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Duo-Solvent Cleaning Process Development for Removing Flux Residue from Class 3 Hardware

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Abstract

Packaging trends enable disruptive technologies. The miniaturization of components reduces the distance between conductive paths. Cleanliness of electronic hardware based on the service exposure of electrical equipment and controls can improve the reliability and cost effectiveness of the entire system. Problems resulting from leakage currents and electrochemical migration lead to unintended power disruption and intermittent performance problems due to corrosion issues.

Solvent cleaning has a long history of use for cleaning electronic hardware. Limitations with solvent based cleaning agents due to environmental effects and the ability to clean new flux designs commonly used to join miniaturized components has limited the use of solvent cleaning processes for cleaning electronic hardware. To address these limitations, new solvent cleaning agents and processes have been designed to clean highly dense electronic hardware.

The research study will evaluate the cleaning and electrical performance using the IPC B-52 Test Vehicle. Lead Free no-clean solder paste will be used to join the components to the test vehicle. Ion Chromatography and SIR values will be reported.

Introduction

The challenge for assemblers and OEMs is to design reliable hardware that performs consistently in the field. Smart electronic devices require increased functionality, small form factor and fast data transfer. Information technology needed to support these devices lead to electronic component complexity, switches that require signal flow rates and higher transmission frequencies. The concern is that electronic hardware failures will become more prevalent.

Electronic assemblies increase in value as a part of the overall product in which the technology is implemented. Cleaning is not so much due to the value of the PWB itself, but due to its place in the overall system. Most think of cleaning as a chemical. In reality, cleaning is a process designed to remove undesirable soils without changing the surface in an unacceptable manner.

Years ago, the initial PCB cleaning process was typically solvent cleaning. Chloro-fluorinated solvents dominated the market until ozone depletion reared its ugly head. The dominate technology that emerged to replace solvent cleaning was flux compositions that left behind low levels of non-ionic residues. In addition, the spacing between conductive paths was sufficient to safely build electronic assemblies without the need for cleaning.

Over the past twenty years since the Montreal Protocol was enacted, the number of transistors in a dense integrated circuits doubled approximately every two years. The observation is named after Gordon E. Moore, co-founder of the Intel Corporation.[1] Highly dense interconnected devices emerged. As components decreased in size, the distance between conductors decreased. With the emergence of Lead-Free soldering, planar board finishes and leadless components became commonplace. As a result, the Z-Axis reduced to a point where flux volatiles can become entrapped under bottom termination components. Non-activated flux residues in combination with decreased spacing between conductors increased the importance of cleaning production assemblies.

Key factors to consider when designing the cleaning process are (1.) Part being cleaned, (2.) Soils encountered (3.) Standoff gaps lower than 50µm, (4.) Exposed metals, (5.) Cleaning agent, (6.) Cleaning machine, (7.) Process parameters needed to clean, (8.) Process control and (9.) Environmental health & safety.

Transition of Solvents, Fluxes and PCBs

Customer needs and innovation creates an environment where continuous improvements ensue. Over the past 20 years, printed circuit boards have transitioned from through-hole, surface mount combined with through-hole, surface mount only and to today's highly dense surface mount assemblies. Flux compositions used for wave soldering, paste flux and solder paste compositions have transitioned from liquid rosin based fluxes to low residue no clean and water soluble fluxes. The flux components within solder paste have become highly complex with a high amount of variability among the no-clean, rosin and water soluble solder paste residues offered to industry. For assemblers who clean, the challenge is the design of cleaning agents that clean a wide range of soils and cleaning equipment designed to penetrate bottom terminations. Matching the cleaning and rinsing agents with the cleaning equipment is critical to achieving clean parts on a consistent basis.

Cleaning solvents for electronic applications have transitioned from CFCs (ozone depleting & global warming issues) to HCFCs (lower ozone depletion values but high global warming values ~ examples are R-141b and 225), and toward HFCs (non-ozone depleting solvents, but high global warming potentials ~ examples are HFCs and HFEs). A new class of Hydrofluoro-olefin solvents with favorable toxicity properties is a recent innovation that offers new promise to solvent cleaning processes. Hydrofluoro-olefin solvents are non-flammable, low global warmers; do not contribute to ground level smog, and not a volatile organic compound as determined by the U.S. EPA. A safe solvent cleaning process that offers numerous environmental benefits and has the ability to solvate no-clean flux residues fills a void for cleaning highly dense assemblies soldered with modern flux technologies.

The importance of cleaning electronic hardware is critical as assemblies reduce conductive paths. Components with tighter pitch and high interconnects require solder paste flux compositions with multifunctional properties to achieve acceptable soldering yields. The remaining residues contain a range of materials that require cleaning agents engineered with dispersive, polarity and hydrogen bonding properties. Solvent cleaning agents work well when the soil dissolves in the cleaning fluid. When some of the components within the flux residue are not miscible in the solvent cleaning agent, white residues are present post cleaning. To address this limitation, an innovative approach to cleaning electronic assemblies using a waterless solvent cleaning process has emerged.

