

# Electrochemical Impedance Spectroscopy: An Innovative Application for Quality Control of Solder Paste

## Abstract

The miniaturization of components has caused increased defects in the Surface Mount Technology (SMT) process during the solder paste printing. The root cause of solder paste printing failures is often attributed to the stencil, squeegee, or printing process parameters; however, the solder paste is often overlooked and could be the cause of printing and soldering defects. Although there are current methods for quality control of solder pastes such as rheological techniques, they are not commonly used due to their complexity and high costs. Therefore, there is a need to implement a more affordable and efficient tool to control the solder paste before and during its use in order to reduce printing failures and minimize variations in the SMT process. In this research, electrochemical impedance spectroscopy was used as a method of inspecting solder paste to determine if paste printability, or its fitness for use, could be predicted. The solder paste was worked over an extended period of time while samples were extracted for rheological and electrochemical measurements. In another case, the solder paste was subjected to high temperatures in order to simulate an accelerated aging process as if the jar was experiencing poor shipment/handling conditions. Based on the results, there is an increase in the time constants of the flux-powder interface that directly correlates to the decrease in recoverability of the paste over time. Overall, a solder paste's fitness for use can be predicted through the correlation of electrochemical and rheological measurements.

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## 1. Background

The trend of the electronics industry towards the miniaturization of components has the potential to increase first-pass defects of the Surface Mount Technology (SMT) process more than ever before. Decreasing the area of paste application generates a need for increased precision during the stencil printing process to reduce the opportunity of failures such as skipping, gasketing, or scooping. Solder paste printing is already responsible for 52-71% of assembly defects and 87% of reflow soldering defects [1]–[3]. While the root cause of failures is often attributed to the stencil, squeegee, or printing process parameters, the material itself is often overlooked. The ability to better control the solder paste before and during its use will reduce printing failures and minimize variations in the SMT process.

Currently, there are common quality control tests, such as Solder Paste Inspection (SPI) testing, that allow for the reduction of stencil printing defects through inspection of the solder paste after it is already printed. However, when there is a stencil printing error, such as a skip or bridge of the paste, the board must be cleaned, the problem identified, and the board re-printed. This type of setback can be detrimental to production because it halts further printing until the problem is identified and fixed.

The industry standard J-STD-005 requires a measurement of viscosity in order to determine the quality of a solder paste before shipment or during incoming inspection. A viscometer determines the condition of a paste by measuring its dynamic viscosity through the application of a single shear force [4]. A paste that is too thick, or has a high viscosity, could cause

insufficient deposits; whereas, a paste that is too thin, or has a low viscosity, could cause slumping [5]. The usage of the viscometer for quality control has a high false positive rate because it ignores the shear thinning property of a solder paste while being used on a stencil printer. The paste is subjected to a single shear rate during a viscometer reading; whereas, the paste is subjected to multiple shear rates during the printing process [4]. In addition, although this test is convenient for solder paste manufacturing companies, it is impractical on the factory floor due to the large quantity of paste required. Some viscometers, such as the spiral viscometer, require the use of an entire jar of paste, which is costly and offers false assurances that the other jars received with that paste are of the same quality.

Similarly, rheological properties of solder pastes have been widely studied and it was determined that those properties dictate the paste's behavior during the printing process. There are various rheological properties of solder paste that can be measured by different tests:

#### *Creep Recovery*

The creep recovery test determines the slump characteristics, aperture filling process, and recovery after the printing process. In this test, a shear stress is applied to the solder paste while the strain is monitored over time; after a pre-set time, the stress is removed, and the strain is recorded. The compliance is calculated from the ratio of the strain in the paste to the applied stress [1]. A higher compliance ratio correlates to a lower percent recovery; the paste is more likely to bleed or smudge during the printing process because it is unable to recover back to its original structure [1]. Whereas, a lower compliance ratio correlates to a higher percent recovery and are less likely to smear because they can recover back to their original structures. With a set compliance threshold, the creep recovery test can be used for quality control testing of solder paste.

#### *Viscosity Test*

The viscosity test can be used to predict the degree of shear thinning through measurements of the viscosity over a range of shear rates [6]. The viscosity of the solder paste must be low enough for the paste to be able to move through the stencil apertures, but high enough for the paste to recover to its initial state after it is through the stencil [6]. A good shear thinning correlates to the paste's ability to move from a low viscosity to a high viscosity after a force is applied.

#### *Oscillatory Test*

The oscillatory test is often used prior to the creep recovery test to determine the stress that should be applied to the paste. This test determines the linear viscoelastic region of the solder paste; the region represents the maximum deformation that can be applied to the material without destroying its structure [7]. A shear stress or strain is applied to the paste in order to measure the storage and loss modulus. The ratio between the storage and loss modulus can indicate if the paste is cohesive, which results in the insufficient release of the paste from the stencil during the emptying process.

#### *Hysteresis Loop Test*

The hysteresis loop test, or the thixotropic loop test, can be used to predict the thixotropic behavior of the solder paste through measuring the resulting stress after applying sweeps of shear rates. The sweep consists of a low shear rate, increasing to a high shear rate, and then decreasing

back to the low shear rate over a period of time. The non-Newtonian behavior of solder paste results in a hysteresis loop with the area representing the degree of the structural breakdown of the paste due to the force applied [8]. Higher thixotropic values correlate to bad structural properties, which make it more probable for the paste to fail on the stencil printer. Lower thixotropic values correlate to good structural properties of the paste, which make it less likely to cause defects on the stencil printer.

### *Thixotropic Test*

The thixotropic test determines the recovery of the paste after an applied force. The test involves step shear rates starting with a low shear rate, followed by a high shear rate and back to the initial shear rate. The recovery is calculated from the ratio of the viscosity at the low shear rate, after the high shear rate was applied, and the initial viscosity at the low shear rate [6]. The recovery relates to the paste's ability to return to its original structure after a force is applied to it. A poor recovery results in slumping of the paste during the stencil printing process.

These process control methods are not commonly used in the factory due to their complexity and high costs. Therefore, there is a need to implement a more practical, affordable, and efficient tool for the inspection of solder pastes. This capability would determine if a solder paste is fit for use in the stencil printing process, preventing related production issues.

In this study, the use of electrochemical impedance spectroscopy was used as a solder paste quality control tool. The sensitivity of the EIS spectra to solder alloys, solder ball size, and flux type was investigated across 11 commercially available solder pastes. Additionally, the relationship between the fit circuit elements of the EIS spectra and rheological measurements were explored both as the solder pastes age through heat accelerated aging and when in use on a stencil printer.

