FURTHER INVESTIGATIONS OF CORROSION IN THE CLEANING PROCESS

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ABSTRACT

This paper is a continuation on an investigation into the mechanism(s) of metallic corrosion in the cleaning process. With the increased demand placed on increasing the reliability and functionality of Printed Circuit Board Assemblies (PCBAs) while at the same time decreasing the size and environmental impact manufacturers are having to use new materials and reevaluate reliability. One way to increase reliability is by cleaning the PCBAs to remove contamination, such as flux residues, which can cause or at least contribute to, numerous failure mechanisms. The combination of new materials and the need for cleaning to ensure reliable end products, which may have to have a lifetime of 25+ years in harsh environments, is leading to questions about the impact that the cleaning process has on PCBAs.

The most common cleaning process is an aqueous cleaning process which utilizes an Engineered Aqueous Cleaning (EAC) agent. EACs are multifunctional cleaners designed to achieve many seemingly contradictory goals. To penetrate, wet and flow under low profile components, the wash solution must exhibit a low surface tension. Once the cleaning agent has successfully removed the residue set, the wash fluid must be rinsed out using high surface tension rinse water. At the same time EACs must be compatible with a wide range of materials. While plastics and glasses may corrode, it is metals which are at the greatest risk of corrosion and are the focus of this paper.

We examine the corrosion mechanism and rate of two cleaning agents, a pH neutral and an EAC cleaning agent with four common metals used in PCBAs: eutectic tin lead solder, lead free solder (SAC305), copper, and high lead solder. In this study we look at the impact of temperature and fluid flow rates have on both the electrochemical corrosion process as well as the morphological changes caused by the corrosion.

Key words: Reliability, Cleaning, Flux, Corrosion, Compatibility

INTRODUCTION

Modern electronics manufacturing has become increasingly difficult due to the increased demands placed on electronic devices. The need for small, highly reliable electronics that will be used in environments which until recently were considered too harsh for Printed Circuit Board Assemblies (PCBAs) has pushed electronics manufacturing to the edge of current manufacturing technologies.

Additionally, there are more legislative constraints, such as environmental regulations, being placed not only on the PCBAs but their manufacturing process as well. In addition to the elimination of lead from many PCBAs, regulations are restricting the use of brominated solvents (e.g. n-propyl bromide), or Volatile Organic Compounds (VOCs).

Due to the need for a reliable densely populated PCBA, the tolerance for contamination, particularly ionic contamination, is greatly diminished. Bleeding edge components, such as QFNs, now have such low standoff heights that the no clean fluxes cannot properly off gas the volatile activators, or their decomposition products, leaving an active flux residue behind. This flux residue can then interact with the with metals present on the PCBA, such as solder, and lead to corrosion related failure mechanisms. Additionally, the electrochemical reactions that occur during corrosion are accelerated by increases in the electric field strength, which increases as the pitch of Surface Mount Devices (SMDs) decrease.

Cleaning

Aqueous cleaners, regardless of type, are complex mixtures of additives designed to balance a wide range of potentially conflicting parameters. Broadly speaking, the most important cleaning agent additives for the corrosion process are solvents, the buffering system, and corrosion inhibition. There are more additives, such as surfactants, which will influence the corrosion process in a less direct way.

One or more solvents may be included to tailor the solvency of the cleaning agent to be a “broad spectrum cleaner” or may be included to be more effective at solubilizing a certain flux at the expense of the cleaning agent not being able to solubilize another flux. As the percentage of solvent increases, the solvent will influence the available electrochemical pathways of corrosion, especially for immiscible solvents. The solvent layer will generally have a higher resistance than the aqueous layer, and the electrochemically active species may have different mobilities than in a purely aqueous environment. Furthermore, if there is an organic or solvent phase each additive will have a certain solubility in both the organic and aqueous layer, and will reach this equilibrium potentially depleting or enhancing the concentration in each phase.

Buffer systems are an essential part to a robust cleaning process as it ensures long bath life, by keeping the pH of the cleaning agent relatively constant over time. Buffers consist of combinations of acids or bases and their related salts, which sets up an equilibrium reaction.

