

“PARTIALLY-ACTIVATED” FLUX RESIDUE IMPACTS ON ELECTRONIC ASSEMBLY RELIABILITIES

Yanrong Shi, Ph.D., Kyle Loomis, Jennifer Allen, Bruno Tolla, Ph.D.

Kester, Inc
Itasca, IL, USA
yshi@kester.com
kloomis@kester.com

ABSTRACT

The reliabilities of the flux residue of electronic assemblies and semiconductor packages are attracting more and more attention with the adoption of no-clean fluxes by majority of the industry. In recent years, the concern of “partially-activated” flux residue and their influence on reliability have been significantly raised due to the miniaturization along with high density design trend, selective soldering process adoption, and the expanded use of pallets in wave soldering process. When flux residue becomes trapped under low stand-off devices, pallets or unsoldered areas (e.g. selective process), it may contain unevaporated solvent, “live” activators and metal complex intermediates with different chemical composition and concentration levels depending on the thermal profiles. These partially-activated residues can directly impact the corrosion, surface insulation and electrochemical migration of the final assembly. In this study, a few application tests were developed internally to understand this issue. Two traditional liquid flux and two newly developed fluxes were selected to build up the basic models. The preliminary results also provide a scientific approach to design highly reliable products with the goal to minimize the reliability risk for the complex PCB designs and assembly processes.

Key Words: Reliability, SIR, ECM, Flux Residue, Low Stand-off device, Selective Soldering, Pallet, Solder Paste, Chemical Flux

HOW FLUX APPEARS IN UNDESIRABLE AREAS ON A PCB ASSEMBLY

Liquid fluxes are widely used in wave soldering process for through-hole connectors in PCB assembly. Flux removes the surface passivation layer and improves the wetting of molten solder into the barrels. In order to prevent the solder wave from contacting SMT components or to protect temperature sensitive components, engineers are likely to choose pallets with various window designs for wave soldering process, as shown in Figure 1. In some cases, liquid flux residues can be observed in the space between the pallet and PCBs (out of the windows) and under nearby SMT components, where the flux never contacts the molten wave.

With the industry trend towards miniaturization, the number of through-hole connectors is decreasing on PCB assembly. Through-hole connectors and SMT devices are also getting closer with high density assemblies, making the pallets application more challenging. Therefore, selective soldering is getting more popular in turn of increasing the assembly flexibility, shown in Figure 1. Most commonly, process engineers choose the low solid no-clean liquid flux product on the market for selective soldering, even though these fluxes were designed for traditional wave soldering. In this particular application, the solder wave only contacts defined areas, which could be much smaller than the flux applied areas and leave partially-activated flux residue after the soldering process. The partially-activated flux residue phenomena on both pallets and selective soldering system are more likely due to two major reasons.



Figure 1. A pallet for wave soldering on the top (Photo from QTEC); selective soldering on the bottom (Photo from ERSA).

1. Inappropriate assembly process settings

For through hole application, IPC standard JSD-001C requires >50% hole fill for Class II and >75% hole fill for Class III solder joints. In order to meet this classification, excessive liquid flux is usually applied to increase barrel fill, especially on thick challenging boards in lead-free assembly. The extra flux can be over sprayed to the top side of the board through the barrel and get trapped under the connector package and nearby components. In Figure 2, a current liquid flux product was dyed in red and sprayed on a through-hole connector to show the flux deposit on the top side of PCB. The flux volume is approximate $380 \mu\text{g}/\text{cm}^2$ of solid content on the board, doubled the recommended flux volume.

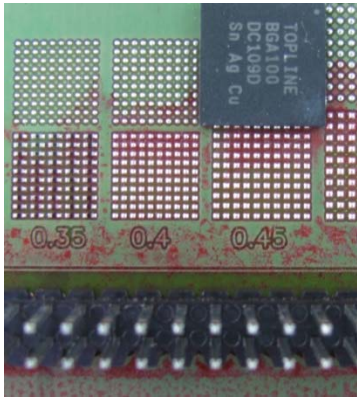


Figure 2. Excess flux sprayed over the top side of board. The distance is 15 mm between the connector and BGA, and 6 mm between the connector and the close edge of 0.35 pads.

