

APPLICATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY FOR QUALITY CONTROL OF SOLDER PASTE

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ABSTRACT

The state of materials utilized in the manufacturing of electronic products ultimately determines the quality, yield, defects, and cost of the final assembly. However, at this time in the electronics industry, there are no techniques that provide the manufacturer with the ability to characterize and trace a given material throughout the manufacturing process. Consequently, many defects, where the genuine root cause is related to variations in the material, are solved through process adjustments.

This research describes a novel, quality control method focused on the characterization and monitoring of solder paste to ensure its performance in order to minimize defects and material disparity at the time of use. This solution utilizes electrochemical impedance spectroscopy (EIS) to measure electrochemical changes in relation to the rheological properties of solder paste. A two-electrode probe system is used to apply a small voltage to measure the physiochemical reaction process within solder paste. The resulting Flux Coefficient (FC) and/or Powder Reactivity Coefficient (PRC) are derived from an equivalent circuit model reflecting the different interactions that occur in a solder paste. These coefficients are sensitive to modifications from storage, handling, and use during manufacturing. This paper, along with provided case studies, will describe the technique and science behind our method of determining a solder paste's fitness for use in the electronics manufacturing process.

Key words: solder paste; quality control; stencil printing; electronics manufacturing; rheology; humidity

INTRODUCTION

Despite major advances in printing equipment, solder paste inspection, and modern materials, solder paste printing accounts for 60% of assembly defects and it is estimated that up to 87% of reflow defects may be attributed to errors during stencil printing [1]. While numerous approaches to solder paste qualification and evaluation have been well defined and implemented in practice [2] [3] [4], few electronics manufacturers currently have implemented a quality control practice for ensuring the integrity of their solder paste before and during use. Additionally, while solder paste

manufacturers reliably test their products against IPC J-STD-004 and IPC J-STD-005 (IPC-TM-650) standards prior to leaving their facility, there are numerous factors during handling that may impact the performance of the materials.

Subsets of the IPC J-STD-005 standard may be used for solder paste quality control such as viscosity testing; however, this test requires the use of at least 500 grams of solder paste, which increases waste and prevents it from being used to measure the paste during printing. To reduce the quantity of solder paste required for testing, many researchers have studied the use of rheologic methods for solder paste testing that require only a few grams of solder paste. Rheologic measurement techniques such as creep recovery, thixotropy, oscillatory, viscosity, hysteresis loop, and yield stress tests, have been found to correlate to printing performance [1] [5] [6] [7] [8]. While solder paste rheology may be related to printing performance, due to the equipment necessary and complexity of operation, these techniques are not well suited for the factory floor.

This study evaluates the use of electrochemical impedance spectroscopy (EIS) as a method of solder paste quality control. These measurements are quick, taking less than 4 minutes with no moving parts. Forty-five solder pastes from seven major manufacturers were used to evaluate this technique on a representative sample presently available on the market. Measurements were taken before printing, during printing, and in different ambient environments. The EIS results were correlated to viscosity and rheology results.

EIS FOR SOLDER PASTE MEASUREMENT

EIS is a commonly used measurement technique with applications in batteries, coatings, and corrosion. EIS is an electrochemical technique wherein a material is characterized by applying a small alternating current (AC) potential and then measuring the impedance over a set of frequencies. By developing an equivalent circuit model of the material of interest and fitting the impedance spectra to the model, specific physiochemical properties of the material may be extracted. Previously, EIS has been applied to the domain of solder paste quality control [9] [10].

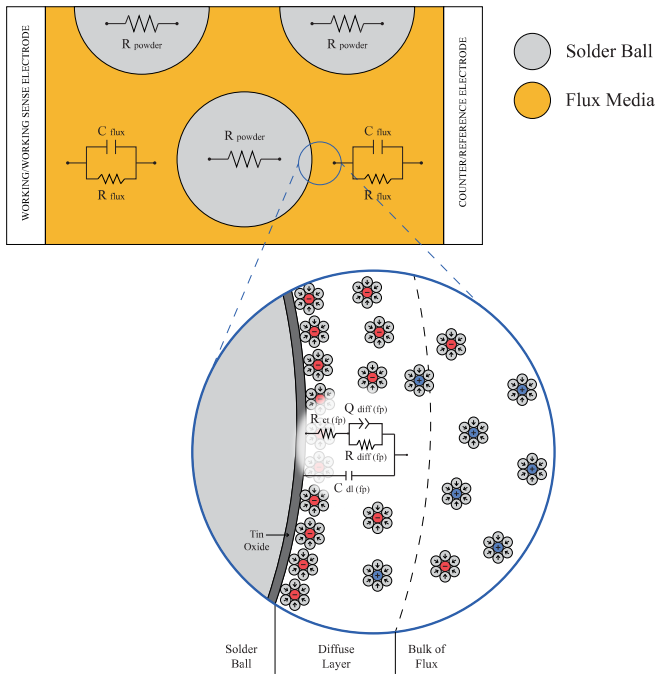
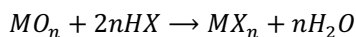
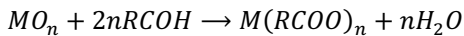


Figure 1. Visualization of the equivalent circuits for the metal powder and flux that make up solder paste. Interaction between the metal powder and bulk flux occurs over a diffusion layer.

To develop an equivalent circuit model of a material, it is necessary to understand the underlying structure and chemical behavior of a solder paste. Solder paste is comprised of a metal powder suspended in a flux. A solder paste flux contains an often-unknown mixture of chemical components that can be broadly broken down into solvents, rosins/resins, surfactants, activators, and rheologic modifiers. Solvents are an inert medium used to combine the active ingredients. Rosins/resins are high-temperature tolerant non-volatile chemicals. Surfactants are detergents used to lower the contact angle of the flux with the surface it is applied to. Activators are chemicals that react with metal oxides to remove them in reflow. Rheology modifiers are any variety of compounds used to improve non-Newtonian properties of a solder paste.

