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Materials Compatibility and Aging for Flux and Cleaner Combinations

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Abstract

A materials study of high reliability electronics cleaning is presented here. In Phase 1, mixed type substrates underwent a condensed contaminants application to view a worst-case scenario for unremoved flux with cleaning agent residue for parts in a silicone oil filled environment. In Phase 2, fluxes applied to copper coupons and to printed wiring boards underwent gentle cleaning then accelerated aging in air at 65% humidity and 30 °C. Both sets were aged for 4 weeks. Contaminants were no-clean (ORL0), water soluble (ORH1 liquid and ORH0 paste), and rosin (RMA; ROL0) fluxes. Defluxing agents were water, solvents, and engineered aqueous defluxers. In the first phase, coupons had flux applied and heated, then were placed in vials of oil with a small amount of cleaning agent and additional coupons. In the second phase, pairs of copper coupons and PWB were hand soldered by application of each flux, using tin-lead solder in a strip across the coupon or a set of test components on the PWB. One of each pair was cleaned in each cleaning agent, the first with a typical clean, and the second with a brief clean. Ionic contamination residue was measured before accelerated aging. After aging, substrates were removed and a visual record of coupon damage made, from which a subjective rank was applied for comparison between the various flux and defluxer combinations; more corrosion equated to higher rank. The ORH1 water soluble flux resulted in the highest ranking in both phases, the RMA flux the least. For the first phase, in which flux and defluxer remained on coupons, the aqueous defluxers led to worse corrosion. The vapor phase cleaning agents resulted in the highest ranking in the second phase, in which there was no physical cleaning. Further study of cleaning and rinsing parameters will be required.

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1. INTRODUCTION

New engineered cleaning and defluxing agents promise great improvements in cleaning and reliability for electronic assemblies. As complexity grows and dimensions shrink in high reliability electronics, the need for materials compatibility and effectiveness in cleaning and rinsing is vital.

The most common and harmful contamination sources are flux residues and cleaning agent residues. Potential interactions with moisture and voltage include corrosion, dendritic growth, and electrical leakage. A defluxing process must be compatible with the materials on the PWA, compatible with the structure of the PWA and be able to clean under low standoff or tightly spaced components, while not damaging fragile or vulnerable components. It also must be achievable for production at the given agency, which includes an acceptable hazard level for facility requirements, applicability to cleaning method/equipment in place, and a reasonable timeline for validation.

Determination of which fluxes and cleaning agents pose a greater risk of corrosion and damage to circuit boards and their assemblies for high reliability, long-life electronics begins with materials testing of the effects of each defluxer and flux in consideration. In this report, we present the results for initial compatibility testing. Fluxes were selected by program, so this study was limited to fluxes and defluxers currently in use and under consideration for future use.

In the first phase of testing, various materials substrates underwent a condensed contaminants application to view a worst-case scenario for unremoved flux with cleaning agent residue. This setting allows corrosion and staining due to poorly rinsed soldered electronics to be apparent in a short amount of time, and can help in the down selection of fluxes and cleaning agents for use, or for further testing. Contaminants were “no-clean” (ORL0), water soluble (ORH1 liquid and ORH0 paste), and mildly activated rosin (RMA; ROL0) fluxes. Small amounts of cleaning agents, such as de-ionized water, solvents, and aqueous defluxers were included. Oxygen free electronic grade (OFE) copper coupons, with a metered amount of flux applied, were heated to standard solder temperatures for the flux types, cooled, then submersed in 20 centistoke silicone oil as an inert medium that mimics actual use for several electronic assemblies. For materials compatibility evaluations stainless steel, silver-gold-copper-palladium alloy and polyamide-imide coupons were added. Covered vials of the test materials were aged at ambient conditions for four weeks. Coupons were removed from the test vials and a visual record of material damage made, from which a subjective ranking was applied for comparison between the various flux and defluxer combinations.

The second phase of materials compatibility tests and aging used hand soldered parts which were then gently cleaned. The same defluxing agents and fluxes used in the first phase were again tested, with the exception of ethanol as a solvent. Substrates were OFE Cu coupons and PWB with simple (no low standoff, miniaturization or tight spacing) surface mount components. Pairs of copper coupons were hand soldered by application of each flux, using tin-lead solder in a strip across the coupon or standard soldering methods on the PWB. One of each pair was cleaned in each cleaning agent, the first with approximately a 3 – 5 minute 40 kHz ultrasonics and/or a

vapor cleaning method, and the second with a roughly a one minute soak or vapor cleaning method. These coupons were aged by storage in air at 65% humidity and 30 °C for 4 weeks. Ionic contamination residue was measured before accelerated aging, and a visual record made before and after aging, from which a subjective ranking was applied for comparison between the various flux and defluxer combinations.

