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Modeling the effects of temperature on the rheology of solder pastes and flux system

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Solder paste is one of the most important process materials today in surface mount technology. Stencil printing of solder paste onto PCBs constitutes an important stage in the reflow soldering of surface mount devices. A high proportion of the solder-related defects can be attributed to the stencil printing process. This is likely to continue with the trend toward miniaturization and the implementation of die-size packages. To achieve repeatable solder deposits from board-to-board and pad-to-pad requires an understanding of the paste rheology. One of the key factors that influences solder paste rheology is temperature. A change in temperature will cause the viscosity of the solder paste to change. This change could be ambient or from the stencil printing process itself. This is likely to impact on the performance of the solder paste. In this paper, we present the effect of temperature on the rheological properties of solder paste and the flux vehicle system. Current models show a single variable dependence of viscosity with temperature. The model presented here incorporates shear rates and can be used for any solder paste or non-Newtonian material. The effects of temperature on solder paste flux medium, particle size and distribution, and metal alloy content are also presented.

1. Introduction

Solder paste is one of the most important process materials today in surface mount technology. An ideal solder paste will increase production yields while decreasing the amount of defects associated with reflow. The performance of a paste, however, depends on a variety of factors, including storage, how easily and accurately it can be deposited (printability), flow characteristics (rheology), adhesion strength of components during pick and place (tackiness), ability to avoid reflow defects and reliability (post reflow) [1].

Solder paste is at the core of surface mount technology (SMT). It can be defined as a homogenous and kinetically stable mixture of solder alloy powder, flux, and vehicles [2]. The flux vehicle is a combination of solvents, thickeners, binders and fluxing agents. Solder paste is used as the joining medium between the components and the substrate, by providing both electrical and thermal conductivity. With these principal merits, it is a viable interconnecting material applicable to electronics assemblies. The successful assembly of a component onto a substrate with no defects is crucial for the reliability, stability, and functionality of the device.

One of the processes that require the use of solder paste is stencil printing. Stencil printing is one of the most attractive methods of depositing solder paste onto PCBs. A consistent print from board-to-board and pad-to-pad is dependent on some properties of the paste. There are many factors that affect solder paste technology. The performance and characteristics of the solder paste depends on the physical, chemical and rheological properties of the flux/vehicle system. Many factors also affect solder paste rheology. These include particle size and distribution, flux, metal content, storage and temperature. During the printing process, the temperature of the environment must be monitored as any variation will affect the rheological properties of the paste and hence print performance [3].

In this paper, we present the effect of temperature on the viscosity of a range of solder pastes. Some of the solder pastes differ in particle size, flux medium, metal alloy (% of tin), and metal loading. There is also a comparison between a flux vehicle system and its corresponding solder paste. These permutations will enable proper analysis of the sensitivity of solder paste viscosity to temperature.

2. Temperature effect on solder paste rheology

2.1. Solder paste rheology

Solder paste is a homogeneous, stable suspension of solder powder particles suspended in a flux binder. The shape and size of the metal particles in combination with the rheological properties of the binder are tailored to match the application method of the paste onto the PCB. A simple representation of the constituents of solder paste is shown in Fig. 1. The binder contains flux and other substances that determine its flow properties. It must keep the particles evenly dispersed within the

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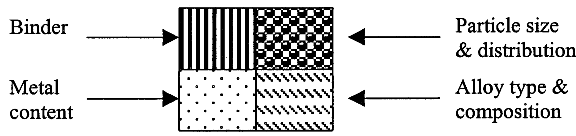

Figure 1 Constitutive elements of solder paste: a basic representation.

medium at room temperature. The paste must maintain its consistency during application and the binder must not inhibit the action of the flux during reflow soldering. Within the binder are: (i) the dissolved flux in (ii) the solvent with (iii) an activator mixed with (iv) thickeners and lubricants that determine the rheological properties of the paste. Particle size and distribution can vary depending on the application (i.e., QFP, BGA, flip chip, etc.). Spherical-shaped particles are desired. The powder material is normally an alloy with a varying composition of elements, e.g., tin (Sn), lead (Pb), silver (Ag), etc., and percentages. In eutectic solder paste for example, the alloy contains 63 % tin and the rest is made up of lead. The metal content is the percentage of the mass of the powder to the wet solder paste. This can vary but is typically 88–91% (45–55% volume fraction). The different metal contents affect how easily the paste can be printed or dispensed with a syringe, and also its slump properties. Solder paste formulation is usually regarded by paste manufacturers as proprietary information.