There are various fluxing reactions that may occur within a solder paste, depending on the formulation. The most common fluxing reactions are acid base reactions that may be represented by the simplified equation:



where M is metal, O is oxygen, RCOOH is carboxylic acid, and X is a halide [11]. While the fluxing reaction typically is thought of as occurring at reflow temperatures, this also occurs at colder temperatures, giving a solder paste a limited shelf life. The result of this reaction, $M(RCOO)_n$ or MX_n , a metal salt, is higher in viscosity than the flux, leading to an increase in overall viscosity as a solder paste ages.

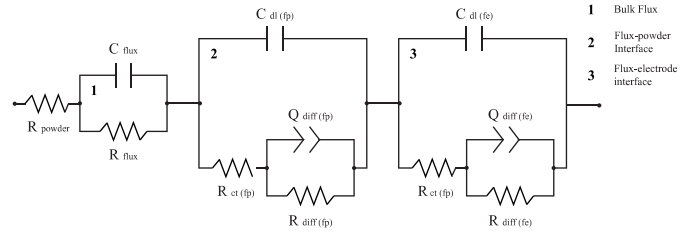


Figure 2. Equivalent circuit model.

The electrochemical phenomenon of a solder paste may be split into three behaviors: the dielectric properties of the flux, the interaction between the flux and metal powder, and the interaction between the flux and probe electrodes.

Flux Dielectric

Like most solvents, a solder paste flux exhibits both properties of conductors and dielectrics. The conductivity term, or R_{flux} in the equivalent circuit, accounts for the movement of free ions within the flux. The dielectric term, or C_{flux} in the equivalent circuit model, accounts for the impact of bound charged species within the flux that may consist of both polar molecules and non-polar molecules.

Many factors can impact both the conductivity and dielectric components of the flux dielectric behavior. The choice of solvent will impact the flux conductivity (e.g. deionized water has a conductivity of 10 micro-Siemens/cm whereas isopropyl alcohol has a conductivity of 3.5 micro-Siemens/cm). The selection and quantity of a flux activator will alter the quantity of free ions in solution. Surfactants selected may be ionic. Resins and rheologic modifiers may alter the dielectric component behavior of a flux. Variations in solder paste formulation irrelevant to solder paste performance would invalidate most comparisons between solder paste models or manufacturers outside of academic intrigue, however, when used for a single solder paste model, may be used to track lot-to-lot variations in formulation.

When solder pastes are handled in practice (on a stencil printer or in storage), the flux dielectric behavior also may change. It is well known that when a solder paste is printed on a stencil printer, it gradually will thicken and become unprintable or, for certain solder paste, will gradually thin and result in poor print definition. Exposure to high humidity, low humidity, high ambient temperature, or too much air drift above the stencil may accelerate this process [11]. Typically, when a solder paste absorbs moisture from the environment, it causes degradation of the paste viscosity. In this situation the conductivity of the solder paste is expected to increase due to the higher conductivity of water compared to solvents within the flux. When solvents evaporate from a paste, the viscosity will change. In this situation the conductivity is expected to decrease as the free ions in the solution require solvents to remain solvated. In practice, it is challenging to determine the specific mechanism that causes a solder paste

to change; however, through experimental evidence, these changes may be correlated to printing performance.

To simplify the interpretation of the flux dielectric behavior and to generate a single number, we define the FC as the time constant of the Flux RC equivalent circuit as defined in Equation 1.

$$FC = \tau_{flux} = (R_{flux}C_{flux}) \quad \text{Eq 1.}$$

Interaction Between Flux and Powder

The fluxing reactions within a solder paste are diffusion controlled and may be modeled as a Randles circuit. The diffusion of activator to the surface of the solder powder and resulting product away from the surface is modeled by a constant phase element, $Q_{diff (f-p)}$, and a resistor, $R_{diff (f-p)}$, in parallel. The energy dissipation associated with electron transfer during a fluxing reaction is represented by the charge transfer resistance in the equivalent circuit, $R_{ct (f-p)}$. Additionally, when metal is placed into an ionic solution, the surface becomes charged and attracts ions to the metal powder, forming an electric double layer capacitance $C_{dl (f-p)}$.

Many factors may impact the interaction between the powder and flux. The choice of solvent will impact flux conductivity and, therefore, the rate of diffusion. Selection and quantity of the flux activator will influence the reaction rate. Other additives also may influence the reaction. Like with the FC, the PRC may also be used to track lot-to-lot variations of a solder paste.

In practice, like the FC, the PRC of a solder paste is also influenced by the environmental conditions in which a solder paste is handled. As water is more ionic than most flux solvents, the rate of diffusion is likely to increase with the presence of moisture. When a flux's solvents evaporate, the rate of diffusion will decrease. However, unlike with FC, the diffusion rate also is impacted by stirring or agitation of a solder paste. As the reaction is diffusion limited when the solder paste is left still, the products of the fluxing reactions will be present in higher concentrations directly around the solder powder. When the solder paste is stirred, the product becomes more evenly distributed throughout the flux and increases the diffusion rate until the product builds up once again. While PRC and FC are measuring different phenomenon within the solder paste, both can be influenced by similar changes.

Like with the FC, we define the PRC as the time constant of the fluxing reaction diffusion within the solder paste as defined in Equation 2.

$$PRC = \tau_{f-p} = (R_{diff (f-p)}Q_{diff (f-p)})^{1/n} \quad \text{Eq 2.}$$

Interaction Between Flux and Electrode

The interaction between the flux and electrode may additionally be modeled using a similar method as with the flux and powder; however, this phenomenon is of no practical use for solder paste quality control.

RHEOLOGIC CHARACTERIZATION OF SOLDER PASTE

Rheological characteristics, such as shear thinning, dictate a paste's transfer efficiency and ability for the paste to recover [7]. Currently, there are various widely used rheologic techniques such as quality control measurements to predict the behavior of a solder paste during printing. In the creep recovery test, a stress is applied and removed in order to study paste deformation through its recovery and compliance [1] [5]. Oscillatory tests determine the viscoelastic properties of a solder paste by subjecting it to continuous sinusoidal shear stresses [5] [6]. Viscosity tests involve taking measurements of viscosity over a range of shear rates in order to predict a paste's ability to shear thin [1] [6]. Yield stress tests are used to understand the printability of paste by determining the shear stress at which a material flows [5]. The hysteresis loop test is used to predict the thixotropic behavior of the solder paste through measuring the resulting stress after applying shear sweeps [8]. Thixotropy tests are used to determine a solder paste's ability to structurally recover after being sheared [1] [6]. As a benchmark for comparison, EIS measurements were compared against rheologic results from thixotropy measurements. This rheologic technique was chosen based on its relation to solder paste screen printing. The thixotropy test simulates the printing process as a solder paste undergoes a high shearing force when the squeegee pushes the paste through the apertures as it rolls over the stencil.

