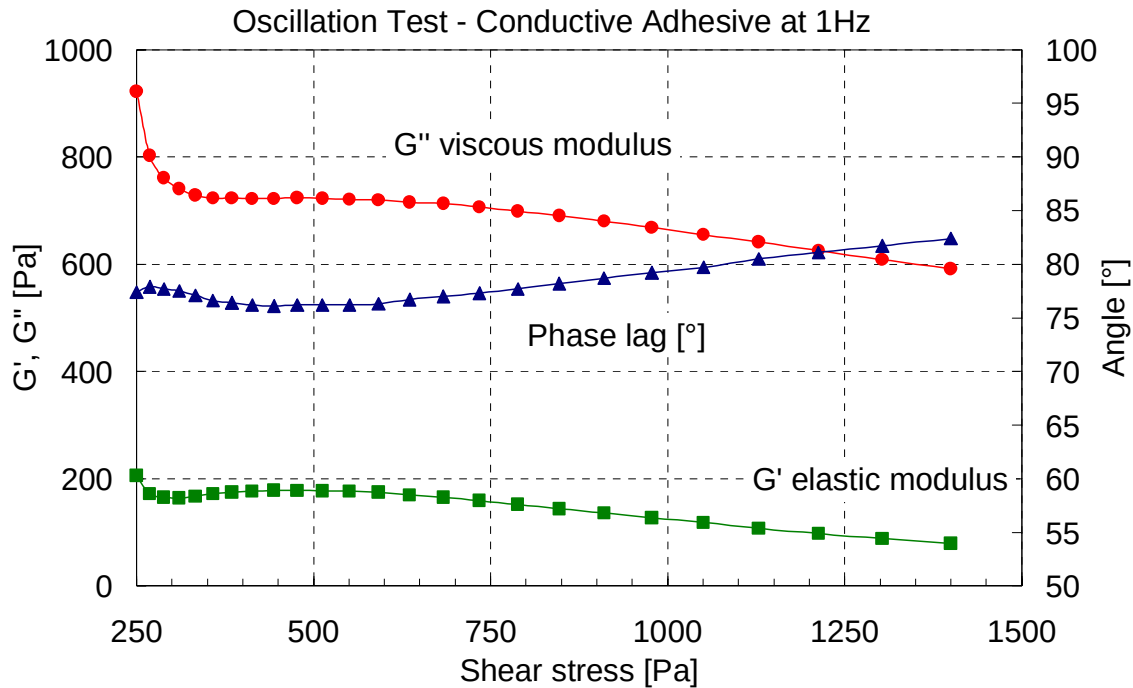


Figure 13 Oscillation test of conductive adhesive

The phase angle for the adhesive is higher, as might be expected, and interestingly doesn't show as strong response to shear rate as the solder paste.

4. DISCUSSION

Today's printing media are specifically developed to have a wide process window, hence machine parameters are not critical. The print quality then mainly depends on stencil quality, with the proviso that the application requirements are satisfied (temperature, humidity, medium expiry date). In the past solder paste consisted of metal particles mixed with resin flux and alcohol solvents. Application of such a simple mixture was very machine dependent and variables such as squeegee printing speed, pressure and separation speed had to be recorded and controlled.

The main requirement in the rheology testing of solder pastes and conductive adhesives used in stencil printing is to find a rheology measure, which can be correlated to print defects and solder paste tack [8]. This has shown to be unsuccessful, because of the complex nature of solder pastes and conductive adhesives. Product developments no longer allow the simple identification of a rheological parameter that correlates with paste performance. The rheology remains approximately constant over a wide range of conditions and the impact of rheology modifiers or loss of solvents are not readily seen with a rheometer. The difficulty in correlating print parameters, such as deposit volume and height with rheology parameters, has been shown to be similar to that seen before [4]. The clearest way to demonstrate solder paste or conductive paste is fit for printing is to evaluate it on the stencil printer.

In recent years solder paste development has advanced with introduction of time-dependent rheology modifiers into solder pastes, which superbly improve printing quality. To describe these systems in terms of static rheological variables such as viscosity is insufficient, but the use of “dynamic characterisation” with the oscillatory method may be a useful characterisation tool.