The primary driving forces underlying the rheology of solder paste includes both kinetic and thermodynamic contributions which also covers thermal motion [2]. The difficulty in predicting solder paste rheology is apparent due to the lack of knowledge of the structure and the nature of forces exerted by molecules/particles.

Resin is the base of most conventional systems. It is dissolved in a rosin-soluble solvent whose composition partly determines the viscosity of the paste. One or more surface agents are normally added in the system to ensure proper dispersion of the solder particles and provide adequate wetting of the substrates. To acquire the desired rheological performance, additives can be added.

2.2. Temperature effects on rheology: background

The performance characteristics of a paste can also be affected by temperature. It is crucial that the temperature be controlled when measuring rheological parameters [3]. Temperature extremes in storage and use should be controlled. Solder pastes can vary widely in formulation, thus producing different behavior with respect to temperature change. For this reason, paste response to temperature fluctuation is very important.

In homogeneous Newtonian and non-Newtonian fluids, the influence of temperature on viscosity is the Arrhenius (Equation 1) form. When the temperature is raised, two competing effects occur [4]. One is the fall in viscosity of the continuous phase, obeying the Arrhenius equation [5, 6]. The other is that, as the continuous phase becomes more fluid, the dispersed solder powder acquires more energy, the rate of structure formation increases. The subsequent tendency for viscosity to rise means that the fall in viscosity due to the drop in the continuous phase viscosity may be more than compensated for by an increase in suspension viscosity. In other words, the possibility exists for the viscosity to rise, remain constant, or fall with increasing temperature.

$$\eta = \eta(T) = A \exp\left[\frac{E_{\mathrm{vis}}}{RT}\right] \tag{1}$$

In Equation 1, R is the molar gas constant (8.314 J K^{-1} mol^{-1}), A is the pre-exponential constant, T the absolute temperature (K), and E_{vis} the activation energy for viscous flow. Equation 1 is convenient because it contains only two unknown parameters, A and E_{vis}. The magnitude of E_{vis} will thus determine the sensitivity of the solder paste to temperature. Providing a reasonable fit for a variety of data, it has been widely used at elevated temperatures to express the viscosity–temperature behavior of materials such as polymer melts [7]. The definition of E_{vis} implies there is a barrier against viscous flow in solder paste. It has been concluded that an activation energy is not necessary and can be derived from curve shifts [8]. Meanwhile, the exact significance of the pre-exponential parameter is open to debate [4].

Another equation that can be used is the William–Landel–Ferry (WLF) relationship, expressed as [9, 10]:

$$\log(a_T) = c_1(T - T_r)/(c_2 + T - T_r) \tag{2}$$

Here T and T_r are the absolute and reference temperature respectively, $c_1(i = 1, 2)$ are constants and a_T is the shift factor [11] defined by Equation 3, where the subscripts r refers to properties at the reference state; η is the absolute viscosity while ρ is the density. This approach has successfully been used with polymers [12].

$$a_T = \eta(\dot{\gamma}, T)T_r\rho_r/\eta(\dot{\gamma}_r, T)T\rho \tag{3}$$

It must be remembered that since solder paste is a non-Newtonian fluid, its viscosity is not only a function of temperature (as shown in Equation 1) but also a function of shear rate. Providing data for one without the other is meaningless. There are many models relating the measured viscosity at different shear rates described by any of the following Equations:

- Cross Model: $$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + K_1\dot{\gamma}^{n_1}} \tag{4}$$
- Sisko Model: $$\eta = \eta_\infty + K_2\dot{\gamma}^{n_2} \tag{5}$$
- Power Law Model: $$\eta = K_3\dot{\gamma}^{n_3} \tag{6}$$

These simple viscosity models can be used to estimate the shear thinning property of non-Newtonian materials. They provide better estimates at different sections of a viscosity versus shear rate diagram [13]. η_0 and η_∞ described in Equations 4 and 5 are referred to as the asymptotic values of the viscosity at very low and high shear rates respectively. The other parameters, K_i and $n_i(i = 1 - 3)$ are the consistency and power law indices, respectively. It is important to note that care must be taken regarding which model to use, as they are basically empirical in nature and arise from curve fitting.

3. Experimental design

3.1. Instrument

Rheological experiments were conducted on a Reologica controlled-stress rheometer with a 40 mm diameter parallel plate geometry and sample thickness of 0.5 mm [14]. Viscosity measurements were carried out at different shear rates and temperature (10–30 °C). Although the temperature range is limited, it is sufficient to provide trends in rheological dependence on temperature.