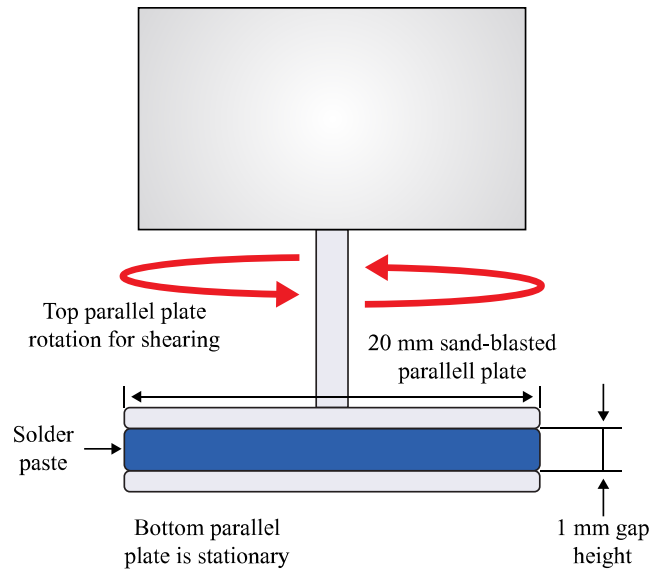


Figure 3. Rheological experimentation setup.

Figure 3 shows the experimental setup for rheological measurements. The step flow method was used to study paste recoverability through the application of a high shear step followed by a low shear step, to allow for paste recovery. The tests were conducted using a shear rate of 0.1 s^{-1} for 300 s followed by $0.5\text{-}2.0 \text{ s}^{-1}$ for 300 s (high shear rate varied between solder pastes) and then back to the initial shear rate of 0.1 s^{-1} for 300 s. Figure 4 demonstrates the data output from this method as a function of viscosity and time.

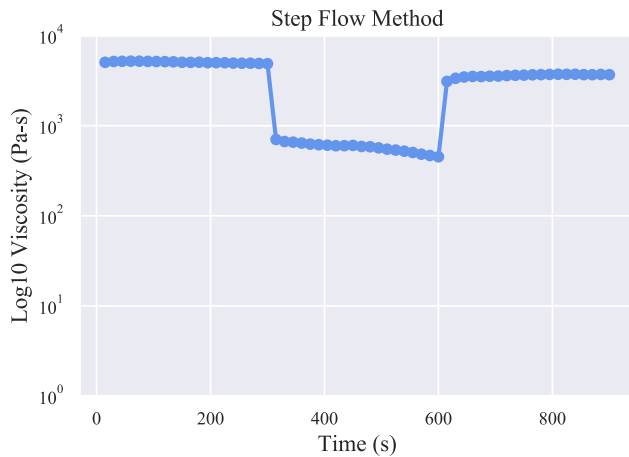


Figure 4. Step flow method.

In the step flow tests, the recovery of the paste was calculated from the viscosity after the high shear rate in relation to the viscosity at the beginning of the test. The initial viscosity was plotted as a function of time to provide a visual reference of paste recovery. The recovery of the paste was calculated based on equation 3:

$$\text{Recovery (\%)} = \frac{\eta_{0.1 \text{ Recovery}}}{\eta_{0.1}} \times 100 \quad \text{Eq 3.}$$

Where $\eta_{0.1 \text{ Recovery}}$ is the measured viscosity at the shear rate of 0.1 s^{-1} (after removal of the high shear rate) and the $\eta_{0.1}$ is the measured viscosity at the beginning of the test at 0.1 s^{-1} [11].

EXPERIMENTS

Three different scenarios were devised to evaluate the solder pastes at different points within the manufacturing process: measurements directly from the container prior to use, through an accelerating aging test on a stencil printer, and when exposed to different environmental conditions whether that be on the printer or post-printing.

Equipment

All EIS measurements during experimentation were conducted utilizing the Vison MARK-1 with the E-Chem Insight. A two-electrode probe system was used to apply a small voltage to investigate the electrochemical properties of solder paste.

Rheological measurements were performed on a TA Instruments Discovery Hybrid Rheometer-1 (DHR-1). The rheometer was equipped with an Active Temperature Control (ATC) to ensure all tests were performed at 25°C . Measurements of rheological recoverability and viscosity were measured using a step flow procedure previously described. The selected geometry for the rheometer was a 20 mm sand-blasted parallel plate system with a 1 mm gap height.

Solder Pastes Selected

Forty-five different unique solder pastes were tested from seven major solder paste manufacturers with each experiment. These solder pastes vary in flux designator, alloy, and type. The flux designators tested were ORH0, ORH1, ORM0, ORM1, ROL0, and ROL1. The alloys tested were: SAC305, Innolot, LF-C2, SN100C, and Sn63/Pb37. Types 3 and 4 solder pastes were tested. All solder pastes were tested within the expiration date. For all experiments, the solder paste was left to reach room temperature overnight before the experiment.

Measurements from Container Prior to Use

To determine if a solder paste meets quality standards prior to use, it is necessary to characterize what the expected results are of an incoming solder paste. For each solder paste, 15 measurements were taken directly from the jar or cartridge and measured using the Vison MARK-1. If a solder paste arrived in a cartridge, an appropriate quantity of solder paste was dispensed into a plastic container. Then, the container was stirred for 5 minutes using a metal spatula. An additional 15 samples were taken post-stirring.

These measurements form one starting baseline or golden sample to compare future measurements against for quality control purposes. A subset of results from 10 solder pastes is shown in Figure 5.