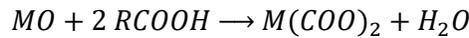
## **2. Electrochemical Impedance Spectroscopy for Solder Paste Quality Control**

Electrochemical impedance spectroscopy (EIS) is a highly sensitive technique used to establish the electrical response of chemical systems by applying a small AC voltage at different frequencies to a given material. At each frequency, the impedance is determined by the ratio of the applied voltage to the measured current [8]. This technique is useful to study materials that undergo multiple phenomena and structural contributions that are difficult to extract using other techniques [10]. Previous work has shown that EIS measurements of solder pastes correlates to rheologic behavior and printing performance. It was determined that the electrochemical reactions present at the flux-powder interface are sensitive to the history of the paste and can be studied by EIS [11].

### *Structure and Chemistry of Solder Paste*

Solder pastes are heterogeneous materials, consisting of metallic particles encapsulated in a flux media containing an organic activator. The flux media consists of: resins for oxygen barrier, rheological additives to provide good printing properties, solvents to dissolve other materials, and activators to remove the oxides from the solder particles as well as components and PCB pads during reflow [12, p. 101].

The activators are composed of weak organic acids (WOA) that promote the reactivity of the metal oxides. The generalized chemical reaction between the activator (RCOOH) and the metal oxides (MO) is:



In most fluxes, this reaction is diffusion limited and not reaction limited. The reaction rate is dependent on how quickly the product of the reaction – metal salt – is removed from the metal surface. The structure and reactions occurring within the solder paste can be combined into a unified model of the physicochemical interactions within the solder paste as in Figure 1.

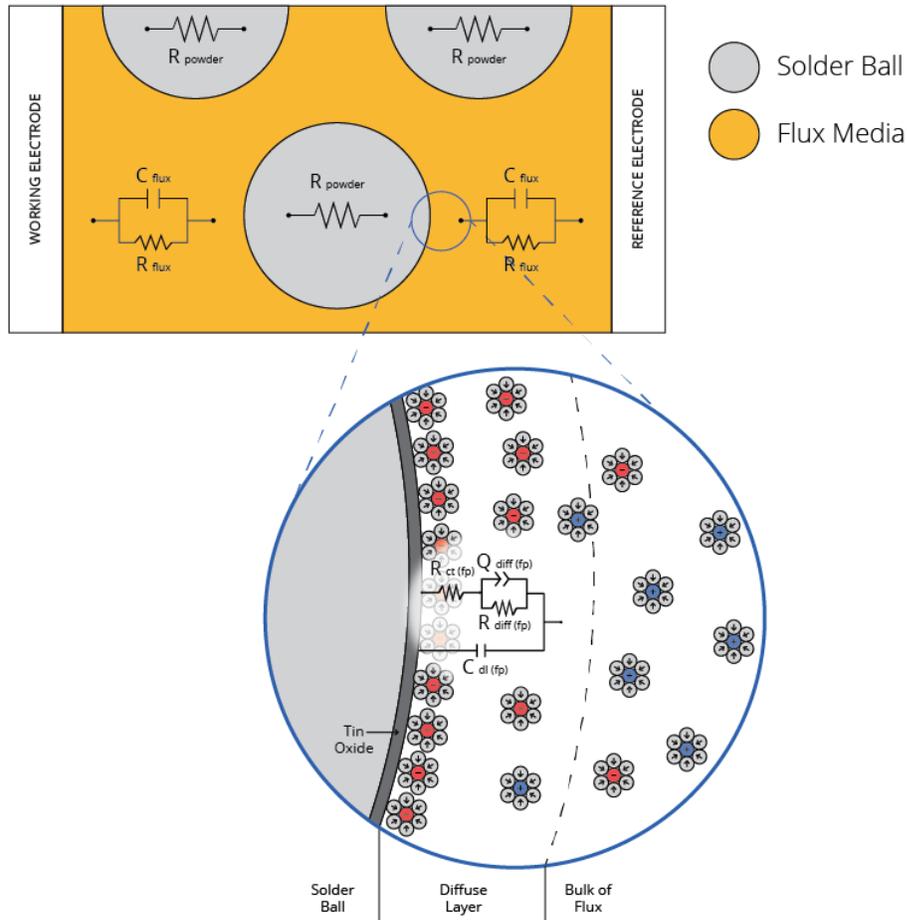


Figure 1. A depiction of the physicochemical interactions in solder paste relevant for creating the EIS equivalent circuit model. These interactions can be broken up into three main categories: (1) the dielectric behavior of the bulk flux media, (2) the reaction at the flux-powder interface, and (3) the reaction at the flux electrode interface. (1) the flux media contains ionic species that result in the flux being electrically conductive and polar molecules that cause the flux to be polarizable. The conductivity of the flux is modeled by a resistor,  $R_{flux}$ , and the polarizability modeled as a capacitor,  $C_{flux}$ . (2) a diffusion-limited reaction occurs between the solder balls and the flux where the reaction between the tin oxide and flux activators at the surface is modeled by a charge transfer resistance,  $R_{ct(fp)}$ , and the diffusion of reaction product away from the surface of the solder ball is represented by the RQ circuit containing  $Q_{diff(fp)}$  and  $R_{diff(fp)}$ . A diffuse layer forms where the reaction product is diffusing away from the surface which results in a double layer capacitance  $C_{dl(fp)}$ . (3) at the electrodes surface, a similar reaction occurs as with the flux-powder interface (not shown).

## Equivalent Circuit Model of Solder Paste

A lumped element equivalent circuit model can be derived by combing the physicochemical interaction within the solder pastes (Figure 2). The equivalent circuit helps with understanding the processes occurring as the solder paste is in use and acts as a reference model to track the degradation of the paste. Those physicochemical interactions are divided into different components: powder resistance – generally negligible for most solder alloys due to their high conductivity –, flux, flux-powder interface, and flux-electrode interface.

The flux component is related to the polarizability and conductivity of the flux and can be modelled by a capacitor,  $C_{flux}$ , and resistor,  $R_{flux}$ , in parallel, respectively. In water-soluble fluxes, the flux is highly active, and has a high ionic content. This leads to a lower flux resistance in water-soluble fluxes compared to no-clean fluxes.

The flux-powder interface reflects the interaction between the flux with the metallic particles. It involves the reaction between the activators present in the flux and the metal particles, which is a diffusion-controlled reaction. The reaction rate is represented by the charge transfer resistance in the equivalent circuit,  $R_{ct (f-p)}$ . After the reaction proceeds, the product (metal salt) must be removed from the surface of the metal. This process is time dependent and represented by a constant phase element,  $Q_{diff (f-p)}$ , and a resistor,  $R_{diff (f-p)}$ , in parallel. A constant phase element represents an imperfect capacitor that is used to describe real-world systems. The time constant associated with this process describes how quickly the metal salt is removed from the surface of the solder ball. In addition, during the reaction, the oxide layer on the metal particle becomes charged. This attracts ions in solution to form a diffusion layer surrounding the solder ball where free ions are attracted to the charged layer. This interaction can be modeled by a capacitor,  $C_{dl (f-p)}$ .