Besides the excessive flux volume, the spray nozzle used in a wave machine and even the advanced drop-jet technology in a selective machine can create flux spattering and satellites on the surrounding area with inappropriate process settings, e.g. jet offset or high jetting frequency. The bottom picture in Figure 3 shows the flux deposit area on a fax paper with different jetting frequencies from a drop-jet fluxer in a selective soldering machine. The jetting frequency of top line is 4 times higher than the bottom, while the fluxer traveled 4 times on the bottom line to achieve the same flux volume as the top. This test result indicates that with the same flux volume, the flux can be applied to a much wider area on the PCBs with a higher jetting frequency compared to a lower frequency.

2. Low surface tension of the flux product

Surface tension is the elastic tendency of liquids which makes them acquire the least surface area possible. Figure 4 below is a simple demonstration of the surface tension effect on liquids spreading. 0.5 mL of various liquid, including DI water, IPA, Flux A, B, C and D, were dropped onto a Cu OSP board, and the resulting spread areas were observed.

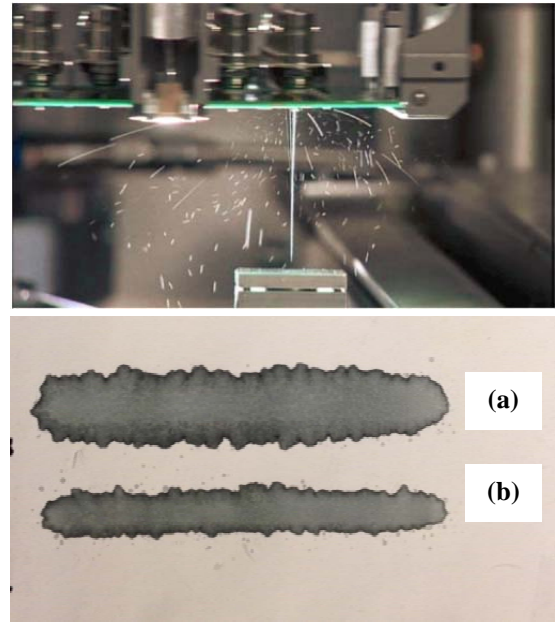


Figure 3. Top: Flux spattering and satellites generated by inappropriate drop-jet settings (Photo provided by Vitronics); Bottom: fluxing area on fax paper with different drop-jet settings. (a) Jetting frequency = 40 dot/s; Drop-jet speed = 20 mm/s; (b) Jetting frequency = 10 dot/s; Drop-jet speed = 20 mm/s; the fluxer travel four times to achieve the same flux volume as the top settings.

The surface tension of DI water is 72 mN/m, and IPA is 22 mN/m at 25°C. As shown in the image, DI water with the highest surface tension maintained as a single bead exactly where it was dropped, while IPA and other fluxes spread out with different speeds and areas. With addition of surfactants, Flux B and C have similar surface tension to IPA which enables them spread out faster in a larger area. Flux A and D are formulated to have higher surface tension, therefore they spread in smaller area at a slower speed. The excessive flux spread under BGA in Figure 2 is also contributed by the low surface tension of the product. In this demonstration, the distance between BGA and the connector is approximately 15mm. The flux can easily wet BGA's bottom with the flux volume of $380 \mu\text{g}/\text{cm}^2$ of solid content on the board. In most recent years, the higher density integration and miniaturization trend makes this situation more prevalent.

A spread area comparison study was conducted for Flux A and B under different jetting frequency with a Vitronics selective machine. As shown in Figure 5, Flux A had a smaller spread area on both 20 dot/sec and 50 dot/sec of jetting frequency than Flux B, which is consistent with the internal lab test result. With the high surface tension, the spread area of Flux A is less dependent on the jetting

frequency than Flux B, which provides more accurate flux deposit for selective soldering.