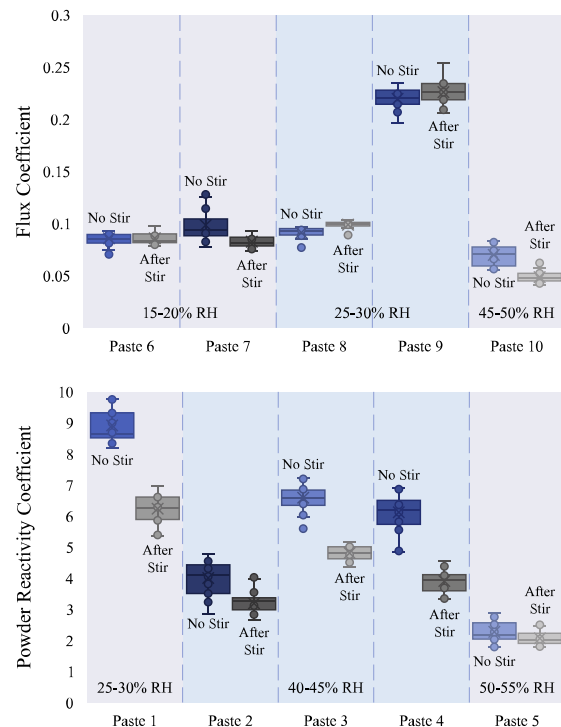


Figure 5. Subset of 10 FC (top) and PRC (bottom) measurements measured from new solder pastes. It can be observed that PRC measurements are lower after stirring than before stirring. Additionally, both FC and PRC measurements exhibit lower variance after stirring.

Accelerated Aging of Solder Paste on Stencil Printer

During printing, the properties and behavior of a solder paste continuously change. While these changes may be tolerable for certain processes, it would be ideal to minimize these variations. The first step in minimizing variations in the printing process is to measure the solder paste during printing.

A stencil printer was configured using an apertureless stencil without solder paste replenishment to accelerate the solder paste aging. The time between prints was 10 seconds. The print speed was 1.96 in/sec. The squeegee pressure was 4 kPa. All experiments for this procedure were conducted at $45 \pm 5\%$ room humidity and $23 \pm 2^\circ\text{C}$ room temperature. EIS and rheological measurements were taken every 30 minutes for five hours.

These results can be used to characterize the expected behavior of a solder paste during printing. Any deviations from the expected behavior of a solder paste form an early indicator on in-process failures prior to defects occurring. An example of the expected PRC behavior of a solder paste printing on a stencil printer is shown in Figure 6, and the expected FC behavior is shown in Figure 7.

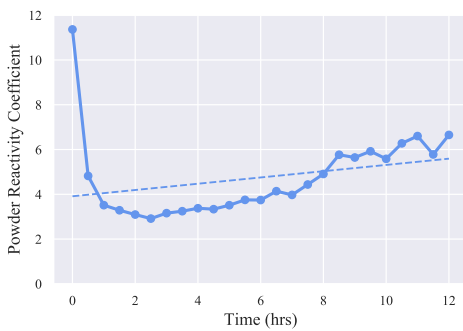


Figure 6. Example of PRC results when a solder paste is printed on a stencil printer for 12 hours. This curve can be split into three phases: initial acclimation, normal printing, and end-of-life. When a solder paste is initially printed, the PRC will decrease rapidly. It then will stay relatively consistent during normal printing operations. At the end of its useful stencil life, the PRC will increase.

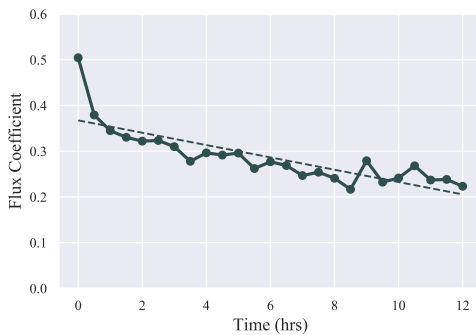


Figure 7. FC results when a solder paste is printed on a stencil printer. There is an initial acclimation period before a steady decrease.

Impact of Solder Paste Exposed to High and Low Humidity

Solder pastes may be exposed to a range of ambient environments both during printing and post-printing when present on a board. It is well known that exposure to excessively high or low ambient humidities may induce poor performance; however, even operating within the range of manufacturer-recommended humidities, changes in solder paste behavior can be observed. Therefore, it is useful to understand how different ambient conditions affect solder paste measurements.

For each solder paste, after mixing, two samples were taken and placed onto solder paste probes. One sample was placed into a low humidity environment 35-45% and one sample was placed into a high humidity environment $\sim 65\%$ RH. Using the Vision MARK-1, EIS measurements were taken every 30 minutes for five hours.

An example of the typical results is shown in Figure 8. These results may be used either to estimate an offset that can be applied to the expected results on a stencil printer to predict its behavior when printed at a different relative humidity or to simply provide context to assist in interpreting measurements before use on a printer.

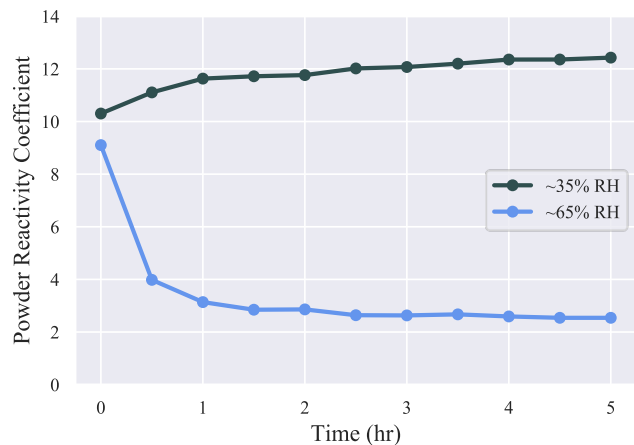
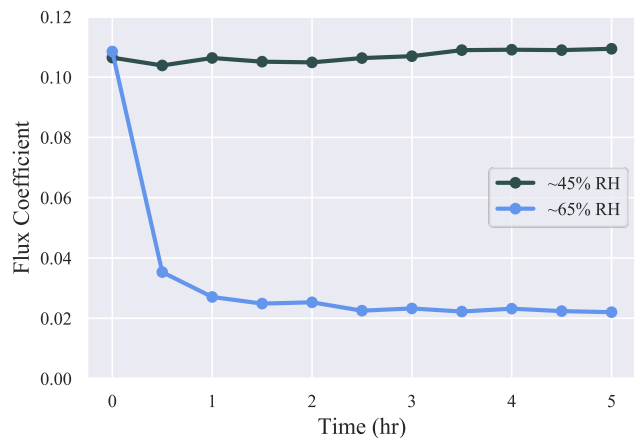


Figure 8. FC (top) and PRC (bottom) results of a solder paste sample placed within a low humidity and a high humidity environment.