The flux-electrode interface is associated to the interaction between the flux and the electrode material as an artifact of the measurement apparatus. The reaction between the flux and the electrode is modeled similarly to the flux-powder interface. However, the reaction rate is much slower than the one happening between the activators and metal particles. In most cases, the flux-electrode interactions can be ignored.

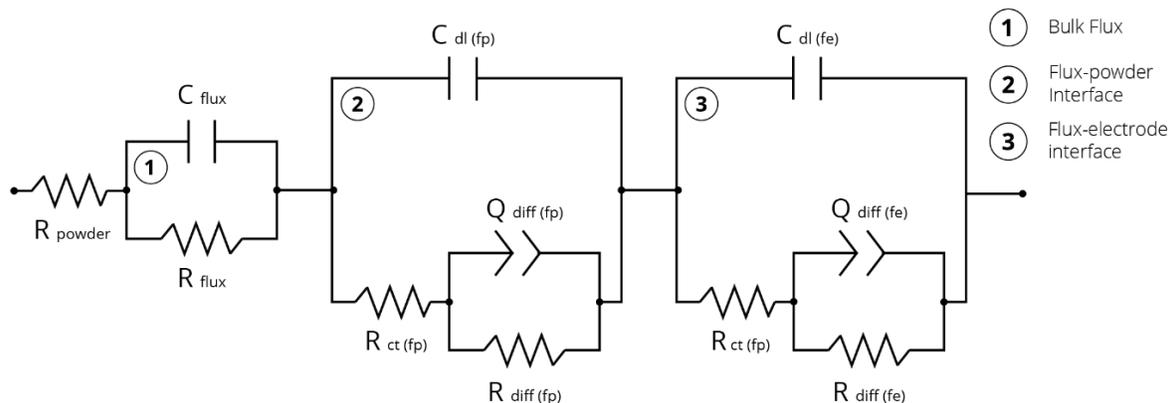


Figure 2. Lumped element equivalent circuit model of solder paste modeling the physicochemical interactions. (1) shows the contribution due to the conductivity and polarizability of the flux media. (2) shows the contribution due to the reaction at the interface between the solder balls and the flux. (3) shows the contribution due to the reaction between the flux and electrode material.

### *Interpreting Impedance Spectra and Fit Circuit Parameters*

When using EIS to measure solder paste in practice, the result is a set of complex impedances measured at different frequencies such as in Figure 3. Some or all the interactions by the flux, flux-powder, or flux-electrode may be visible depending on the chemistry of the solder paste and the measurement parameters. As a glance, the impedance spectra can be qualitatively analyzed by looking at the sizes of each region in the plot. For example, when the flux-powder region is smaller, the reaction occurring at the flux-powder interface occurs more quickly and the solder paste is more active.

The lumped-element equivalent circuit can be fit to the impedance spectra to determine the value of each circuit element. This can then be used to calculate a characteristic time constant for each reaction.

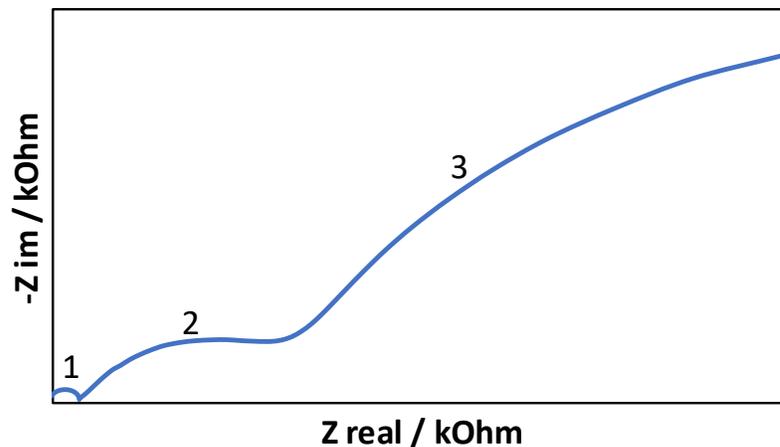


Figure 3. Example of an idealized impedance spectra of a solder paste resulting from the equivalent circuit in Figure 2 represented as a Nyquist plot. The region of the Nyquist plot indicated by (1) is characteristic of the dielectric of the flux, the region (2) is characteristic of the flux-powder interface, and the region (3) is characteristic of the flux-electrode interface.

### *Detecting Failures using Electrochemical Impedance Spectroscopy*

Multiple observed properties of a solder paste are influenced by the reaction between the activator and metal powder oxide layer [13]:

#### *1. Shelf Life*

While it is common to think of solder pastes “activating” at higher temperatures (i.e. the activation temperature), the activator in the flux reacts with the oxide layer surrounding the solder ball even at room temperature or in refrigeration. This reaction results in a thinning of the oxide layer as it is converted into a metal salt. Two different failure mechanisms are common as a result of this reaction during storage [13], [14]:

- 1) Increased viscosity of the solder paste due to the build-up of the metal salt reaction product. The metal salts are generally insoluble and more viscous than the original flux material which causes the viscosity to increase while in storage.

- 2) Clumping due to the complete removal of the metal powder oxide layer. When the metal powder oxide layer is removed, the exposed clean solder alloys can cold weld together, resulting in a clump of solder balls attached together.

These failure mechanisms can be monitored by the impedance spectra through a change in the flux-powder time constant. As the reaction occurs and less reactant is available, the reaction slows which increases the flux-powder time constant.

## 2. Stencil Life

The reaction rate between the flux activator and solder balls is increased as the solder paste is stencil printed because the motion of the solder paste promotes the diffusion of reaction product away from the surface of the solder particle. The oxide layer on the solder balls can be thinned and the solder balls cold welded together resulting in clumps [13]. This process can also be monitored through an increase in the flux-powder time constant.

## 3. Materials and Methods

### 3.1. Materials

Eleven different solder pastes were tested before the printing process (from an as-received jar) and in a simulated stencil printing process. The composition, type, and flux type are included in Table 1. The pastes were stored at 4 °C and the experiments performed at room temperature. In this study, each solder paste container was left out until it reached room temperature. The sample was stirred with a spatula for 2 minutes to redistribute the metal particles homogeneously.

Table 1. Solder pastes used in this study.