3.2. Test materials

The samples investigated are shown in Table I. These include some development pastes for flip chip applications and also a commercially available one. The flux medium of the selected samples covers the range widely used in the industry. Solder paste P4 is commercially available for ultra-fine pitch printing while P1–P3 are still development products for flip chip applications [15]. F4 is the flux medium of sample P4.

From Table I, the following similarities are noted with the following parameters different:

- Particle size of samples P1–P3,
- Solder paste and its flux vehicle (P4 and F4).

4. Results and analysis

The results presented here are subdivided into sections in order to investigate the effects of temperature on a range of solder pastes different in particle size and distribution, flux type, metal and alloy content. Since the viscosity is a function of both shear rate and temperature, the subsections below investigate the effects on viscosity with one parameter (i.e., shear rate or temperature) fixed. In the final subsection, a model equation is presented relating the viscosity with shear rate and temperature for each solder paste.

The zero and infinite shear viscosity (η_0 and η_∞, respectively) have not been used because they are simply not shear rate dependent. Equations derived with these parameters are simple and merely a replica of the Arrhenius Equation 1. By not using the zero and infinite shear rate viscosity, a detailed analysis of the complex nature of solder paste is presented.

4.1. Viscosity as a function of shear rate at constant temperature

The viscosities measured at different shear rates and constant temperature are shown in the flow curves of Fig. 2. To model the dependence of viscosity on shear

TABLE I Range of solder paste samples investigated

Label	Sample	Particle size (μm)	Flux medium	Metal content (%)
P1	Paste	10–25	No clean	89
P2	Paste	10–25	Rosin mildly activated	89
P3	Paste	10–25	Water washable	89
P4	Paste	20–45	No clean	90
F4	Flux of P4	–	No clean	–

Temperature: o @ 10°C + @ 20°C × @ 30°C

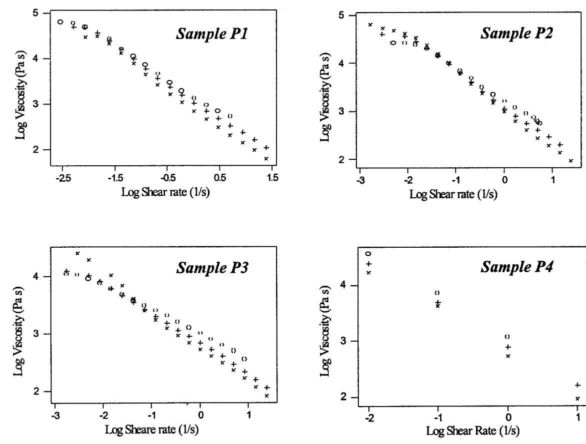

Figure 2 Flow curves for samples P1–P4 at different temperature.

rates, Equations 4 to 6 can be used. This gives a generic Equation of the form.

$$\eta = \eta(\dot{\gamma}) \tag{7}$$

At constant temperature, the non-Newtonian nature of solder paste is clearly seen. Applying the power law model (Equation 6) on the result presented in Fig. 2, the slopes for each curve at 10, 20, and 30 °C are estimated slope $= n_3$). For each solder paste, the absolute value of the slope of each curve increases as the temperature rises. This is shown in Fig. 3 for samples P2 and P3. The consistency index K_3, decreases with increasing temperature.

4.2. Viscosity as a function of temperature at constant shear rate

Comparison will be made to investigate by how much the viscosity is affected from solder pastes that differ in one parameter, i.e., flux type. Applying the natural log on both sides of the Arrhenius Equation 1, Equation 8 was obtained.

$$\ln(\eta) = \ln(A) + \frac{E_{\text{vis}}}{R}\left[\frac{1}{T}\right] \tag{8}$$

By plotting $\ln(\eta)$ versus $1/T$, E_{vis} for each sample can be deduced from the slope. The generic viscosity–temperature equation of the form of Equation 9 can be deduced.

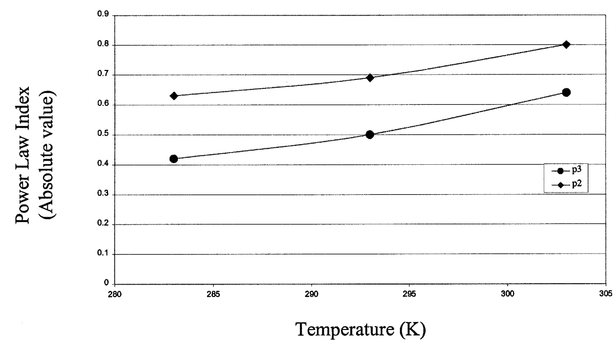

Figure 3 Variation in the power law indices (n_s) for flow curves from samples P2 and P3 at different temperatures.

$$\eta = \eta(T) \tag{9}$$

It was found that the slopes and intercepts from Equation 8 also vary with the measurements at different shear rates. This will be fully discussed in Section 4.3.