RESULTS AND DISCUSSION

Main Effects Analysis of Solder Paste Measured Before Use

To evaluate the use of EIS measurements for quality control of solder paste before use, it is beneficial to understand the main factors that influence the before-use results. The factors studied were manufacturer, flux designator, alloy, type, and stirring sensitivity.

A main effects plot of all measurements taken prior to use is shown in Figure 9. Most variation in measurements taken of solder pastes before-use can be attributed to differences in formulation between different solder pastes more so than stirring or handling conditions. This factor makes the measurements useful to detect if the solder paste before use is the correct paste or if there are any changes in formulation or lot-to-lot. However, this prevents the generation of a single specification that can be applied universally to all solder paste for quality control. Therefore, for each solder paste, measurements must be compared against a baseline for that solder paste.

Relationship Between Solder Paste Shelf Life and Expiration and Powder Reactivity Coefficient and Flux Coefficient Measurements

Solder pastes have a shelf life because the fluxing reaction that occurs between the flux and powder also occurs at room temperature. When a solder paste ages, the product of that reaction is more viscous, increasing the overall solder paste viscosity. As the fluxing reaction product builds up within the flux, the reaction will slow as indicated by an increase in PRC value.

The initial diffusion rate of the fluxing reaction also may be a predictive tool of solder paste shelf life. Due to differences in how manufacturers decide on a shelf life recommendation and in each solder paste, this trend can be observed by looking at the post-stirring before-use measurements from

one manufacturer's solder paste. Table 1 shows all the experimental results from one solder paste manufacturer sorted from smallest to largest FC and PRC. Blank FC values indicate that the results were below the detectable limit and blank PRC values indicate that the results were above the detectable limit.

The FC and PRC results exactly aligned with the manufacturer's reported shelf life from the technical datasheets. For this manufacturer, pastes with a PRC below ~ 3 had a reported shelf life of 4 months. Pastes with an FC greater than ~ 0.06 has reported shelf life of 12 months. Pastes with a PRC above ~ 3 and FC below ~ 0.06 have a reported shelf life of 6 months. It is theorized that pastes at the higher extreme of the 6-month cluster (e.g. P8) will far exceed the stated shelf life recommendation as compared to solder paste at the lower extreme (e.g. P2) that may experience degradation in storage sooner.

Table 1. Recommended Solder Paste Shelf Life vs. Powder Reactivity Coefficient and Flux Coefficient Measurements Measured after Stirring for One Manufacturer

Shelf Life	Paste	FC	PRC
4 Months	P1		2.087 ± 0.201
6 Months	P2		3.40 ± 0.179
	P3		3.925 ± 0.344
	P4		4.785 ± 0.226
	P5		6.343 ± 0.406
	P6		6.453 ± 0.432
	P7	0.017 ± 0.001	631.02 ± 61.53
	P8	0.03 ± 0.003	
	12 Months	P9	0.08 ± 0.004
P10		0.09 ± 0.006	
P11		0.102 ± 0.004	

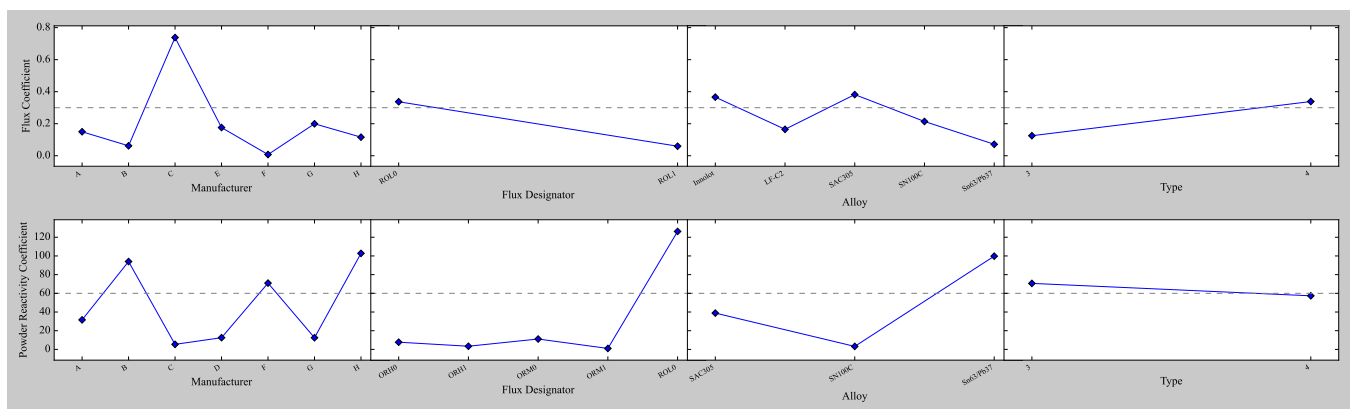


Figure 9. Main effects plot of solder paste measurements taken before use. Most variation in before-use measurements can be attributed to differences in solder paste formulation between different solder paste models. Notably, the flux of ROL1 solder paste was more conductive and thus had a lower FC than ROL0 solder pastes due to the additional halides. Solder pastes with ORH1, ORH0, ORM1, and ORM0 fluxes had similar fluxing reaction diffusion rates at room temperature and therefore similar PRC values. These four fluxes had much quicker fluxing reaction diffusion rates than solder pastes with ROL0 fluxes. Solder pastes using ORH1 and ORM1 fluxes had slightly quicker diffusion rates than pastes using ORH0 and ORM0 fluxes.