Solder Paste	Alloy	Particle size distribution / $\mu\text{m}$	Flux Type
A	Sn <sub>63</sub> /Pb <sub>37</sub>	24-45	Water-soluble
B	Sn <sub>63</sub> /Pb <sub>37</sub>	20-38	No-clean
C	Sn <sub>63</sub> /Pb <sub>37</sub>	25-45	Water-soluble
D	Sn <sub>63</sub> /Pb <sub>37</sub>	25-45	Water-soluble
E	Sn <sub>63</sub> /Pb <sub>37</sub>	25-45	Water-soluble
F	Sn <sub>63</sub> /Pb <sub>37</sub>	25-45	No-clean
G	Sn <sub>63</sub> /Pb <sub>37</sub>	25-45	No-clean
H	Sn <sub>63</sub> /Pb <sub>37</sub>	24-45	No-clean
I	SAC 305	25-45	Water-soluble
J	SAC 305	25-45	Water-soluble
K	SAC 305	24-45	No-clean

### 3.2. Equipment

Electrochemical measurements were performed using the Vision MARK-1 with the E-Chem Insight. A two-electrode probe configuration was used for the EIS measurements (Figure 4).



Figure 4. The two-electrode probe configuration used for the EIS measurements in this study.

Rheological measurements were performed using a Discovery Hybrid Rheometer HR-2 (TA Instruments) and a parallel plate geometry of a 20 mm plate diameter. The rheometer is equipped with an Active Temperature Control (ATC) and all tests were performed at 25 °C with a 1 mm gap width.

### 3.3. Rheology Measurements

It is essential to understand the thixotropic behavior of solder pastes in order to correlate with the structural breakdown and recovery of the paste while in use. For that purpose, the thixotropic rheological test was used to analyze the recoverability of the solder pastes.

In the thixotropic tests, the sample was subjected to low and high shear rates over a specific period and the recovery of the paste was calculated as a function of the viscosity after the high shear rate was removed. The tests were conducted using a shear rate of 0.1 s<sup>-1</sup> for 100 s followed by 10 s<sup>-1</sup> for 120 s and then back to the initial shear rate of 0.1 s<sup>-1</sup> for 100 s. The shear rates were chosen to avoid the solder paste from propagating out between the parallel plates during the measurements. The recovery of the paste was calculated based on equation 1:

$$Recovery (\%) = \frac{\eta_{0.1 Recovery}}{\eta_{0.1}} \times 100 \quad \text{Eq. 1}$$

Where  $\eta_{0.1 recovery}$  is the measured viscosity at the shear rate of 0.1 s<sup>-1</sup> (after removal of the 10 s<sup>-1</sup> shear rate) and the  $\eta_{0.1}$  is the measured viscosity at the beginning of the test at 0.1 s<sup>-1</sup> [6].

### 3.4. EIS Measurements

The impedance spectra were recorded using a two-electrode probe configuration (Figure 4). The spectra were measured with an AC amplitude of 0.1 V RMS by sweeping the frequencies from 10 kHz to 1 Hz at 10 points per decade and the measurements were performed at the open circuit potential (OCP). The samples were prepared by spreading the solder paste on the electrode comb using a stencil with a thickness of 0.5 mm (Figure 5).



Figure 5. The probe covered with solder paste for EIS measurements.

The obtained impedance spectra were fitted using the Powell algorithm. The equivalent circuit presented in Figure 2 was used to fit each spectrum. The initial parameters to start the fit were determined for each solder paste separately to have an accurate fitting based on the resistance values obtained in the Nyquist plot.

Time constants of the powder-flux interface were calculated from the fitted values using the following equation:

$$\tau = (RQ)^{1/n} \quad \text{Eq. 2}$$

Where  $\tau$  is the time constant,  $R$  is the diffusion resistance at the powder-flux interface,  $Q$  is the diffusion constant phase element, and  $n$  is the degree of deviation from an ideal capacitor ( $0 - 1$ ) [11].

### 3.5. Incoming Inspection of Solder Pastes

Incoming inspection tests were conducted using 40g jars of solder paste. The solder pastes were subjected to 40 °C in a conventional oven for 78 hours to create a worse-case storage and shipping condition. Samples were taken from each jar after specific times to run the rheological and electrochemical measurements. After taking a sample, the jar was placed in the oven again. The samples were left out to reach room temperature before running any of the experiments.

### 3.6. Process Control of Solder Pastes

Solder paste process control tests were performed using an apertureless stencil printer. The solder paste was placed in the stencil printer to start “using” the paste, as squeegees rolled the paste back and forth on the stencil to simulate a printing process. Samples for rheology and EIS measurements were taken from the initial moment of opening the jar after stirring the paste and from the stencil printer every hour while using the paste. The experiments were carried out for 12 hours for both solder pastes.

## 4. Results and Discussion

### 4.1. EIS Sensitivity Analysis

EIS measurements were performed for the solder pastes presented in Table 1. Figure 6 shows the spectra obtained for different solder pastes with different flux types and alloys. There are clear differences between the pastes, showing that water-soluble pastes have lower impedance values compared to no-clean ones. This is related to the different components (activators, solvents, etc.) and characteristics of the paste, such as water-soluble solder pastes containing fluxes with higher conductivity due to their polar nature.

For some pastes, components of the flux, flux-powder, and flux-electrode are visible after measurements. However, for some water-soluble pastes using the same frequency range, the flux component is not seen. Higher frequencies are needed to see the complete spectrum, since the system is dominated by low impedance elements due to the high conductivity of the flux. On the other hand, for some no-clean solder pastes, the component of the flux-electrode interface is not seen due to their high impedance, which is related to the high resistance of the solder paste and lower frequencies are needed to see the flux-electrode component. In addition, there are clear differences between the alloys of paste, which show different time constants for the flux-powder interface due to the varying metal composition. These results point out that EIS is able to differentiate between water-soluble and no-clean solder pastes as well as contrasting alloys.