2. MATERIALS AND METHODS

The materials tested were specific to various programs, with some overlap between programs. All were in current use or being considered for future use, in work done by Sandia National Labs.

Flux Types:

- A: water soluble paste, ORH0
- B1 & B2: no-clean liquid, ORL0
- C: water soluble liquid, ORH1
- D1 & D2*: mildly activated rosin, RMA, ROL0

**RMA fluxes may be reported together, as response was approximately same in all cases*

Metal Coupon Materials:

- OFE Copper
- Kovar
- Paliney 7
- 304 Stainless Steel

Cleaning Agents

- S1: solvent, ethanol (not used in Phase 2)
- S2: solvent, d-Limonene
- A1: DI water, >16 MOhm-cm
- A2: aqueous defluxer # 2
- A3: aqueous defluxer #3
- V1: vapor defluxer, AK-225
- V2: vapor defluxer # 2
- V3: vapor defluxer #3

Methods for Phase 1 and Phase 2 are similar, and are described in this section. Visual inspection at actual size and 6X magnification of coupons and boards from both phases at the termination of four weeks aging allows comparison of damaging effects on the materials involved. A corrosion level rating method was developed in order to compare the flux and cleaning agent combination results. The ratings take into account residue, corrosion, etching, staining, and pitting, as well as ionic residue data for Phase 2 (Tables 1 – 3). The number scale increases with the amount of residue or damage by corrosion.

The rating reported for each jar is a sum of the ratings given by each material for Phase 1. Phase 2 incorporates a scale for amount of corrosion residue seen before cleaning, as well as a scale based on Ionograph results. The rating reported for each coupon is a total of all three ratings. The PWB in Phase 2 had only visual inspection for residue left from cleaning, and were not included in the rating process.

Table 1. Phase 1 and 2 rating for corrosion after cleaning

KEY	Rating Description, Phases 1 &2 Post-Clean
0	No discoloration or pitting
1	Very slight stain, no residue or pitting
2	Visible stain, little residue, no pitting
3	Visible stain and residue, slight pitting
4	Heavy stain and residue, visible pitting
5	Heavy stain, residue and pitting



Figure 1. Post aging coupons cleaned to observe degree of etching.

Table 2. Phase 2 rating for post aging extent of corrosion

KEY	Rating Description, Phase 2 Pre-Clean
0	No Discoloration/Residue
0.5	Slight Discoloration/Residue
1	Discoloration/Residue on <25%
1.5	Discoloration/Residue on 25% to 50%
2	Discoloration/Residue on 50% to 75%
2.5	Discoloration/Residue on >75%

Table 3. Phase 2 Ionic Residue Rating Scale

KEY	µg NaCl equivalent, Phase 2 Ionograph
0	<0
0.5	0-75
1	76-150
1.5	151-225
2	226-300
2.5	300+

2.1. Phase 1 Methods

Metal coupons were prepared by cleaning in 10% Brulin™ 815GD with 40 kHz ultrasonics at 30 °C, and rinsed in DI water of > 16 MOhm-cm resistivity. The Cu was also treated with a 15 second acid dip with DI water rinse. Pre-treatment images were taken of all materials.

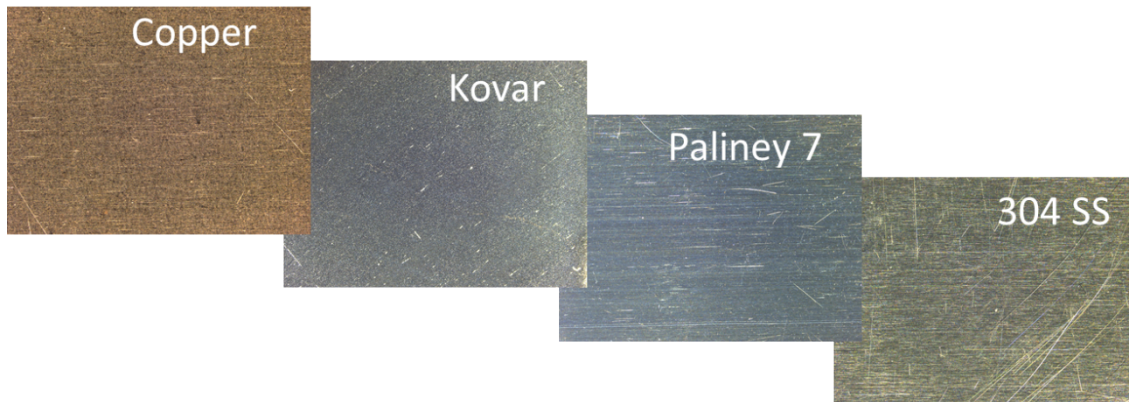


Figure 2. Phase one metal coupon materials before flux treatment.