Using this approach a measurement test method that characterises the visco-elastic properties of solder paste extracts can be used. Before this method can be utilized the proper shear strain rate has to be identified. By recording video sequences printing process steps can be identified and measured in terms of flow characteristics of a printed media. One of the main phenomena is separation of the liquid vehicle from solder paste volume during aperture filling. Propagation velocity of this fluid was linked to the shear strain rate. Once the shear strain rate was identified from these images the viscometry tests can be performed, and allowing the ranking of solder paste liquid vehicles by its apparent viscosity. Liquid vehicles were separated from solid particles by centrifuging. Hence it was shown that high metal loaded solder paste are mixed with thinner flux system than solder paste with low metal content.

5. CONCLUSIONS

- Today current solder pastes have advanced flux vehicle systems that deliver a wide process window. This characteristic does not lend them readily to rheology testing.
- Static measurement of viscosity does not characterize solder paste in its printing behaviour and therefore dynamic properties must be tested by oscillation tests.
- However the visco-elastic properties are of interest and a method is presented here. Dynamic tests describe visco-elastic properties of a material at working shear stress and show dramatic increase in elasticity when exposes to oscillations above 0.1 Hz.
- An increase in elasticity means decrease in flow of liquid vehicle. This indicates that horizontal vibrations of a stencil during a printing process could temporarily “freeze” deposits to elastic solids and therefore improves printing quality.
- The use of video to characterise the flux vehicle bleed is an essential part of the characterisation, and is required to estimate the relevant shear stress.
- Conductive adhesives, being mixed from much finer particles, does not show phase separation and hence the medium has to be measured complete. When measured over wide range of shear strain rate this medium shows much higher apparent viscosity than liquid vehicle from solder paste.

6. ACKNOWLEDGEMENTS

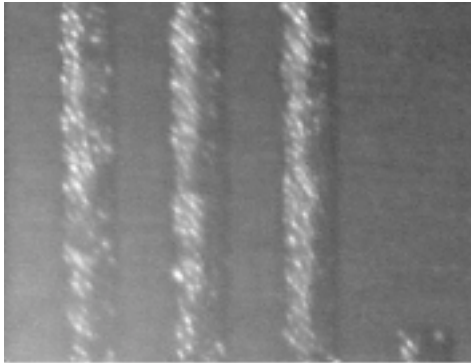
The authors are grateful for the support of the DTI as part of their Measurement for the Processability of Materials (MPM) programme, DEK Printing Machines, Alpha Metals and Multicore Solders for their support. The authors are also grateful to Martin Wickham for many useful discussions through out the work.

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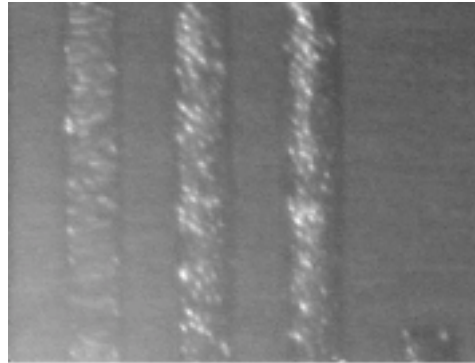
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8. APPENDIX A

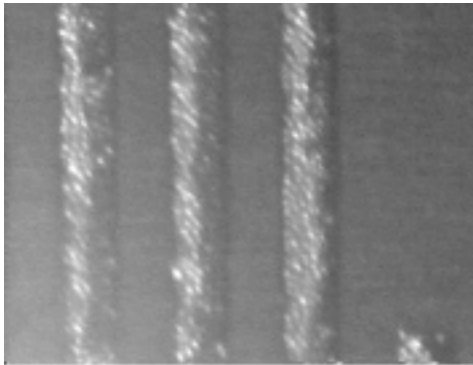
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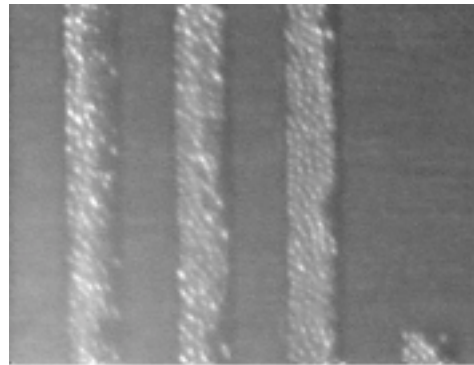
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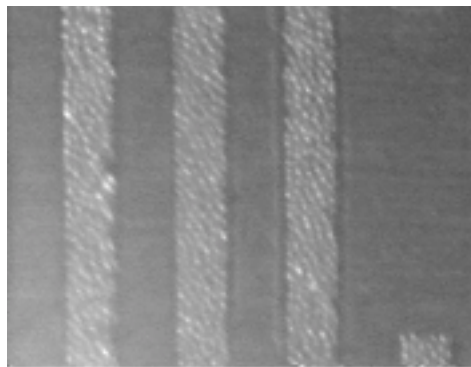
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480 ms