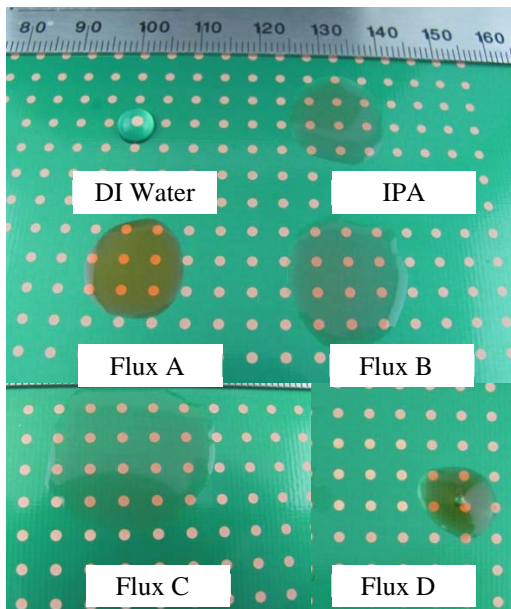


Figure 4. A demonstration of surface tension differences in various fluxes. The fluxes were dyed in red for picture contrast purpose.

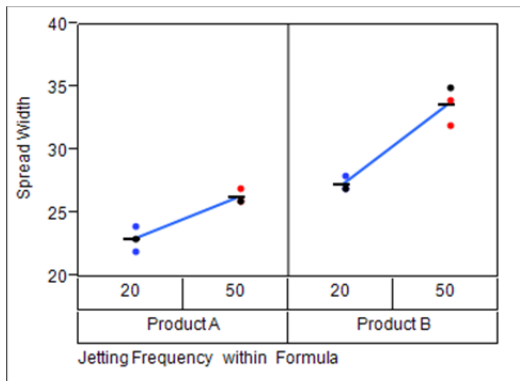


Figure 5. Spread area measurement with different jetting frequency for Flux A and B.

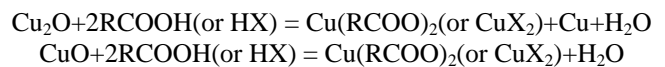
For the standard wave soldering with high density through-hole connectors (without pallets), a low surface tension flux, e.g. Flux C, is preferred regarding solderability. The lower surface tension allows the flux to spread to all areas and eliminate the risk for open solder joints, bridging, solderballs or webbing. Due to the good spreading, the residues will be less visible resulting in improved cosmetic appearance. In contrast, the selective soldering and wave pallet applications should choose the higher surface tension flux, e.g. Flux A and D, to avoid partially-activated flux residues. With appropriate process settings, the drop-jet

technology in selective machine improves the accuracy of flux deposit position.

HOW PARTIALLY-ACTIVATED FLUX RESIDUE APPEARS ON A PCB ASSEMBLY

In both wave pallets and selective soldering processes, the flux left on the undesirable areas never contacts the solder wave and is only exposed to lower temperatures. In order to simulate this, a simple experiment was conducted on IPC B24 boards with a QFP208 placement. Thermocouples were attached on both the bare board surface and under the QFP208 component. The reflow oven was utilized to simulate the different temperature exposure of a solder paste product, which provides results with direct visual observation. Three different reflow profiles were tested with this assembly. The temperature differences between the bare board and under QFP are shown in Figure 6. The “Short” profile with faster heating speed and lower peak temperature provides a larger ΔT ($\sim 40^{\circ}\text{C}$ at peak) between the bare board and under the component, while the “Long” and “Hot” profiles will minimize this effect ($\Delta T = \sim 25^{\circ}\text{C}$ at peak). After the reflow, QFPs were removed from the board. Due to the insufficient heat exposure, solder paste under the QFP through the “Short” & “Long” profiles did not fully reflow. A similar situation can occur with the liquid flux in wave soldering applications especially for the pallet and selective soldering application, where the flux does not directly contact the molten solder.