As most flux residues are acidic as flux residues are dissolved in the cleaning agent the pH of the cleaning agent will decrease over time. This has two detrimental effects to the cleaning process. First, as the pH lowers the solubility of the acidic flux residues will decrease until the cleaning agent stops functioning. This is because, in general, organic acids are more soluble in alkaline pH due to the neutralization reaction. Secondly, as the pH of the solution becomes more acidic, metals tend to corrode more as the hydronium ion (H_3O^+) concentration increases[1]. Buffers can be created at any pH and be designed to have a specific buffer capacity, or amount of acid or base that can be added before the buffer is consumed by the reaction. There is no pH, be it pH 7 or any other pH, which is universally compatible with all metals. Instead the pH of the cleaning agent must be tailored to match the metals which are in use.

Virtually all cleaning agents have some corrosion inhibition contained in their formulation. There are many ways to inhibit corrosion in the aqueous cleaning process, but the two that are of concert to the present discussion are the pH of the aqueous cleaner bath, and corrosion inhibitors. In an aqueous solution the pH can play a significant part in the corrosion process. This is because water can be oxidized or reduced, which can be a source or sink of electrons. As noted above, most fluxes are acidic, and when the finite buffer capacity of an aqueous cleaning agent is consumed, the pH will begin to decrease rapidly. Corrosion inhibitors, on the other hand, do not change appreciably with increases in soil load. There are many different types of corrosion inhibitors, and mechanisms in which they work that it is beyond the scope of this project. However, one of the most common methods of corrosion inhibition involves forming a protective barrier between the metal surface and the aqueous environment. This layer typically, is an adsorbed monolayer on the order of 7-20 molecules thick. While it is true that this allows for the depletion of the corrosion inhibitor, the concentration of the corrosion inhibitor in the cleaning agent is typically orders of magnitude higher than the minuscule amounts required to form a monolayer.

Corrosion

Historically electronic engineers and electrochemists each developed their own terminology and conventions when it came to the study of the same process, and as one would expect they did NOT independently arrive at the same answers, nor did they come to an agreement, nor are their terminology or conventions polar opposite so that one may just invert everything. Sadly, these two fields came up with a hodgepodge of terminology that confuses even the seasoned practitioner. For this paper, the Stockholm sign invariant convention is used[2].

In this convention positive potentials, with respect to E_{corr}, which is the potential at which corrosion is occurring at the highest rate, are defined as oxidation potentials and negative potentials are reduction potentials; the currents resulting from the oxidation reaction is called the anodic current and has a positive sign, and the reduction reaction causes a cathodic current, which has a negative polarity.

As corrosion is such a vast topic, including many different types of corrosion, the following discussion will be limited to a broad overview of corrosion in the PCBA cleaning process, namely in a primarily aqueous solution[3]. Corrosion, in its simplest form, is the oxidation of a metal surface. During this process, the metal atoms transfer one or more electrons to another atom and becomes a cation. The released electrons either flow through the cleaning agent or through an external conductor (such as fixtures). These electrons are then taken up by another chemical species in a reduction process as depicted in Figure 1.

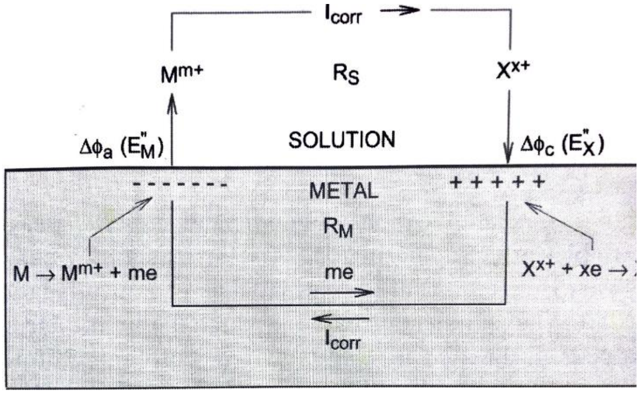

Figure 1. Overview of corrosion process, adapted from Stansbury[4]

This oxidation process is the primary concern in the cleaning process, as it directly effects the metal surface. Dissolving the metal surface is only one of the possible ways corrosion can manifest. There are local changes in pH and electrical potential which may cause oxides, hydroxides, or other metal salts to form directly on the surface of the metal, or these processes may occur in the solution phase resulting in a precipitate.