A small amount of heat treated flux was combined with each defluxer and placed with coupons in a silicone oil environment and aged, to determine which combinations present the higher risk in use. The flux treatment process consisted of:

- 0.18 mL flux applied by droplet or brush onto Cu coupons
- Coupons placed on hot plate at a temperature selected to mimic the typical soldering process on the high heat end:
 - in excess of lead-free solder (370 – 450 °C)
 - in excess of tin-lead solder (230 – 280 °C)
- Cool to ambient, place coupons in jars with other materials to be tested

- Add 6.0 mL silicone oil & 0.18 mL defluxer
- Gently agitate, cover
- Store at ambient temperature for 4 weeks

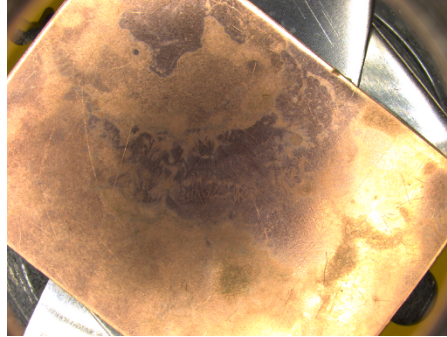


Figure 3. Phase one metal coupon materials stacked in glass jar full of silicone oil.

2.2. Phase 2 Methods

The same fluxes, and defluxers except for ethanol, were evaluated under typical hand soldering conditions in the second phase of testing. Each fluxed coupon was treated with mild cleaning, or a very brief cleaning, and PWBs were cleaned similarly with a brief and a more extended vapor defluxing, then all aged in air, with heat and humidity to accelerate chemical reaction.

For the Cu coupons a tin-lead solder wire was hand soldered across the coupon at both higher and lower temperatures. After cooling, but within 24 hours, half were treated by each cleaning method. Below are the process steps followed for the coupons:

1. Coupon Prep
 - a. Engrave all (52) copper pieces for testing (P2-XX).
 - b. Run all samples (plus extras) through 5 stage, detergent clean
 - c. Acid Bright Dip all samples for 15 seconds
2. Solder and Flux Application
 - a. Flux will be applied using an applicator in a line along the middle of the piece
 - b. A soldering wand (pencil) will be used to (apply solder to) heat the flux, while the sample is on bench (no heat sink)
 - c. The copper piece will then be moved to a heat sink to cool and harden
 - d. All hardened fluxed copper pieces will be stored in the dry air cabinet less than 24 hours before Humidity aging tests begin (record time)
3. Cleaning
 - a. Liquid cleaning
 - i. Clean B, Dip- brief clean (intended to be incomplete)

1. Dip in cleaners for approx. (1 minute)
 2. Rinse in appropriate rinses
 3. Nitrogen air dry
 4. Heated flow dry
 - ii. Clean A, Ultrasonics
 1. Immerse in cleaner under ultrasonics for 3 minutes
 2. Rinse with respective rinses
 3. S Nitrogen air dry
 4. Heated flow dry for 30 minutes
 - b. Vapor Degreaser Cleaning Procedure
 - i. Vapor Degreasing will be set up in a beaker on a hot plate with a covering to keep vapor in. A ring stand will be used to suspend coupons over the degreaser setup.
 - ii. Clean A, Ultrasonics (full clean):
 1. Degreaser fluid temperature should be 121-123 °F
 2. Parts are immersed in vapor and spray for 30 seconds
 - a. Using a pipette, squirt a bit of the degreaser solution on the coupon every few seconds
 3. Parts immersed in only vapor for 1.5 minutes
 4. Parts are immersed in vapor and spray for 30 seconds
 - a. Using a pipette, squirt a bit of the degreaser solution on the coupon every few minutes
 5. Parts are moved up to the cold zone so the fluid evaporates
 - iii. Clean B, Dip (brief clean):
 1. Degreaser fluid temperature should be 121-123 °F
 2. Parts are immersed in vapor only for 1 minute
 3. Parts are moved up to the cold zone so the fluid evaporates
4. Ionograph
 - a. Test each coupon in Ionograph machine with 75% IPA DI Water Solution.
 - b. 3 minute time periods
 5. Aging for 4 weeks
 - a. Constant Settings
 - i. Temperature – 30 °C
 - ii. Humidity – 65%

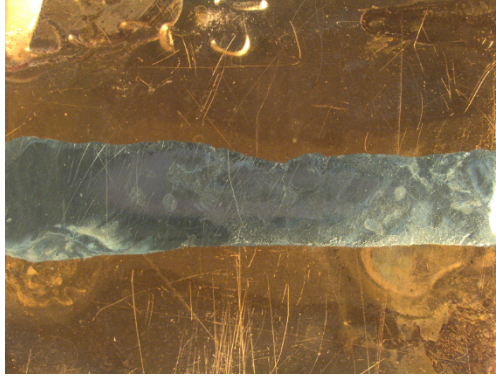


Figure 4. Phase two OFE coupon with solder strip.