The typical activator packages used in current flux system include carboxylic acids, halides and covalent-bonded halogen compounds. As presented in the previous SMTAI conferences^[1, 2], the basic fluxing mechanisms are shown below:



With limited temperature exposure, the flux residue left on the undesirable area may contain unevaporated solvent, raw activator, and metal complex intermediates, which is defined as “**partially-activated**” flux residue in this paper. The thermodynamics and kinetics of these reactions will determine the metal complex intermediates composition and stability. The Cu organometallic compounds with various structures can be formed during the reaction with carboxylic acids: 1) linear Cu(II) complexes, largely related to a Cu(II) d^9 system^[3]; 2) and a chelate or ring complex by reaction with dicarboxylic acids as chelating agents, which are mostly bidentate ligands and enables to occupy more than one coordination position on the central Cu ion^[2]. The linear copper complexes are commonly green in color, while the copper chelates are usually blue. The structure and stability of the Cu complex depend upon the nature of the coordination ligands, as well as the environmental conditions during its formation, e.g. temperature.

Dicarboxylic acids may also form anhydrides when heated. These anhydrides may react further with copper oxides to form other copper complexes or chelates.

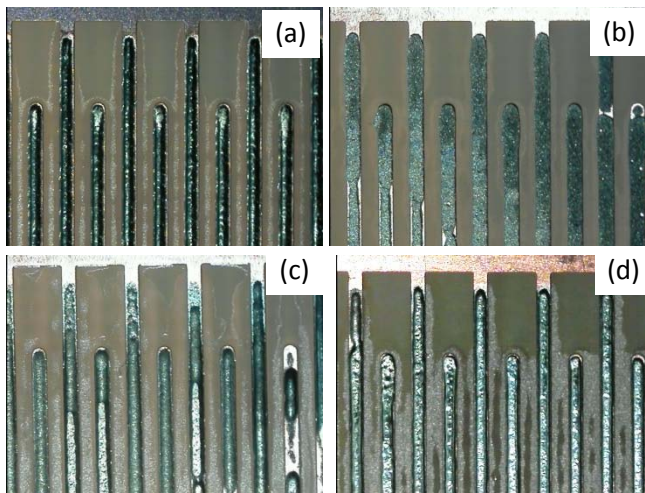
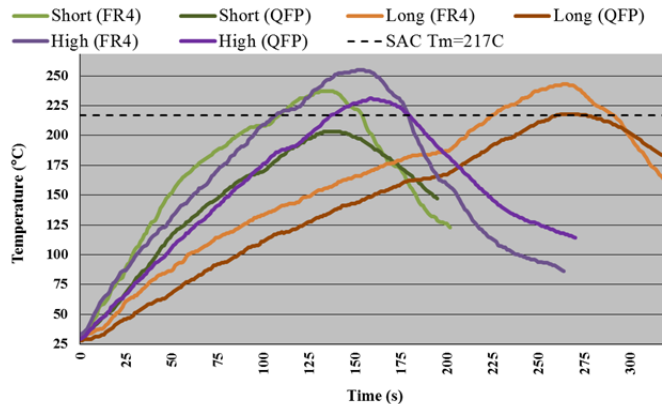


Figure 6. Reflowed B24 boards under: a) Short profile without QFP; b) Short profile with QFP – non-reflowed solder powder; c) Long profile with QFP – partially-reflowed solder alloy; d) High profile with QFP – reflowed solder with rough surface;

HOW PARTIALLY-ACTIVATED FLUX RESIDUE IMPACTS SIR/ECM RELIABILITY

After PCB assembly, all organic components discussed above can possibly be present on the board's surface based on different thermal history. On one hand, this “partially-activated” flux residue has its own physical and chemical characteristics, e.g. moisture sensitivity and ionic conductivity. The compound with higher moisture sensitivity and ionic conductivity can form efficient conductive paths causing current leakage. More detailed

research on the impacts on reliability has been presented in another publication^[1]. Additionally, “partially-activated” flux residue can further react with metal and metal oxides under operating conditions of an electronic device, resulting in more corrosion and electrochemical migration. Some metal complex can also form hydrolysis products with different color deposits on a PCB surface.