Influence of Ambient Environment on Flux Coefficient and Powder Reactivity Coefficient Measurements

When a solder paste is placed in high humidity environments, both the FC and PRC are lower than if placed in a low humidity environment as shown in Figure 10. Because solder pastes often are hydroscopic, they pick up moisture from the environment and, therefore, the conductivity of the flux will increase, decreasing the FC value. The addition of water also increases the diffusion rate of the fluxing reaction, decreasing the PRC.

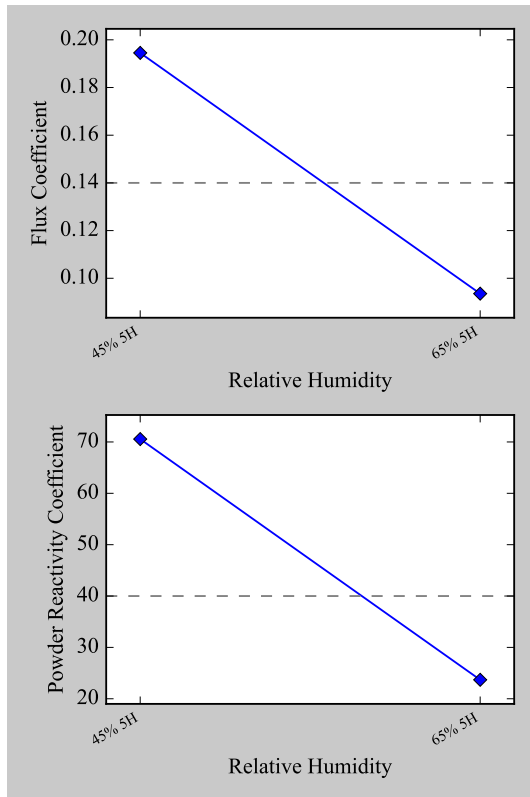


Figure 10. Effect of solder paste placed in high and low humidity environments. In high humidity environments, both the FC and PRC are lower than in high humidity environments.

For the purposes of quality control, these changes due to changing environmental conditions are likely meaningful. According to Dr. Lee in Reflow Soldering Processes, high or low humidity is a root cause of poor stencil life, poor paste release from squeegee, insufficiency, low tack, short tack time [11]. Further investigation is necessary to better understand these relations.

Influence of Handling on Flux Coefficient and Powder Reactivity Coefficient Measurements

When a solder paste is stirred or worked on a stencil printer, both the FC and PRC measurements decrease as shown in Figure 11. The process of stirring a solder paste or working it on a stencil printer increases the surface area exposed to the environment and accelerates any changes that may occur due to the exposure.

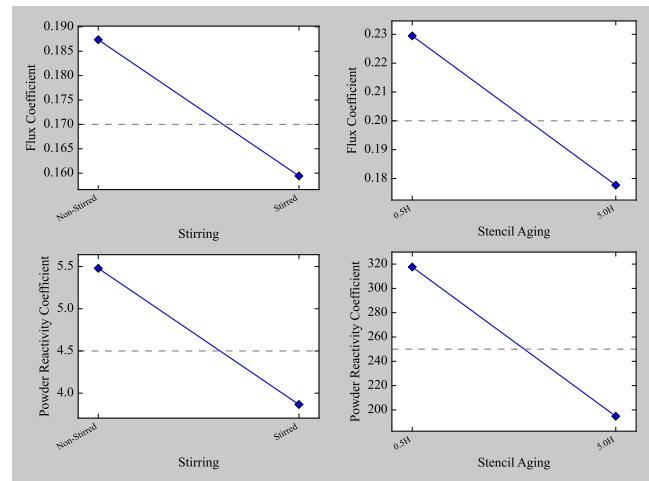


Figure 11. Effect of stirring (left) and printing (right) on FC and PRC measurements. When stirred, both FC and PRC measurements typically decrease. When printed for five hours, both FC and PRC measurements decrease.

Under the environmental conditions tested within these experiments, the impact of moisture absorption had a greater effect on the conductivity than that of solvent evaporation and, therefore, the net effect of stirring was a decrease in FC. Testing under very low environmental humidity <30% RH have shown a reversal in this trend and FC values increase on stirring. When stirring a solder paste, the product built up around the powder is also more evenly distributed throughout the flux and the diffusion rate is increased, resulting in a PRC decrease.

Due to the limited length of time the solder paste is worked on a stencil printer in these experiments relative to the solder pastes stencil life, only the initial decrease in PRC can be observed. As the trends in FC and PRC in the first phase of printing are identical to that of solder paste when stirred or just left exposed to the ambient air, it is believed that these changes primarily are due to the initial absorption of moisture from the environment.

These changes in both FC and PRC measurements may be used to gain early indication of solder paste process deviations prior to the incidence of printing defects.

Correlation Between Flux Coefficient and Powder Reactivity Coefficient Measurements and Viscosity and Rheology Measurements during Printing

Viscosity and rheology measurements are a key component of most previous solder paste qualification testing techniques; therefore, it is advantageous to correlate the results of EIS testing to that of more typical viscosity and rheologic testing techniques. However, due to the large number of measurements within this study, the process of correlating these two values is more challenging.

For each solder paste, the Pearson's correlation coefficient was calculated between each FC/PRC-Viscosity/Recoverability pairing. Due to the noise present

within the viscosity and rheology data in a single 5-hour experiment, likely caused by wall slip within the rheometer measurement, no significant correlation was found. To lessen the impact of the noisy viscosity and rheology data, the results of testing all solder pastes were averaged and the correlation coefficients were calculated on the average data. The results show a near-perfect correlation between both FC and viscosity and PRC and viscosity as shown in Table 2. To showcase the similarities, a plot of both the average FC and average viscosity is shown in Figure 12.