For the PWB, components were hand soldered with the same solder wire, using only RMA flux, cleaned only with the 3 vapor phase defluxers, following this process:

1. Parts immersed in vapor and spray for 30 seconds
2. Parts immersed in vapor only for 1.5 minutes
3. Parts immersed in vapor and spray for 30 seconds
4. Parts are moved up to the cold zone so the fluid evaporates

For the 3 or 6 repeat cleaning cycles the procedure will follow:

1. Complete the amount of repeat cycles in the vapor degreaser (3 or 6)
2. Allow to dry in air dryer for 30 minutes
3. Cool for 10 minutes
4. Take Ionograph readings of each board
5. If Ionograph readings for 6 run boards are above $5 \mu\text{g}/\text{in}^2$ run in vapor degreaser for 3 more runs and document
6. Allow to dry in air dryer for 30 minutes
7. Cool for 10 minutes
8. Take Ionograph readings a second time for all boards
9. Age at temperature of 30°C in 65% humidity for 4 weeks

3. RESULTS AND CONCLUSIONS

Damage to coupons ranged from minor staining to heavy corrosion and etching. In all cases the higher halides ORH1 flux resulted in the most damage, and the RMA flux resulted in the least damage. The cleaning agents showed a wide variation in results from the different tests.

In Phase 1 the least amount of damage to the metal coupons was seen when using RMA flux with added vapor degreaser fluid, which typically resulted in minor staining or residue. A slight increase in staining was noted for the higher temperature tests (Figures 5 – 6).



Figure 5. Best of Low Temperature; RMA flux D2 with vapor defluxers.



Figure 6. Best of High Temperature, no-clean flux B1 & B2 or RMA Flux D2.

The greatest amount of damage was seen with the ORH1 flux and, in general, the aqueous defluxers. However, solvents and vapor defluxers (as well as no cleaning) created substantial corrosion as well (Figures 7 – 9). It is noted that all coupons in Phase 1 were in aging solution stacked on one another, thus it is possible that galvanic corrosion accelerated or decelerated coupon damage. The flux C, water-soluble ORH1, and Cleaner A1 rating as seen in Figure 9-a is higher due to staining on other coupon materials. Fluxes B1 & B2, no-clean, are most dependent on cleaner for the Low Temperature tests, as seen in Figure 9-b.

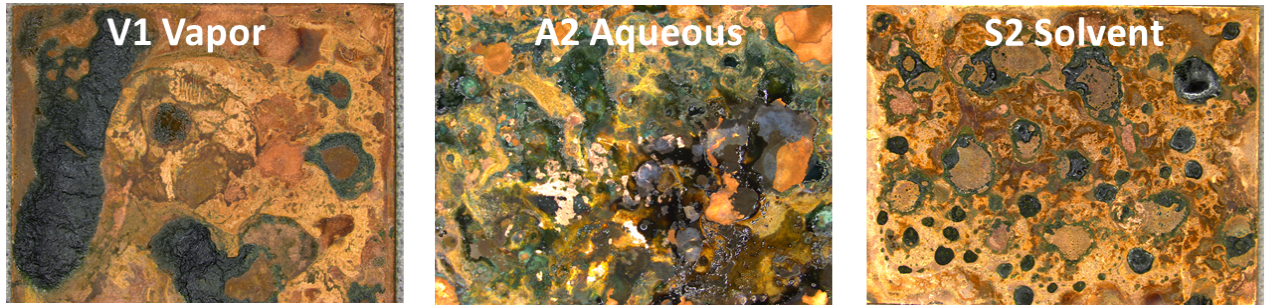


Figure 7. Worst of Low Temperature, C1 water soluble ORL1 flux.



Figure 8. Worst of High Temperature, C1 water soluble ORL1 flux.