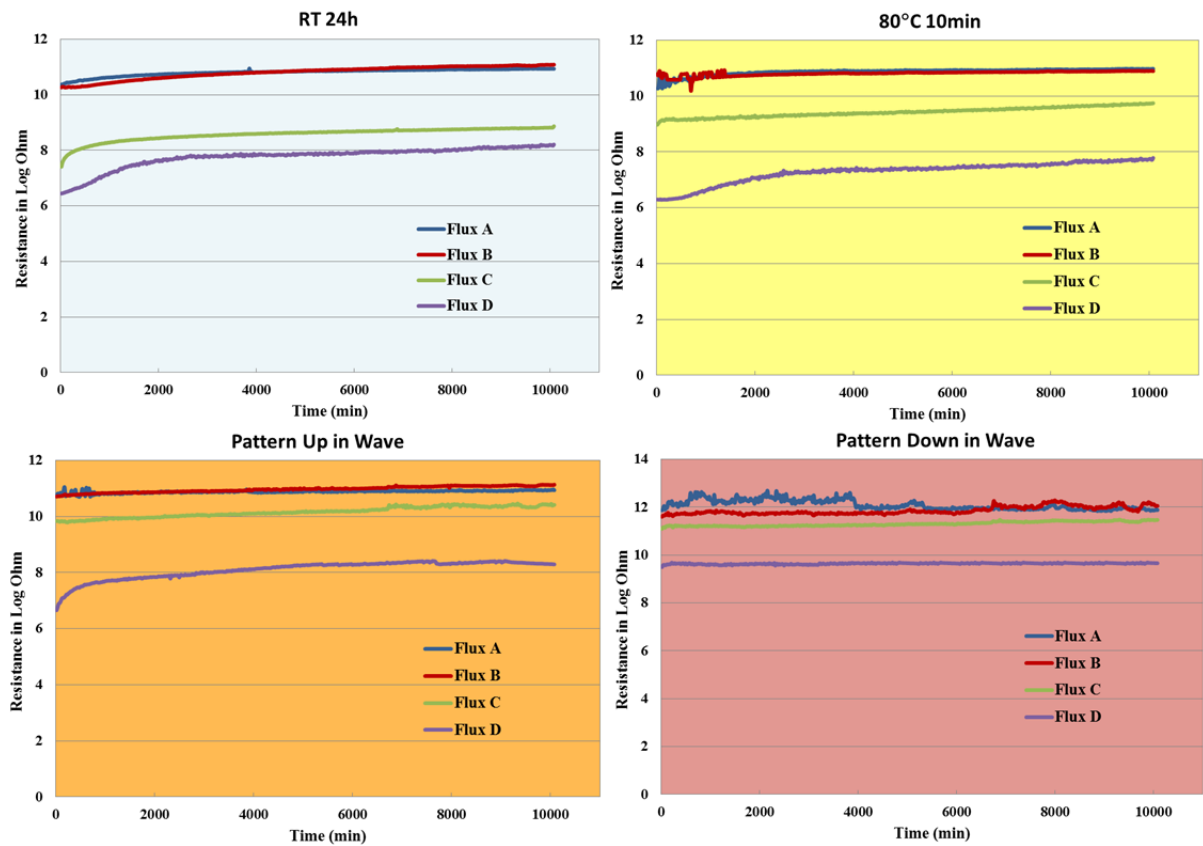
In order to investigate the partially-activated flux residue's impact on the SIR reliability, four fluxes A, B, C and D (previously shown in Figure 4.) were tested using the IPC-TM-650 2.6.3.7 method. 20 μ L samples were applied onto each comb pattern, and the B24 boards were then processed under four thermal exposure conditions:

- Group I: exposed to 23°C/35%RH for 24hrs
- Group II: expose to 80C in a conventional oven for 10min
- Group III: Pattern-Up through wave, approximate exposure temperature is 200°C for 5s with solder pot temperature at 245°C
- Group IV: Pattern-Down through wave, exposure temperature is approximately 245°C for 5s.

The “partially-activated” flux residue on Group I boards should contain the highest amount of raw activators, theoretically the most reactive; the residue on Group II and III may contain different type of metal complex intermediates; and the residue on Group IV boards were mostly removed by contacting the solder wave. The test results including both resistance reading and visual images are shown in Figure 7. Notice the background color indicates the exposure temperature difference.