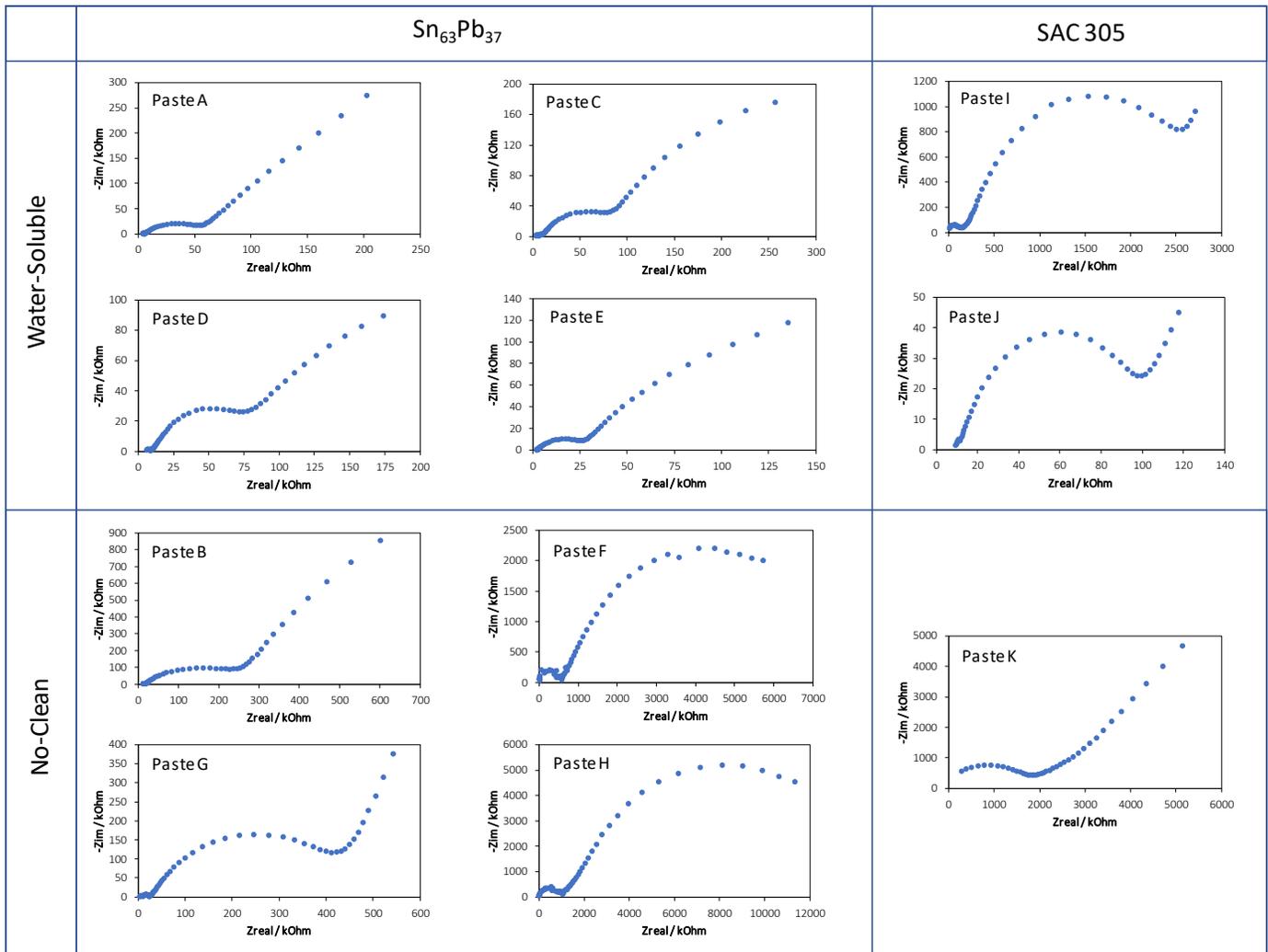


Figure 6. Impedance spectra for each solder paste in this study represented as Nyquist plots. The impedance spectra can be used to determine various properties of each solder paste. In general, the water-soluble solder pastes were more active than no-clean solder pastes as evident by the smaller flux-powder semicircle that corresponds to a lower flux-powder time constant. Of the water-soluble flux pastes, Paste E was the most active followed by Paste A, Paste D, Paste C, and Paste J. Paste I was far less active than a typical water-soluble paste. Of the no-clean solder pastes, Paste B and G were the most active, followed by Paste K, with Pastes F and H being far less active than the rest of the no-clean solder pastes.

## 4.2. Incoming Inspection of Solder Pastes

The purpose of the incoming inspection tests was to simulate an accelerated aging process of a solder paste. This is related to the possible problems of a solder paste as the jar is received such as experiencing poor shipment/handling conditions. During the shipment of solder paste, the storage and transportation conditions of a jar are unknown, which could put the quality of the paste in jeopardy. Therefore, a method of incoming inspection must be implemented to evaluate the integrity of a solder paste before beginning the printing process.

### 4.2.1. Rheological Measurements for Incoming Inspection

In the thixotropic tests, the change in the structure of the solder pastes is studied over different shear rates. Figure 7 displays the recoverability of the solder pastes as a function of time from storage at 40 °C. It can be observed that there was a decrease in recoverability of the pastes over 78 hours in the oven. It was expected that the paste would become less recoverable the longer it remained in elevated temperatures. The reaction rate between the activators and the oxide layer on the metal particles is increased at higher temperatures. This causes the formation of salts and/or metal clumps, affecting its rheological properties.

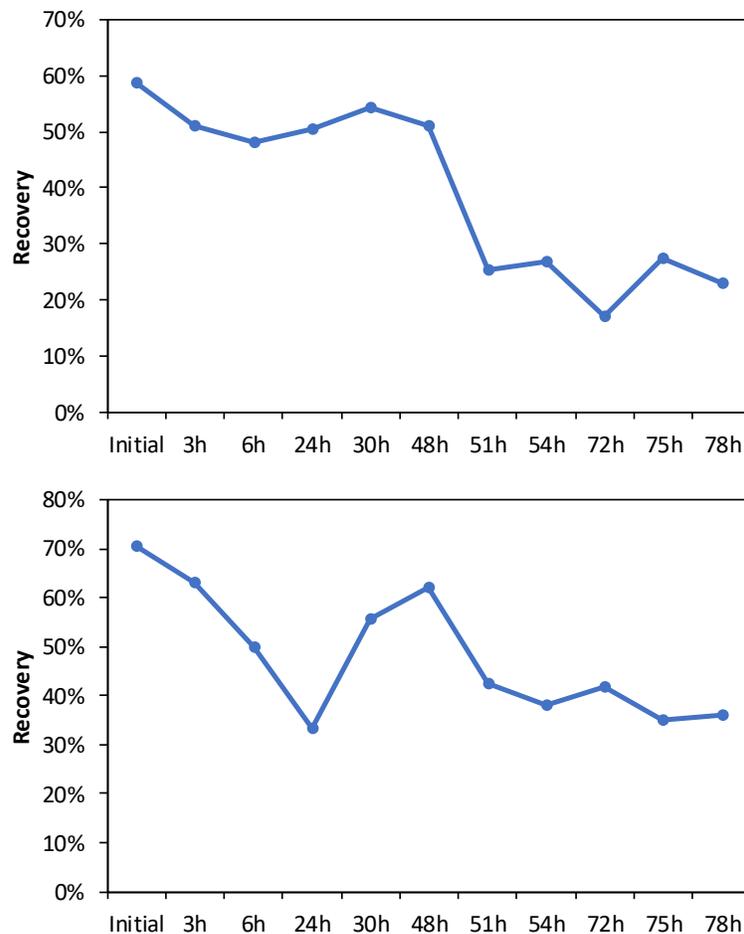


Figure 7. Recoverability over time for Paste A (top) and Paste B (bottom) stored at 40 °C for different periods of times.