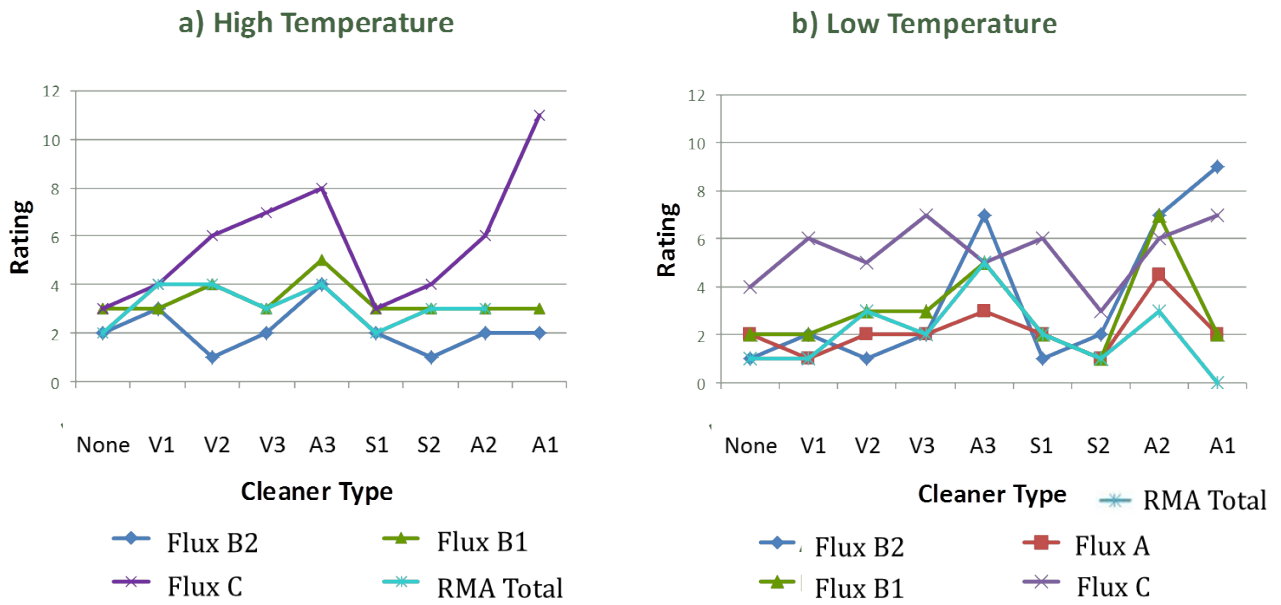


Figure 9. Rating results graph for Phase 1 a) High and b) Low temperature trials.

In Phase 2, a lesser amount of damage was seen across the range of testing. The highest rating for damage and ionic residue was associated with the ORH1 flux and, in general, the vapor phase defluxing. The least corrosion was observed on RMA flux with aqueous cleaning. As seen in Figures 10 – 12, the brief cleaning (Clean B) was little different than the longer cleaning cycle (Clean A), when little physical cleaning action is present (no scrubbing or impingement spray).

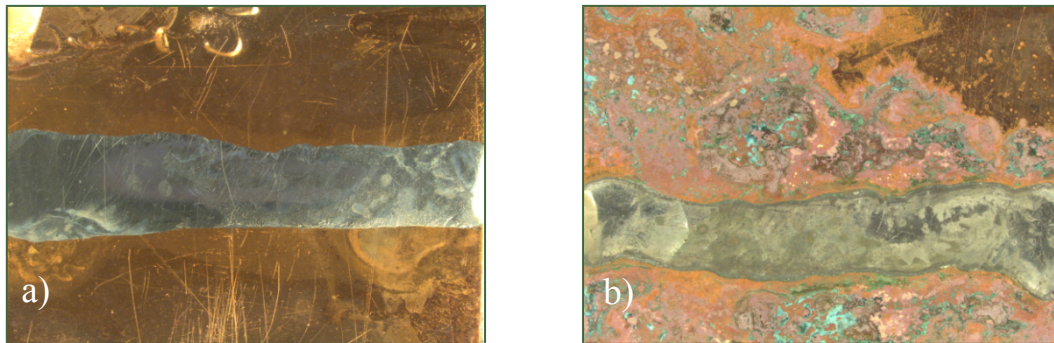


Figure 10. Clean A: a) BEST, RMA flux D, defluxer A3, b) WORST, ORH1 flux, defluxer V3.

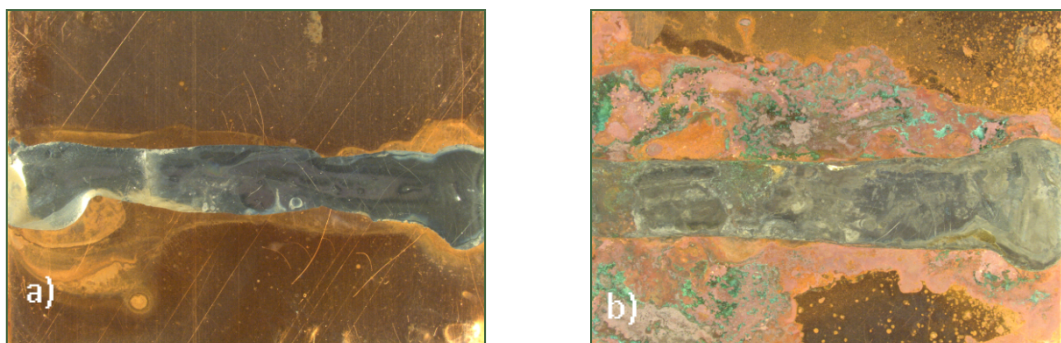


Figure 11. Clean B: a) BEST, RMA flux D, defluxer A1, b) WORST, ORH1 flux, defluxer V1.