4.2.1. Effect of flux type

The effect of flux type was investigated by comparing the results of samples P1–P3. These samples have all other parameters the same apart from flux medium. Fig. 4 shows the variation of viscosity versus temperature at different shear rates using Equation 8.

From Fig. 4, increasing temperature on all three samples (P1–P3) corresponds to a decrease in viscosity. They all have different values for the activation energy of viscous flow. By composition, these samples differ in flux medium only. The activation energy ratio (E_{vis}/R), is also a function of shear rate as shown in Table II and Equation 10.

$$\frac{E_{vis}}{R} = f(\dot{\gamma}) \tag{10}$$

From Table II, it can be seen that the activation energy ratio of viscous flow for each sample increases with shear rate. This variation implies different levels of sensitivity of the samples to temperature. The pre-exponential constant was also found to be shear rate dependent, as described in Equation 11.

$$A = g(\dot{\gamma}) \tag{11}$$

4.2.2. Paste with its flux medium

This experiment is made possible because of sample F4; this is the flux medium used in sample P4. Comparisons made between samples F4 and P4 are shown in Fig. 5.

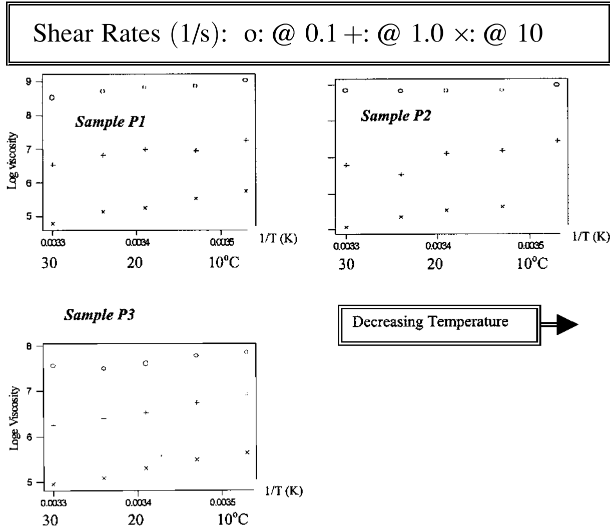

Figure 4 Solder paste temperature dependence of viscosity.

TABLE II Flow activation energy ratios (E_{vis}/R) for different samples. (Units: K).

Shear rate (s^{-1})	P1	P2	P3
0.1	1980(K)	488(K)	1605(K)
1.0	2715	3435	2888
10	4029	3307	3136

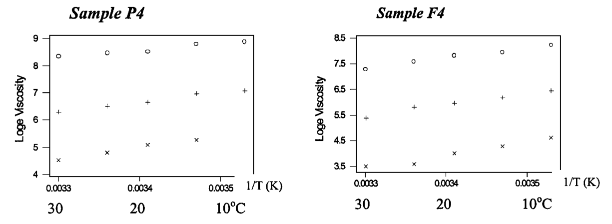

Figure 5 Effect of temperature change on solder paste and flux medium.

The slopes (activation energy ratios) are comparable at each shear rate. Also, both the slope and the pre-exponential parameter, A are shear rate dependent as shown in Equations 10 and 11.

4.3. Viscosity as a function of temperature and shear rate (combined)

So far, we have the viscosity of solder paste as a single variable function of shear rate Equations 4 to 6 or temperature Equation 1. In this section, a model for the combined effects of both temperature and shear rate on the viscosity of all the solder paste samples will be estimated. We will concentrate on the evaluation of both Equations 10 and 11 for each sample. A simplified form of the equation is shown in Equation 12, where $f(\dot{\gamma})$ is the flow activation energy ratio and $A(\dot{\gamma})$, the pre-exponential constant both functions of shear rate. For the various solder pastes, these functions will be different.

$$\eta = \eta(\dot{\gamma}, T) = A(\dot{\gamma}) \exp\left[\frac{f(\dot{\gamma})}{T}\right] \tag{12}$$