#### 4.2.2. Electrochemical Measurements for Incoming Inspection

Figure 8 shows the time constants of the flux-powder interface calculated from the EIS measurements. It can be observed that there is a direct correlation between time constants over time. As the time being stored at 40°C increases, the time constants increase. These results indicate that the physicochemical properties of the solder pastes are changing as a result of the high temperature during prolonged times. Based on the results, EIS measurements are capable of monitoring these changes; therefore, it is possible to use this technique to predict if a solder paste is acceptable for use in the printing process. Additionally, the values of the time constants for Paste A are one order of magnitude lower than the ones obtained for Paste B. These results agree with the difference in flux types for each solder paste as mentioned above.

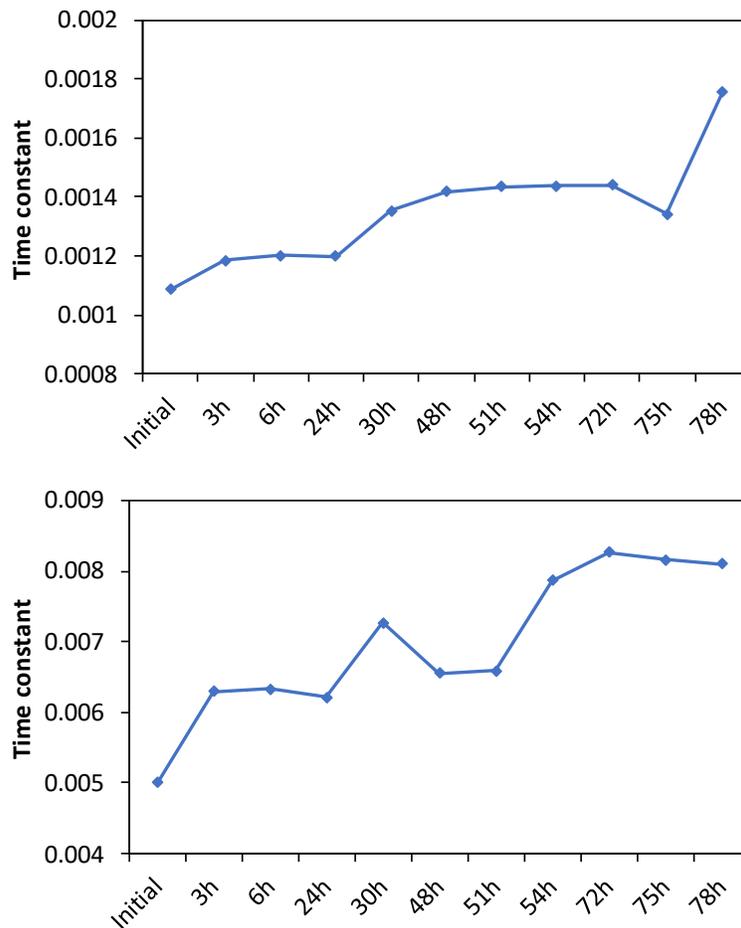


Figure 8. Flux-powder time constants for Paste A (top) and Paste B (bottom) stored at 40 °C for different periods of time.

#### 4.2.3. Correlation Between Rheological and Electrochemical Measurements

Based on the incoming inspection tests, there was a correlation between the time constants from EIS measurements and the recoverability of the solder paste after being stored at 40 °C for different periods of time (Figure 9). An increase in the time constant reflects a decrease greater than 10% in the recoverability of the material due to the properties of the paste changing from the elevated temperatures (solvent evaporation and/or separation, metal oxidation, etc.).

These changes directly impact the printability of the material, in terms of slumps, skips, etc. This shows that elevated temperatures impact the characteristics of solder paste, but through rheological and electrochemical measurements, these changes can be detected.

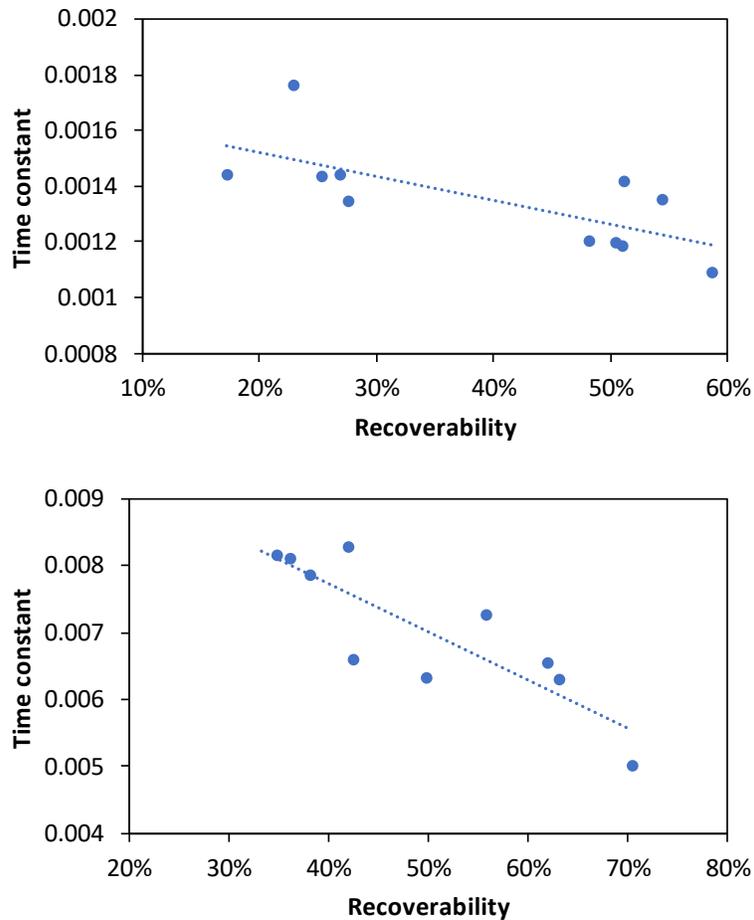


Figure 9. Time constants vs. recoverability of Paste A (top) and Paste B (bottom) from the incoming inspection tests.

### 4.3. Process Control of Solder Pastes

The purpose of these tests was to determine the correlation between the rheological and electrochemical properties of solder pastes to be able to assess its fitness for use

#### 4.3.1. Rheological Measurements for Process Control

Figure 10 shows the viscosity measured as a function of time. In all cases, the viscosity after applying a high shear rate was always lower than the initial viscosity at the same shear rate. As the solder paste remained on the stencil printer for an extended amount of time, the result was a decrease in recoverability where the paste changed due to the shearing that causes a structural breakdown [15].