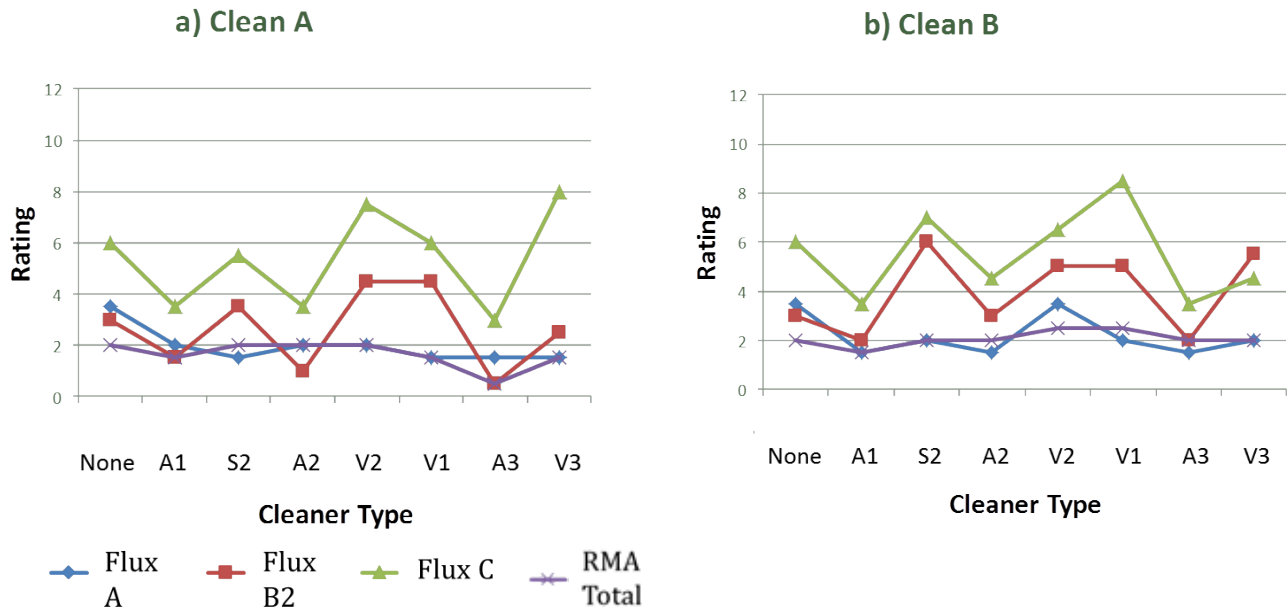


Figure 12. Rating results graph for Phase 2 a) Clean A and b) Clean B.

Averaging the rating values for like combinations of cleaning agents and fluxes in Phase 2, shown in Figure 13, resulted in generally best clean and least damage for the aqueous cleaning agents, with measurable increase between Clean A and Clean B for A2 and A3, but not A1.