According to the resistance readings, both Flux A and B pass the IPC criteria of all resistance readings above 10⁸ Ω for all four board conditions; Flux C barely passes this criteria on Group I condition but pass the other conditions; Flux D only pass the highest temperature condition in Group IV and fails the other three conditions. Besides the resistance reading, IPC also requires that the test boards do not exhibit discoloration, corrosion or dendrites after environmental exposure. Based on this criteria, only Flux A and B pass all conditions; C failed for Group I and II conditions; and D failed the first three conditions.

Group I boards with Flux C exhibited a slightly green color residue after testing, indicating some linear Cu complex was possibly generated from the reaction between



	Group I RT 24h	Group II 80°C/10min	Group III Pattern Up	Group IV Pattern Down
Flux A				
Flux B				
Flux C				
Flux D				

Figure 7. IPC SIR 2.6.3.7 test result of four fluxes with different temperature exposure during B24 preparation.

the acid and copper oxides and further developed under SIR test conditions (40°C/90%RH). Group II boards with Flux C had significant amount of bluish residue on the Cu traces after testing, indicating the chelating Cu complex formation is promoted by the 80°C exposure during board preparation and also further developed during SIR testing. The similar effect can be observed in Flux D, even though the residue is already bluish color at room temperature due to its different activator structure. It is possible that the short exposure at 80°C for Flux C and D accelerates the chemical reaction and generates flux intermediates and unstable Cu complex. These intermediates can easily form more chelating metal complex with Cu under SIR test conditions, resulting in more corrosion. This type of intermediates could have higher ionic conductivity; and the corrosion reaction also increases the ion mobility and lowers the resistance values. Group III boards with relatively higher heat exposed Flux D show brownish residue developed on the copper traces, indicating a different type of copper complex formation. Similar to the previous discussion, this complex can further react with copper causing more corrosion and lowering resistance, but not as significant as the residue under 80°C possibly result from less remaining activators. Group IV boards for all four fluxes have minimum residue left on the surface, after 245°C exposure and most is removed by the solder wave, creating the most reliable condition.

CONCLUSION:

This research establishes the basic approach and test methods for new PCB assembly materials development, specifically for the selective soldering process which is drawing more attention in electronic assembly industry.

In order to obtain higher SIR reliability for through-hole assembly, two recommendations are offered based on this study:

1. Optimize the process settings and choose the right soldering method to limit the amount of “partially-activated” flux residue on the board surface:
 - Design an appropriate soldering profile by considering the thermal mass from the board and components. For example, thermocouples should be attached to several locations on the board and under any large thermal mass components during profiling.
 - Adjust the nozzle or jet settings to obtain accurate deposit location, spread area and appropriate flux volume.
2. Choose the right formulation for the different soldering methods. Particularly for selective soldering, the formula should:
 - Do not clog the drop-jet system head while providing low cleaning frequency requirement.

- Have higher surface tension to control the spread area.
- In addition have a good SIR/ECM reliability under different temperature exposure conditions,

For these reasons, fluxes like Flux C and D are not appropriate formulas for the wave pallet and selective soldering application in the high reliability field; while Flux A and B are suitable products for these applications regarding the reliability aspect. Flux A is the best selection for selective soldering due to its higher surface tension for controlled spread area.

ACKNOWLEDGEMENT

The authors would like to thank the following group and individuals for their efforts and expertise regarding the testing and application in this research:

- Gerjan Diepstraten from Vitronics Soltec
- Denis Jean from Kester PM team
- Kester R&D team members.

REFERENCES:

- 1]. Xiang W., Bruno, T., “Effect of Flux Systems on Electrochemical Migration of Lead-Free Assembly”, SMTA International conference in Rosemont IL, 2014.
- 2]. Yanrong S., Xiang W., Bruno, T., “Smart Chemistry Towards Highly Efficient Soldering Material Formulation”, SMTA International conference in Rosemont IL, 2014.
- 3]. Bruce H. Lipshutz, Steven S. Pfeiffer, “Encyclopedia of Inorganic Chemistry. Copper: Organometallic Chemistry” John Wiley & Sons, Ltd., 2006, DOI: 10.1002/9781119951438.