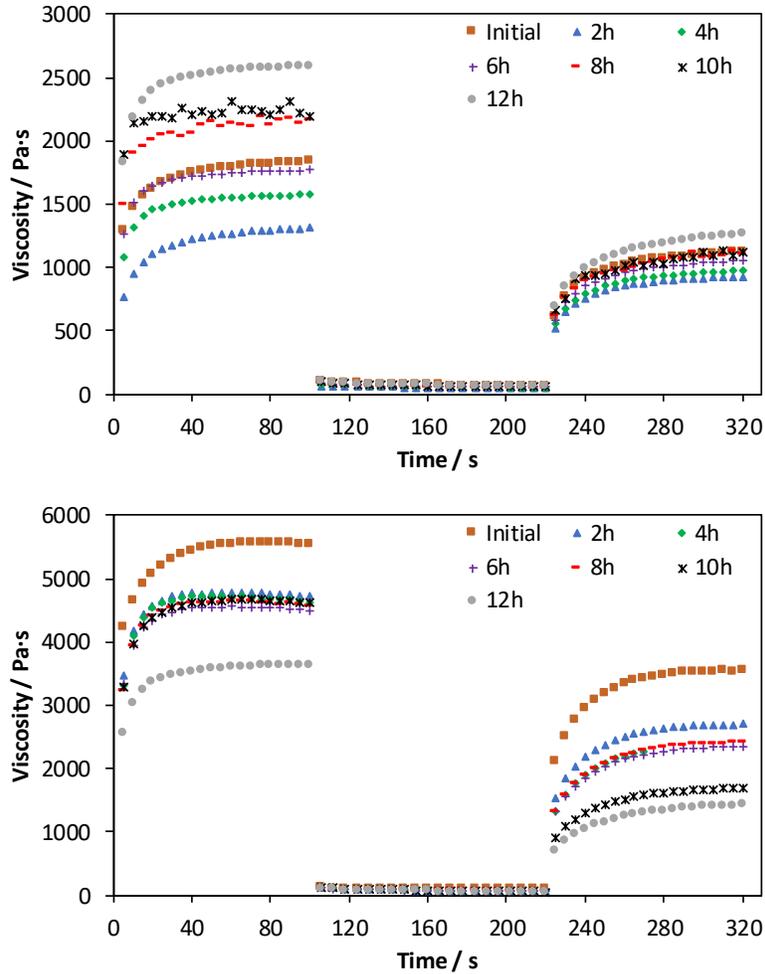


Figure 10. Viscosity over time in the thixotropic tests for Paste A (top) and Paste B (bottom).

Based on the results, the solder pastes never completely recover (100%) while being continuously worked on the stencil printer. The recovery decreases as the time on the printer increases (Figure 11). The structural breakdown of the paste during rheological measurements relates to the high forces, or shear rates, that are applied to the pastes; similar to the forces produced during the solder paste stencil printing process. The recoverability is an important aspect for determining the printability of a paste, which can be related to the amount of time a paste is able to move through an aperture and get back to its initial properties. The viscosity of the paste must be low enough to flow into the apertures, and recover its initial viscosity after the applied force to avoid slumping problems [16]. Although the trend for both pastes is similar, different recovery rates were obtained for the two different solder pastes, a decrease of 12% and 25% in recoverability was seen for Paste A and Paste B respectively. Different recoveries among pastes give an indication of the stencil life of the pastes; Paste A would have a longer stencil life than Paste B. This could be related to the different components of each solder paste (solvents, activators, fluxes, etc.), which lead to a different response to the constant stress applied by the squeegee and environmental conditions.

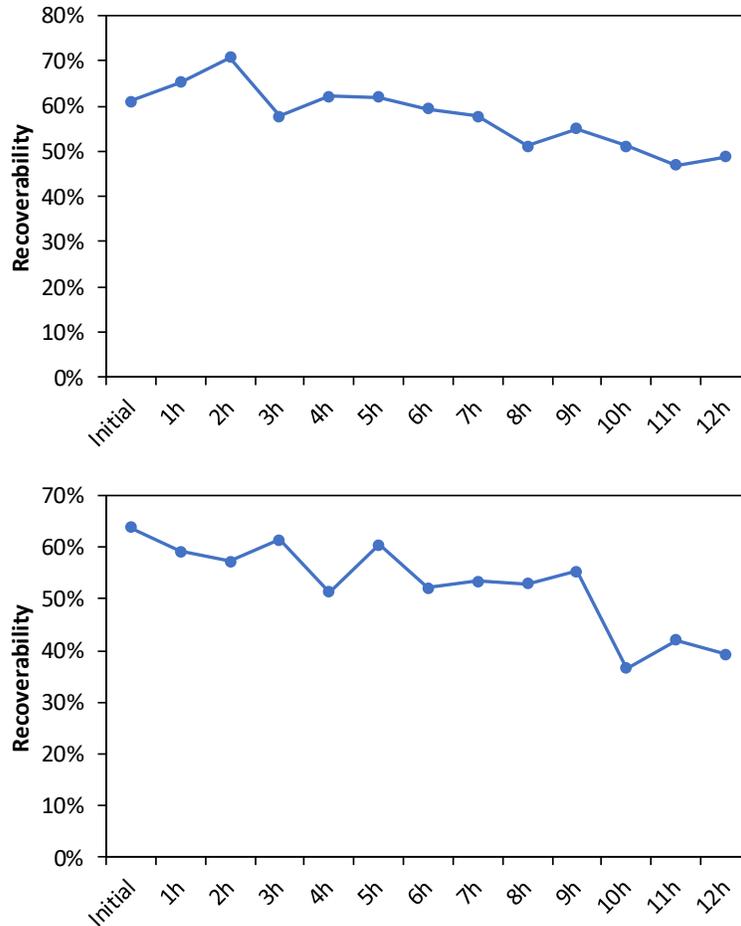


Figure 11. Recoverability over time for Paste A (top) and Paste B (bottom).

#### 4.3.2. Electrochemical Measurements for Process Control

Figure 12 displays the flux-powder time constants calculated for both pastes from the fitness for use tests coupled with the thixotropic tests. The time constants increase as the time the pastes were being used increases, indicating the reaction rate of the flux-powder interface is decreasing. Similarly, to the rheological measurements, both solder pastes have the same trend, but the time constants are different for each solder paste. Paste A has time constants that decrease by 50%; whereas, Paste B has a 56% decrease. As the change in time constants increases, the change in recoverability increases over time, which is directly associated with the stencil life of the solder pastes. This is due to the generation of reactant products surrounding the metal powder and the availability of the activator to sustain the reaction rate. In effect, this is rate limiting reaction behavior between the metal powder and flux activator. As mentioned in the incoming inspection section, time constants for the water-soluble solder paste were one order of magnitude lower than the no-clean solder paste. The time constant values are consistent from one test to another, pointing out the reproducibility and reliability of the EIS measurements to track changes in the solder paste.