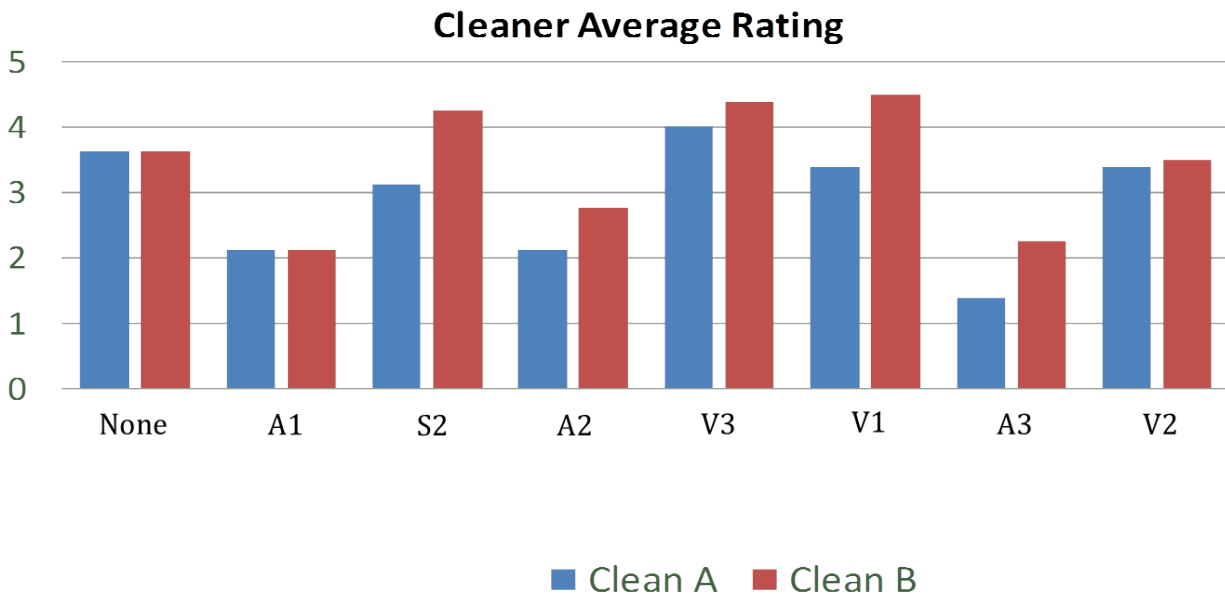


Figure 13. Average of ratings for all cleaner and flux combinations for Phase 2.

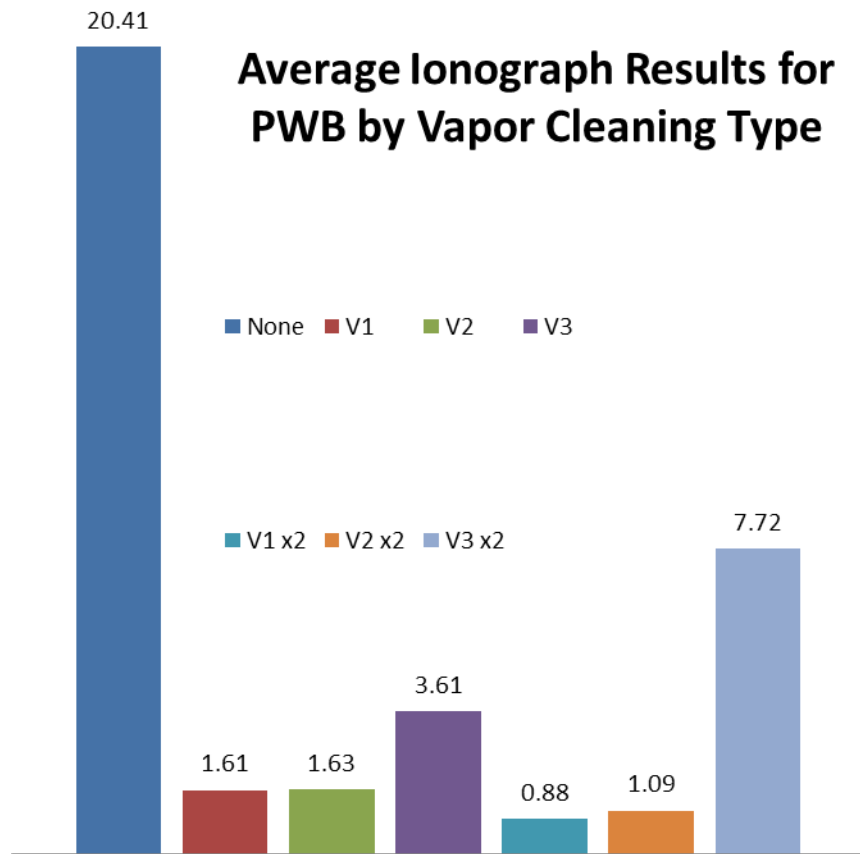


Figure 14. Printed wiring board ionic residue, in micrograms/square inch.

One set of boards was cleaned by a typical vapor cleaning, the second set cleaned with a double amount of cleaning cycles, but as seen in Figure 14, all fell below 10 micrograms per square inch of sodium chloride equivalent. The PWB double cleaned in V3 defluxer appears to have increased residue in comparison to the same cleaning done with a single cycle, which indicates the variation in the soldering and cleaning is probably on the order of the amount of residue measured. However, it is likely that as V3 showed results worse than V1 and V2 in both single and double cleaning cycles, and left visible residue on the boards (see Figure 15) that it fares least well in this comparison.