EIS

The method chosen to study the corrosion process for this study was Electrochemical Impedance Spectroscopy (EIS).

This technique is very nuanced and for more information please consult a text on the subject [5]. In summary, EIS attempts to model an electrochemical system based off of changes in impedance vs. frequency. A small amplitude (c.f. 10 mV_{RMS}) sinusoidal signal is applied to the working electrode. It is swept from a high frequency of typically 10 kHz or 100 kHz to a lower frequency, usually 10 mHz. At each frequency the impedance is measured, yielding the "spectrum" of the electrochemical system's impedance.

Next an empirical model is created to describe the observed impedance behavior. This empirical model typically takes the form of an electric circuit, called an equivalent circuit, as it produces an impedance that matches the frequency response of the electrochemical system. The equivalent circuit consists of typical circuit elements such as resistors (R), capacitors (C), and inductors (L). However, there are certain other circuit elements, such as Warburg impedances (Z_w), which are related to diffusion and are in between a perfect capacitor and perfect resistor, distributed circuit elements, transmission lines, etc.

The objective in fitting the data is not to create an equivalent circuit that most closely models the data, but instead represents the physical processes occurring in the electrochemical system. One of the simplest equivalent circuits is the Randel's Cell, Figure 2. It represents a simple interface between a metal electrode and an electrolyte. The resistor, R_s, is the resistance of the electrolyte, in this case the cleaning agent, at infinite frequency. The other resistor, R_{ct}, is known as the Charge Transfer Resistance, and is related to the resistance encountered in transferring electrons from the metal to the external circuit. The corrosion rate is directly proportional to the charge transfer resistance. The next circuit element, the Warburg Impedance (Z_w) is an optional circuit element, which is related to the rate of diffusion of electrochemically active species. It is intermediate, in terms of phase shift, between a pure resistor (phase shift of 0°) and a pure capacitor (phase shift of 90°), with a phase shift of 45°. Whether or not it is significant is complex and depends on things such as the hydrodynamic conditions at the electrode surface, the topography of the electrode surface, as well as the rates of individual reactions. The last circuit element is the interfacial or double layer capacitance (C_{dl}) which occurs at the interface of the metal surface and the solution. At this interface, there are extremely high electric fields as an electrical double layer is formed over the span of a few Angstroms. The counter electrode serves as the other plate of the capacitor.

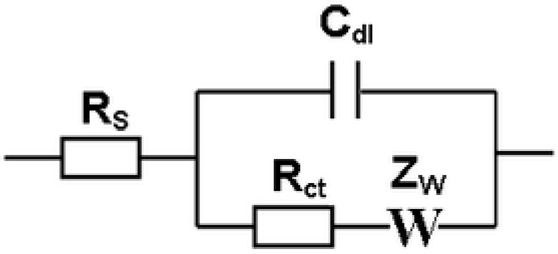

Figure 2. Randel's cell.

METHODS

Two commercially available cleaning agents were used in this study. One, is marketed as a pH Neutral cleaning agent, the other is an Engineered Aqueous Chemistry (EAC). Both cleaning agents are designed with a target concentration of 15% (wt.%) and are comparable in properties and performance, and some relevant properties are shown in **Table 1**. The key difference, for the purposes of this study is the pH neutral has a pH of 7.6 and the EAC has a pH of 9.6. The pH scale is a logarithmic scale, meaning the EAC is one hundred times more alkaline than the pH neutral cleaning agent. The cleaning agents were diluted with DI water to a nominal concentration of 14 wt.%, so that results from prior work can be compared[6, 7]. An additional concentration of 0.1 wt.% was intended to be run to represent conditions typical of a rinsing process, where all the constituents of the cleaning agent are dilute, which may be a more challenging test. However, due to time limitations caused by COVID-19, this additional concentration had to be deferred until a future study.