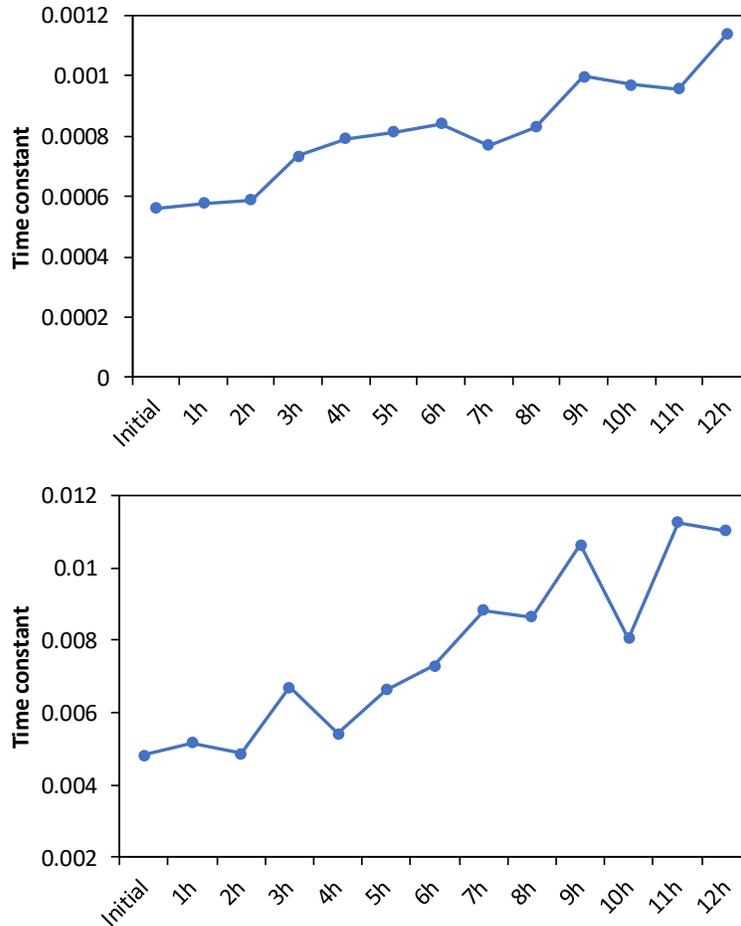


Figure 12. Flux-powder time constants over time for Paste A (top) and Paste B (bottom).

### 2.2.5 Correlation Between Rheological and Electrochemical Measurements

The objective of this study was to determine the correlation between the rheological and electrochemical properties of solder pastes to be able to assess its fitness for use. The thixotropic tests establish a correlation with the electrochemical measurements. There is a direct correlation between the time constants calculated from the EIS measurements and the recovery calculated from the rheology measurements, as seen in Figure 13. As the solder pastes are being used in the stencil printer, the recoverability of the paste decreases due to the structural breakdown. That structural change is also seen as an increase in the flux-powder time constants, which is related to the change in the interaction of the flux with the metallic particles caused by the chemical reactions and flux evaporation occurring while the paste is being used. The results offer evidence that EIS is a powerful tool that can be used to predict the behavior of the solder pastes and determine if the paste is fit for use.

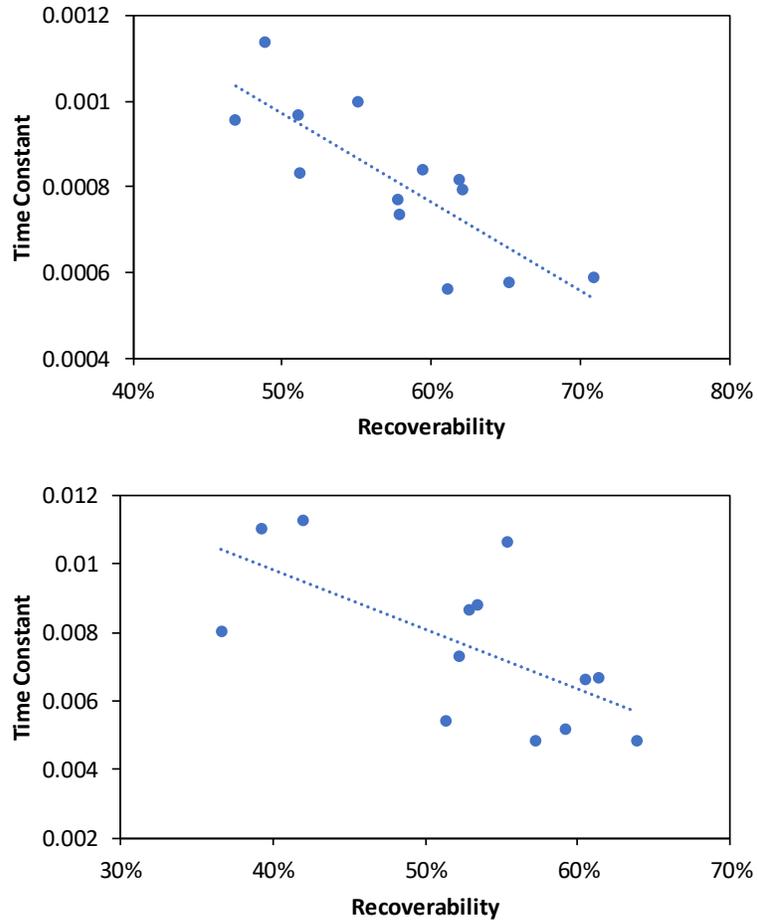


Figure 13. Time constants vs. recoverability of Paste A (top) and Paste B (bottom) from fitness for use tests.

## 5. Conclusions

Electrochemical and rheological measurements were performed to establish the correlation between the electrochemical and rheological properties of solder pastes. The mishandling of solder pastes was simulated to determine the changes in these properties when improperly stored. Additionally, the pastes were studied at the conditions of a stencil printing process, to track the changes while the pastes were being used. The results depicted a decrease in the recoverability of the pastes when they are improperly stored at 40 °C and used over a 12 hour period. On the other hand, the values calculated from electrochemical measurements show the opposite trend, increasing time constants over time.

The results obtained in this study show that EIS is an innovative technique that can be used to predict the recoverability of solder pastes and consequently be able to determine if the solder paste is fit for use in the printing process and/or give an indication if is the root cause of defects (slumps, skips, etc.) in the printing process.

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