From the results presented in the previous sections (4.1 and 4.2), the functions $A(\dot{\gamma})$ and $f(\dot{\gamma})$ can be estimated for each solder paste. These functions were found to be of the form shown in Equation 13, and the constants, C and m are illustrated in Table III.

$$A(\dot{\gamma}), f(\dot{\gamma}) = C\dot{\gamma}^m \tag{13}$$

A typical profile for Equation 13 obtained for solder

TABLE III Values of constants for Equation 13

Sample	$A(\dot{\gamma})$		$f(\dot{\gamma})$	
	C	m	C	m
P1	$e^{-3.3}$	-1.81	$e^{7.9}$	0.10
P2	$e^{-0.64}$	-3.44	$e^{7.48}$	0.42
P3	$e^{-1.02}$	-3.16	$e^{7.8}$	0.15
P4	$e^{-5.11}$	-2.15	$e^{8.13}$	0.12
F4	$e^{-9.36}$	-1.65	$e^{8.4}$	0.05

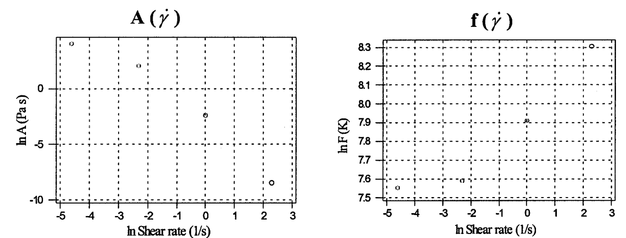

Figure 6 Typical variation of the pre-exponential functions, A and the activation energy ratio, f with shear rates for sample P1.

paste P1 is shown in Fig. 6. The data shown in Table III were obtained from the best fit through the data points shown. It is seen that $f(\dot{\gamma})$ and $A(\dot{\gamma})$ increases and decreases, respectively, with increasing shear rates.

This model has been validated by calculating the difference between the estimated and measured viscosity for the various samples at different shear rates ($0.1–10\,s^{-1}$) and temperature (10–30 °C). It was found that the error was less than 5%. At very low shear rates, the error increases slightly because the viscosity–shear rate function is outside the linear non-Newtonian region [13].

5. Summary

In this paper, we have presented the effects of both shear rate and temperature on the viscosity of solder paste. A method has been used which is different from the method of reduced variables in evaluating these effects. Starting from the single parameter Arrhenius equation relating viscosity and temperature, a modified equation was derived to incorporate shear rate. An equation of this form is essential in estimating the viscosity at shear rates and temperatures that can not be directly measured, such as very high temperatures. The model showed a good fit with experimental results.

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References

1. T. A. NGUTY, M. H. A. RIEDLIN and N. N. EKERE, (Nepcon West, Anaheim, CA, February 21–25, 1999).
2. J. S. HWANG, ''Solder paste in electronics packaging'' (Van Nostrand Reinhold, New York, 1989).
3. C. JOHNSON and J. KEVRA, ''Solder Paste Technology: principles and applications'', ch. 4, (1989).
4. J. FERGUSON and Z. KEMBLOWSKI, ''Applied Fluid Rheology'' (Elsevier Applied Science, 1991) p. 211.
5. C. A. MACKAY, *Electron. Packag. Prod.* **21** (1981) 116.
6. M. J. MINDEL, Proceedings of the Surface Mount International Conference and Exposition, San Jose, CA, August 27–29 (1991), p. 490.
7. J. WANG and R. S. PORTER, *Rheol. Acta.* **34** (1995) 496.
8. R. A. MENDELSON, *Polym. Eng. Sci.* **8** (1968) 235.
9. M. L. WILLIAMS, R. F. LANDEL and J. D. FERRY, *J. Am. Chem. Soc.* **77** (1955) 3701.
10. R. I. TANNER, ''Engineering Rheology'', (Oxford Science Publications, 1985) ch. 9.
11. J. D. FERRY, ''The dependence of viscoelastic behavior on temperature and pressure'' in ''Viscoelastic properties of polymers'', 3rd edn, ch. 11 (1980).
12. N. E. HUDSON and T. E. R. JONES, *J. Non-Newton. Fluid Mech.* **46** (1993) 69.
13. H. A. BARNES, ''An Introduction to Rheology'' (Elsevier Science Publishers, Amsterdam, 1993) p. 21.
14. M. H. A. RIEDLIN, PhD Thesis, University of Salford, UK (1998).
15. T. A. NGUTY, M. H. A. RIEDLIN and N. N. EKERE, IEEE/CPMT International Electronics Manufacturing Technology Symposium, Austin, TX, (1998) p. 206.

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