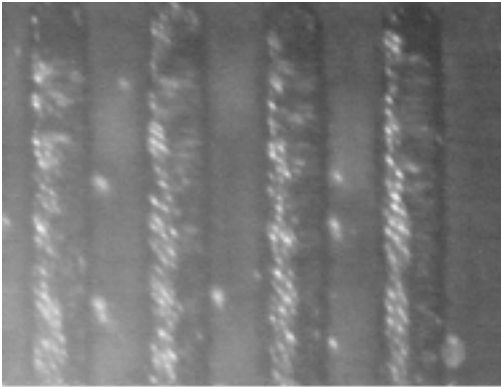


640 ms

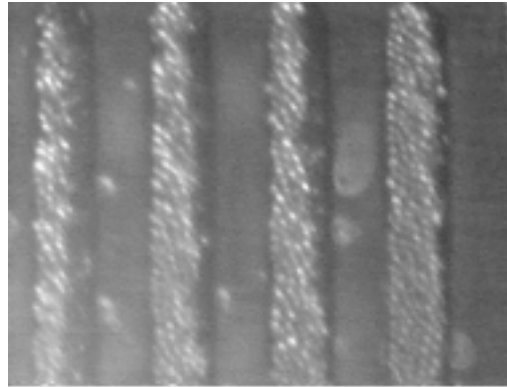


Aperture filling at 10mm/s, 3 kg for paste A, squeegee travels > 6.4mm

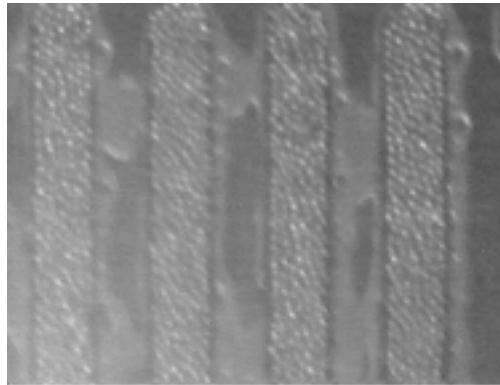
0 ms



160 ms

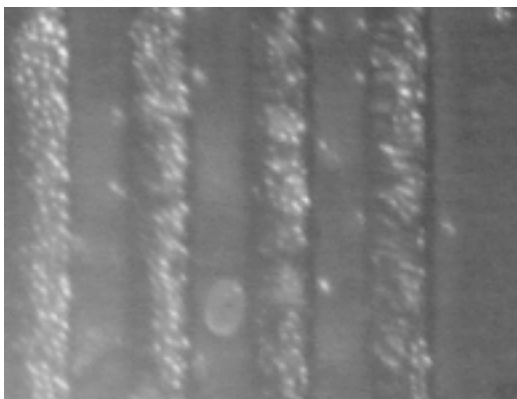


320 ms

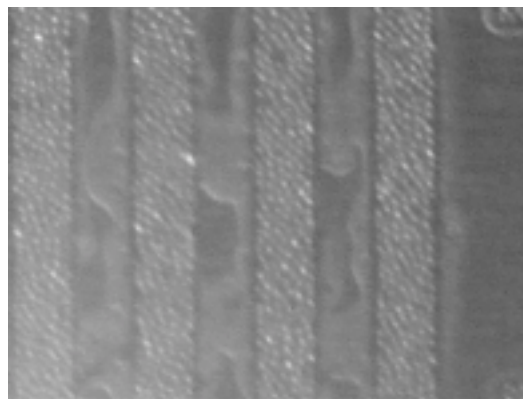