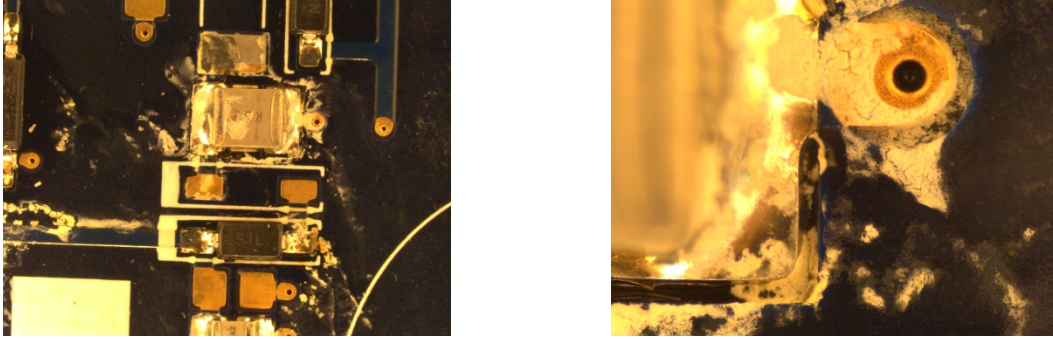


Figure 15. Printed wiring board with the greatest visible flux residue, V3 vapor defluxer.

The less than optimal results of Phase 1 are consistent with no removal of flux and no rinsing of defluxer, as substantial corrosion appeared across all types of defluxers, especially in use of the aggressive aqueous defluxers. The results of the first phase demonstrate the need for appropriate rinsing to achieve low corrosion risk. Observations confirm that higher halide fluxes are more likely to result in corrosion.

In Phase 2 most corrosion occurred with the vapor defluxers. Performance of the vapor defluxers on Cu coupons may be due to lack of physical pre-clean, or insufficient repetitions of vapor condensation. These results confirmed the need for appropriate cleaning method to achieve low corrosion risk, and verified that higher halide fluxes are more likely to result in corrosion. The PWB cleaning demonstrated that for RMA flux, no corrosion was observed on any board, and white residue was present for only one defluxer type.

Conclusions of this initial study resulted in the recommendation of no application of the ORH1 flux when possible, and if the higher activity is required for function, additional testing in cleaning process development will determine the extra rigor required to ensure a good clean of flux residue. The use of aqueous cleaning agents looks promising for assemblies that can be wetted, but further investigation into proper rinsing will be needed. For assemblies that require a solvent or vapor clean, supplementary testing is recommended. And lastly, the vapor defluxer V3 is recommended to no longer be considered for program and will be removed from further testing.

The path forward for continuation of assessment of fluxes and defluxers to use in high reliability applications includes testing for cleaning efficacy with physical cleaning on test vehicles with BGA, QFN and miniature components. An important aspect of this will be evaluation of rinse capability for various defluxers. Another vital factor is the ability to determine cleanliness level validation methods for small amounts of residue well concealed under components. New test methods are desired, and validation of cleanliness testing methods must be corroborated with destructive testing for direct evidence of results. Possibilities include power spray and/or extended time, or a series of solvent solutions to facilitate removal of more residues, for residue extraction used in resistivity of solvent extract or ion chromatography test methods.

APPENDIX A: EXAMPLE APPENDIX TITLE

Table 4. Flux List

Reference Letter	Name	Type and Rating	Test Application
A	Alpha WS809	water soluble paste, ORH0	Low Temperature P1A&B
B1	Alpha NR330	no-clean liquid, ORL0	High and Low P1A&B
B2	Kester 979	no-clean liquid, ORL0	High and Low P1A&B
C	Kester 2331-ZX	organic water soluble, ORH1	High and Low P1A&B
D1	Kester 185	Rosin, mildly activated, ROL0	High and Low P1A
D2	Kester 197	Rosin, mildly activated, ROL0	High and Low P1B

Table 5. Defluxer List

Reference Letter	Name	Type, Ingredients or Concentration
S1	Pharmco-Aaper™ ethanol	solvent, Optima grade, 200-proof, undenatured
S2	Florida Chemical Co. d-Limonene	solvent, technical grade (terpene)
A1	house de-ionized water	aqueous, 16 MOhm-cm, 0.1 micron filter
A2	Kyzen™ Aquanox® A4241	aqueous, 20% in DI water
A3	Zestron™ Vigon® N600	aqueous, 15% (was used at 100%) in DI water
V1	Asahiklin™ AK-225®	vapor/aerosol, HCFC-225cb
V2	Techspray™ Precision-V®	vapor/aerosol, 25 – 45% 1,2-trans-dichloroethylene (30 -50% HFC-43-10mee)
V3	DuPont™ Vertrel SDG®	vapor/aerosol, 65-90% trans-dichloroethylene (5 – 25% HFC-43-10mee)

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