Table 1. Comparison between cleaning agents

Property	EAC	pH Neutral
pH (@ conc.)	9.6 (@15%)	7.6 (@15%)
Typical conc. (wt.%)	10-15%	10-15%
Conc. Used (wt.%)	14.0±0.2%	
Temperature	25±5 °C	

An additional key variable that had to be deferred was the temperature of the cleaning agent. Temperature is generally a significant contributor towards the corrosion rate. A general rule of thumb is at temperatures near room temperature, every 10° C increase doubles the reaction rate. Since the cleaning process is typically heated this may become a significant factor in metal compatibility.

The experimental setup was identical to those in the prior studies. A corrosion cell was modified to permit a recirculating loop which consisted of a peristaltic pump and a modified Erlenmeyer flask to serve as a reservoir. The Erlenmeyer flask contained a magnetic stir bar and was continuously stirred at a constant 800 rpm to ensure that the cleaning agent in the recirculating loop was homogeneous.

The working electrode had an exposed area of 1 cm^2 and was the same working electrode in the prior studies. This was a piece of a commercially purchased SAC-305 solder bar. Prior to use the face of the working electrode was mechanically polished through the series of 240 grit, 320 grit, 400 grit, and finally 600 grit silicon carbide grinding disks. Immediately after the 600-grit polishing the working electrode was rinsed with acetone, dried, and used. The only other metal that was in contact with the cleaning agent was the counter electrode, which serves as the other current carrying electrode. The counter electrode was a standard platinum mesh electrode. As with the prior studies the reference electrode was a Hg/HgO electrode due to its compatibility with alkaline solutions.

The peristaltic pump serves a dual purpose. First, it continuously moves the cleaning agent ensuring that phase separation does not occur. The second is by examining the changes in either the equivalent circuit or the parameters of the circuit elements, diffusion effects may be determined. With the high turbulence of the cleaning process, it is suspected that diffusion effect may be significant in the corrosion process. As the cleaning agent is rapidly and continuously flowing over the surface of the metal an equilibrium is not reached. Two arbitrarily chosen flow rates 62 mL/min and 890 mL/min were studied.

Once the cleaning agent was prepared the system was filled with it. The flow rates were run in a randomized order to minimize any systematic error. The first flow rate was set, and the Open Circuit Potential (OCP) was measured until it reached a stability of 0.1 mV/min. At that point, an initial OCP value was measured, and the EIS data was collected at an amplitude of 10 mV_{RMS} from this initial OCP. The frequency was swept from 100 kHz down to 10 mHz. Upon completion of the EIS scan, the pump was set to the next randomized flow rate and the process was repeated. Under ideal circumstances a freshly polished working electrode would be used to eliminate any surface changes (topology, oxide growth, etc.), however due to the alternating polarity of the working electrode in EIS this is generally not an issue[8]. In between the two cleaning agents the entire apparatus was disassembled, washed, rinsed with DI water, rinsed with acetone, and then dried.

RESULTS

Data Analysis

The resulting twenty electrochemical impedance spectrum were each individually fitted to the Randel's Circuit[9]. Then each of the parameters were analyzed for differences using a Two-Way ANOVA. The following discussions will focus on R_{ct} only, as it is the most germane to the topic at hand, however a more complete model of corrosion in the cleaning process will be constructed in future work.

For clarity in the following plots, the data at each point was averaged and the model was fitted to the average data. In general, the fits were of good quality with the EAC data being slightly better fit by the model than the pH Neutral data. There was one run of pH Neutral which was a statistical outlier and was removed from the data analysis.

Figures 3 and 4 show the Bode Phase and Bode Magnitude plots, respectively. It is unclear from the data if there is a diffusion component to the data, as the phase does not return to a purely resistive impedance, nor does the impedance magnitude become constant at low frequency. While there are minor differences between chemistries and flow rates it does not visually appear that there is a significant difference.