Aperture filling at 20mm/s, 3 kg for paste A, squeegee travels $> 6.4\text{mm}$

0 ms



160 ms



Aperture filling at 30mm/s, 3 kg for paste A, squeegee travels $< 4.8\text{ mm}$

9. APPENDIX B

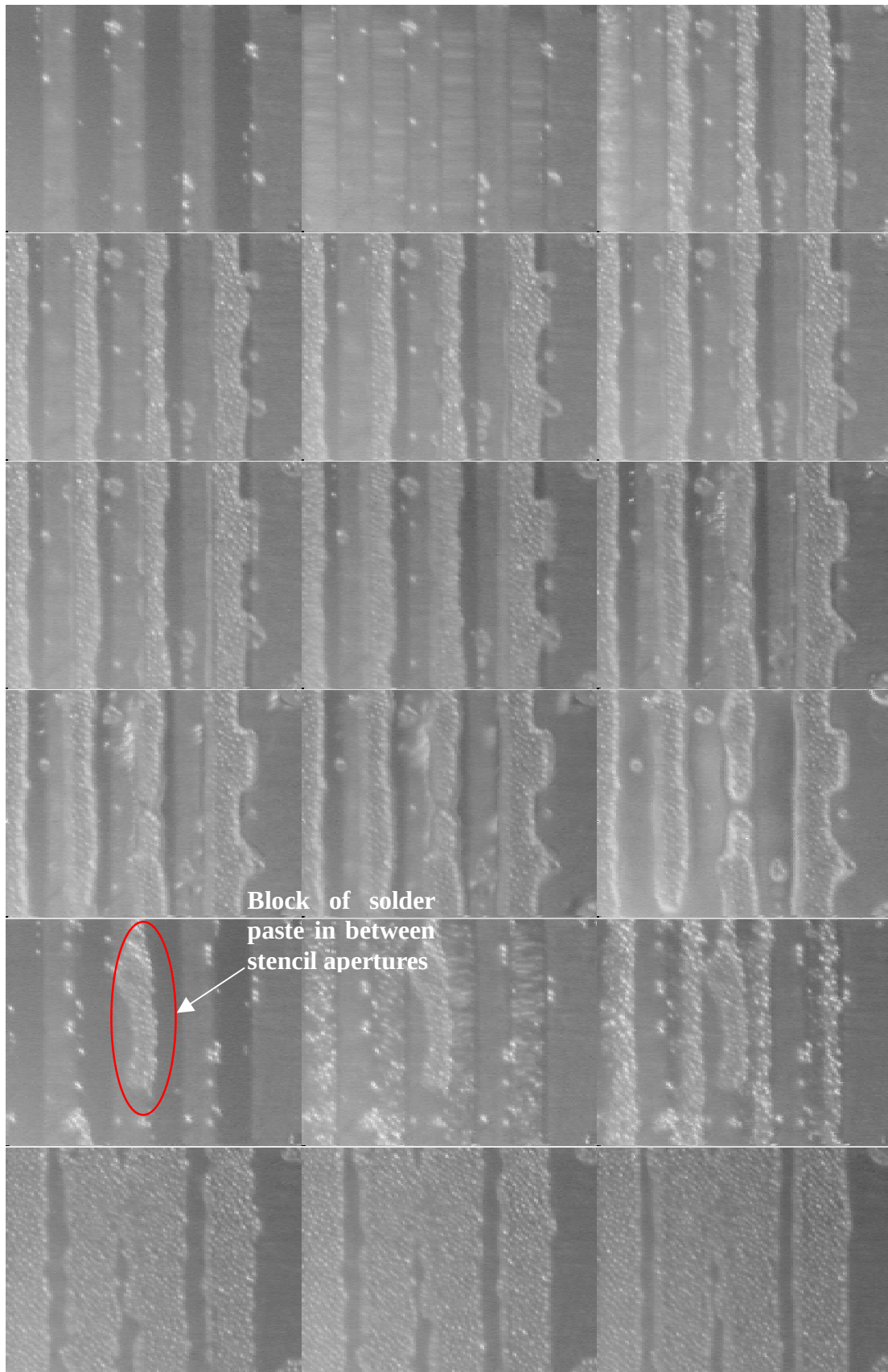


Figure 4 Video sequences of two consequent prints showing wet bridge formation (Paste A)