Table 2. Correlation Coefficients Between FC/PRC-Viscosity/Recoverability Pairs Taking Average First

Comparison	Correlation Coefficient
FC and Viscosity	0.962
FC and Recoverability	-0.592
PRC and Viscosity	0.932
PRC and Recoverability	-0.587

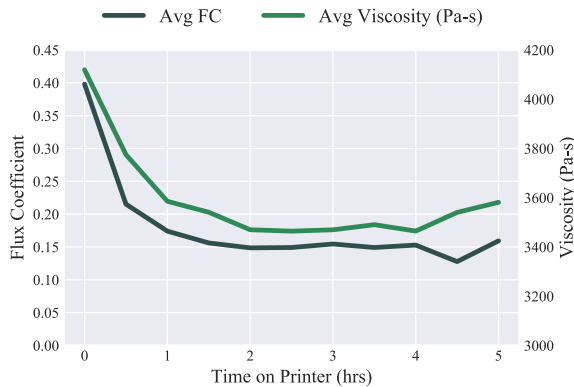


Figure 12. Average viscosity and average FC values of solder pastes printed on the stencil printer.

As both the FC and PRC measurements are well correlated to the viscosity of a solder paste, they also likely will be well correlated to printing performance in practice, making this technique a powerful tool for solder paste quality control.

CASE STUDIES

To showcase the advantages of applying EIS techniques for solder paste quality control, two different case studies are explored: an example of differences in incoming materials and an example of uncontrolled humidity causing changes in solder paste viscosity.

Damaged Incoming Solder Paste

An ORH0 solder paste from a major materials manufacturer with an advertised stencil life of five hours was tested using the experimental techniques described within this paper. After approximately one hour, the solder paste no longer formed a proper roll. To eliminate the possibility of measurement error, the experiment was repeated the next day with identical results. The experiment results for both days are shown in Figure 13.

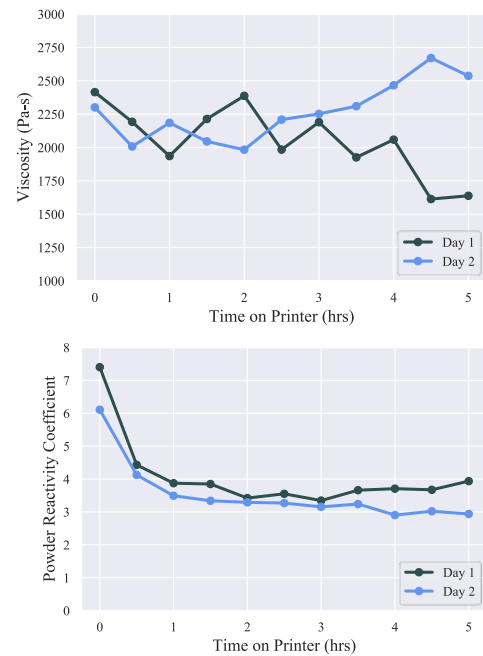


Figure 13. Viscosity (top) and PRC (bottom) results from an ORH0 solder paste suffering from poor stencil life.

Because the first sample was obtained through a third-party distributor, a new container was obtained directly from the manufacturer to determine if the sample was damaged prior to arrival and the experiment repeated. This sample exhibited a good roll for the duration of the manufacturer’s stated stencil life. The results of this experiment are shown in Figure 14.

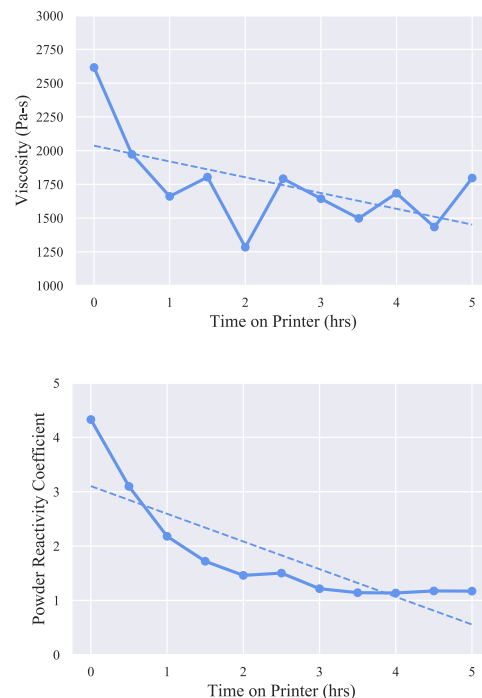


Figure 14. Viscosity (top) and PRC (bottom) results from the same ORH0 solder paste exhibiting good stencil life.

When tested, both samples were 2 months \pm 1 week from the listed manufacturing date. Despite a drastically different observed behavior of the solder paste on the stencil printer, it was peculiar that the viscosity of both the good and bad containers of solder paste were nearly identical. However, both the initial PRC value before placing the solder paste onto the printer and the average PRC value while printing on the stencil printer were much higher for the solder paste exhibiting poor printing performance compared to the solder paste exhibiting good printing performance. When solder paste is mishandled (e.g. stored or transported at higher temperatures), typically the PRC values will be higher than normal as fluxing reaction product has built up within the solder paste. These results indicate that the solder paste likely was mishandled by the third-party solder paste distributor.

Additionally, it is useful to investigate the reason for why the poor solder paste was not caught by the viscosity testing. When sheared to 1 s^{-1} , this solder paste exhibited the formation of dense clumps that were not present at the low shear rates 0.1 s^{-1} used in the viscosity testing. It is thought that these dense clumps are a result of cold-welding of the solder powder due to the aggressive flux used within this solder paste. Images of the solder paste pre- and post-shearing are shown in Figure 15.

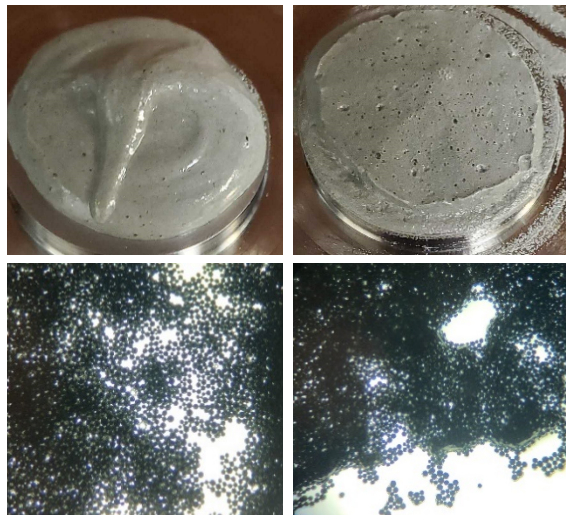


Figure 15. Solder paste pre-shearing (left) and post-shearing (right). Images of entire volume (top) and magnified view of paste (bottom).