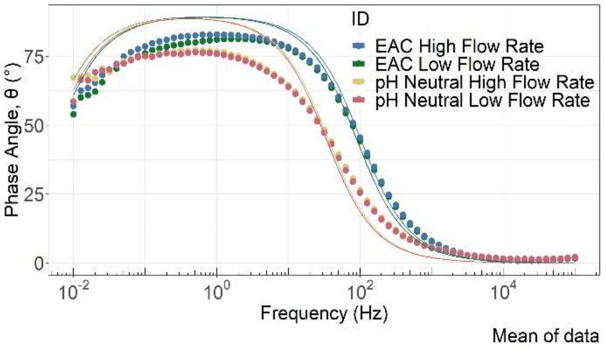

Figure 3. Bode phase impedance plot.

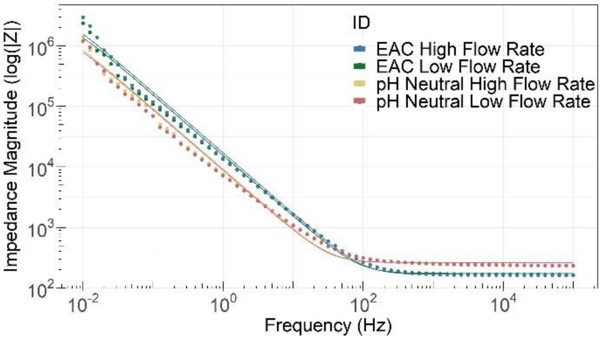

Figure 4. Bode impedance magnitude plot.

The Nyquist plot, **Figure 5**, shows possible evidence for diffusion involvement in the corrosion process. However, there is not a substantial difference between the two flow rates, which may indicate a different mechanism.

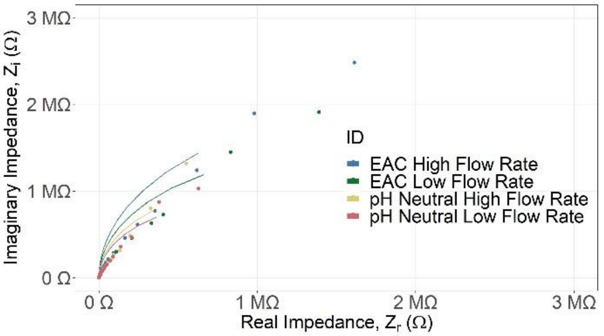

Figure 5. Nyquist plot of the impedance data.

The usual assumptions of ANOVA (e.g. normality, homoscedasticity, etc.) were verified, and then a two-way ANOVA was run on the data,

Table 2 [10]. The ANOVA results indicate that there were no statistically significant differences between cleaning agents, flowrates, or interactions between the two, with regards to the charge transfer resistance (R_{ct}). As noted previously, the charge transfer resistance is related to the corrosion rate. This implies that *ceteris paribus*[i] there is no difference in corrosion rate between the two chemistries.

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[i] *ceteris paribus* translates from Latin as "if all other relevant things, factors, or elements remain unaltered"

Table 2. ANOVA results for R_{ct}

Effect	DFn	DFd	F	p
Flow Rate	1	15	0.037	0.851
Chemistry	1	15	1.785	0.201
Flow Rate :Chemistry	1	15	1.143	0.302

CONCLUSIONS

Findings

The results of no difference in charge transfer resistance between a pH Neutral cleaning agent and an EAC cleaning agent in this study, while boring, illustrates an important point. The pH of a solution does not determine its corrosiveness in isolation. Corrosion is a complex process and claims that one pH is better than another has no basis. Metal compatibility with the cleaning process is a key parameter in choosing a cleaning agent, and there is scarce information out there that quantifies the corrosion.

A more detailed investigation of the corrosion mechanisms in the cleaning process is underway. It is hoped that a qualitative model of the corrosion in the cleaning process may be developed, and then expanded into a quantitative model. Additional cleaning process factors, such as temperature, soil loading, and additional metals needs to be included to provide a useful model, which allows for the prediction of metal compatibility issues, and in cases of unavoidable incompatibilities can be used to estimate any changes in service life of the PCBAs. This additional work is currently in process.

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