Assuming that the solder paste was mishandled and stored above the manufacturer’s recommendations, the flux may have reacted with the oxide layer of the metal powder much more quickly than usual, thinning the oxide layer. As a result of this thinner oxide layer in the damaged solder paste, it was able to form clumps of cold-welded solder powder more readily when sheared than the undamaged solder paste. As this behavior is readily observable only under higher shear rates, it was not picked up in the viscosity testing. However, the PRC measurement calculates the rate of fluxing reaction diffusion within the solder paste that is slowed down by the

thinning of the oxide layer, making it sensitive to the changes that caused the solder paste to roll poorly where the viscosity measurements were not.

Humidity Control Failure during Printing

A different ORH0 solder paste from a different materials manufacturer was tested using the techniques described in this paper. The results of the experiment are shown in Figure 16. During this experiment, the environmental control system malfunctioned between one and three hours, resulting in an increase in relative humidity above the acceptable upper threshold for the experiment. Due to this increased ambient humidity, viscosity of the water-soluble solder paste decreased and correspondingly, due to the increase in moisture absorption, the PRC decreased.

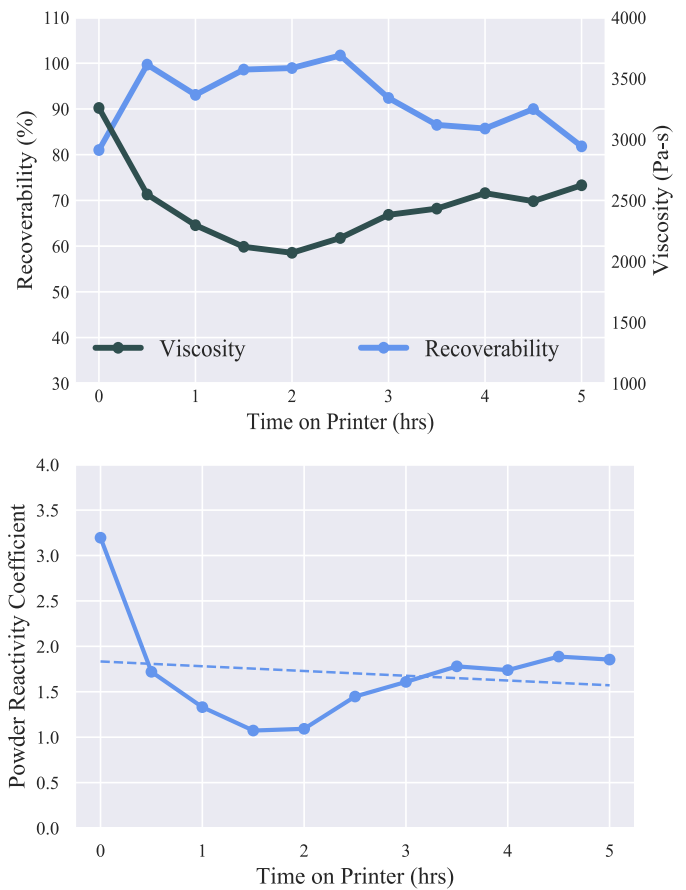


Figure 16. Rheologic behavior (top) and PRC (bottom) during environmental control failure when printing. Between the first and third hours of testing, humidity increased before returning to the target humidity. The viscosity and PRC decreased before recovering.

By using electrochemical impedance spectroscopy techniques, it is possible to detect slight changes in the solder paste related to viscosity that would be impractical to measure using existing solder paste quality control techniques.

CONCLUSION

In this work, the use of EIS for quality control of solder paste was explored. Measurements before use were strongly influenced by formulation and, therefore, may be used to detect changes in incoming materials. EIS measurements also were related to the manufacturer's stated shelf life. During printing, EIS measurements were found to have a strong correlation to the viscosity of a solder paste. EIS is a powerful technique to monitor and control the quality of a solder paste both before and during use.

REFERENCES

- [1] R. Durairaj, S. Mallik and N. N. Ekere, "Solder paste characterisation: towards the development of quality control (QC) tool," *Soldering & Surface Mount Tech*, vol. 20, pp. 34-40, June 2008.
- [2] C. Shea and R. Lawrence, "Solder Paste Qualification Testing for EMS Production," in *SMTA International Conference Proceedings*, 2017.
- [3] D. Dixon, "Development of a Solder Paste Test Vehicle for Miniaturized Surface Mount Technology," in *IPC APEX Expo 2018 Proceedings*, 2018.
- [4] C. Shea, "Accelerating the Solder Paste Evaluation Process," in *SMTA International 2018 Proceedings*, 2018.
- [5] S. Mallik, M. Schmidt, B. R and N. Ekere, "Evaluating solder paste behaviours through rheological test methods and their correlation to the printing performance", *Soldering & Surface Mount Technology*, vol. 22, no. 4, pp. 42-49, 2010.
- [6] S. Mallik, J. Thiemea, R. Bauera, N. Ekere, A. Seman, R. Bhatti and R. Durairaj, "Study of the Rheological behaviours of Sn-Ag-Cu Solder pastes and their Correlation with Printing Performance", in *11th Electronics Packaging Technology Conference*, 2009.
- [7] T. E. N. Nguty, "Monitoring the effects of storage on the rheological properties of solder paste.", *Journal of Materials Science: Materials in Electronics*, vol. 11, pp. 433-437, 2000.
- [8] V. G. Kolli, F. Gadala-Maria and R. Anderson, "Rheological Characterization of Solder Pastes for Surface Mount Applications," in *IEEE TRANSACTIONS ON COMPONENTS, PACKAGING, AND MANUFACTURING TECHNOLOGY*, 1997.
- [9] Frederickson et al. "Solder paste and residue measurement system," United States of America Patent US5656933A, 12 August 1997.
- [10] M. H. R. K. C. Seitz, "Process-monitoring via impedance spectroscopy," *Materials Research Society*, p. 411, 1996.
- [11] N.-C. Lee, "Reflow soldering processes and troubleshooting: SMT, BGA, CSP, and flip chip technologies," Oxford: Newnes Publication, 2002.