Duo-Solvent Cleaning Technology

Duo-Solvent Cleaning Technology is designed to clean challenging soils using a solvent cleaning agent matched to the soil and then rinsed with a Hydrofluoro-olefin solvent. Electronic assemblies are introduced in an agitated solvating immersion tank. The solvating tank contains an engineered cleaning agent designed to remove lead-free no clean, rosin and water soluble flux residues. Once the residues are removed, the assemblies are transferred to a vapor degreasing boil sump to rinse the assembly free of the solvating agent and other process soils. Assemblies free of flux residue go through a Hydrofluoro-olefin immersion rinse followed by a vapor rinse. The parts exit the system clean and dry. A solvent separation system is designed within the process to extract contaminants out of the system and to maintain a highly purified solvent rinse. The process produces a clean and dry part in one machine with short cycle time, low energy usage and small footprint (Figure 1).[2]

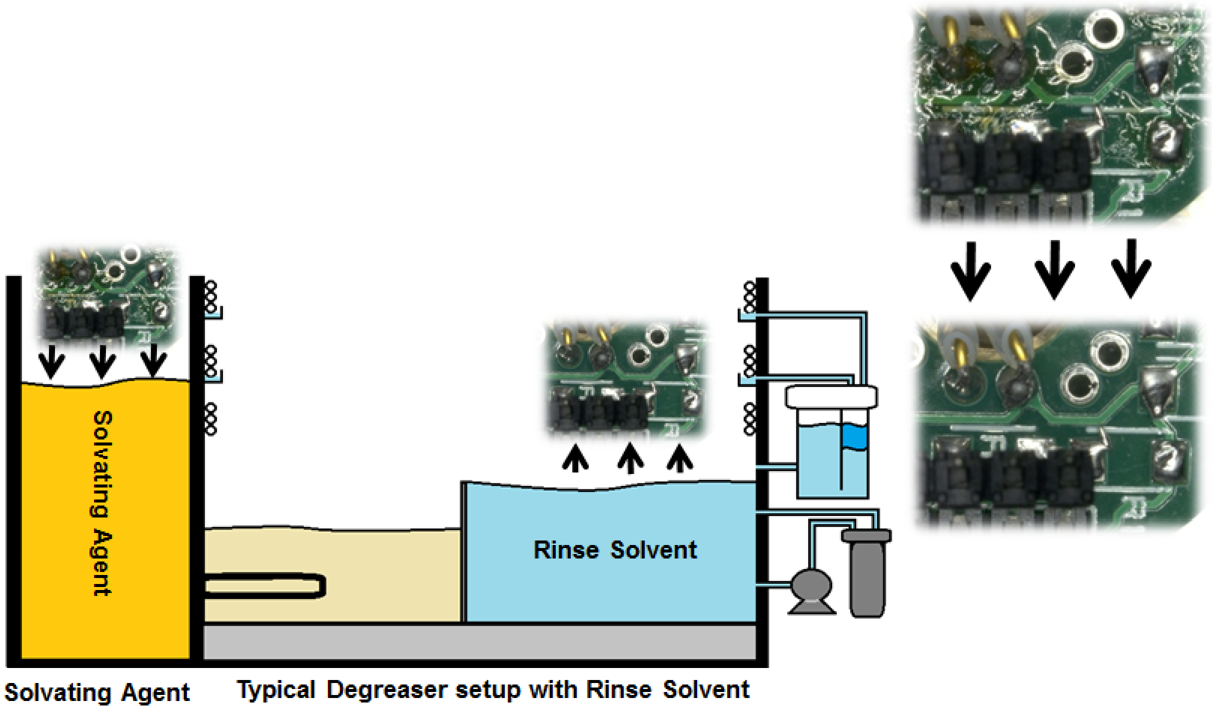


Figure 1: Duo-Solvent Cleaning Process

Figure 2: Duo-Solvent Approach

The solvating agent is an engineered cleaning fluid composition with balanced dispersive, polarity and hydrogen bonding solubility forces. The cleaning agent is engineered to the soil being cleaned, in this example, lead-free no-clean flux residues. The slow evaporating cleaning agent exhibits a strong hydrophilic/hydrophobic balance, non-flammability and rinses well with the Hydrofluoro-olefin rinse solvent. The rinse solvent exhibits desirable environmental, performance, stability, compatibility and safety properties.

Table 1

Property	**Solvating Agent**	**Rinsing Agent**
Chemical Name	Oxygenated Engineered Mixture	Hydrofluoro-Olefin
Boiling Point	203˚C	19˚C
Surface Tension @ 20˚C	32.7 dyne/cm	12.7 dyne/cm
Flash Point	88˚C	None
Water Soluble @ 25˚C	Partial	460 ppm
VOC	Non-Exempt	Exempt

Solubility of the Soil in the Cleaning Agent

Electronic assembly processing residues that dissolve in the cleaning agent are based on the following forces:

- Dispersive ~ Soil dissolves in a cleaning agent
  - Soil has "like" chemical properties to the cleaning agent
  - Like dissolves Like
  - Temperature and Energy typically increase the dispersion rate
- Polarity[3]
  - Intermolecular force of attraction or repulsion which act between neighboring molecules or ions (Van der Waals force)
  - Force between two permanent dipoles (Keesom force)
  - Force between a permanent dipole and a corresponding induced dipole (Debye force)
  - Force between two instantaneously induced dipoles (London Dispersive Force)
- Hydrogen Bonding[4]
  - Electrostatic attraction between polar molecules
  - Hydrogen atom bound to a highly electronegative atom such as nitrogen, oxygen or fluorine
  - Attracted a nearby highly electronegative atom

A Teas Diagram is a way to plot the relative strengths of the dispersive, polarity and hydrogen bond forces.[5] If the relative strengths of the forces are known, a compound can be plotted in an equilateral triangle. The three legs of the triangle each represent the percentage of one of the three forces for that compound. For instance, a compound that is characterized as 35% polar, 15% hydrogen bonding, and 50% non-polar would be plotted as follows:

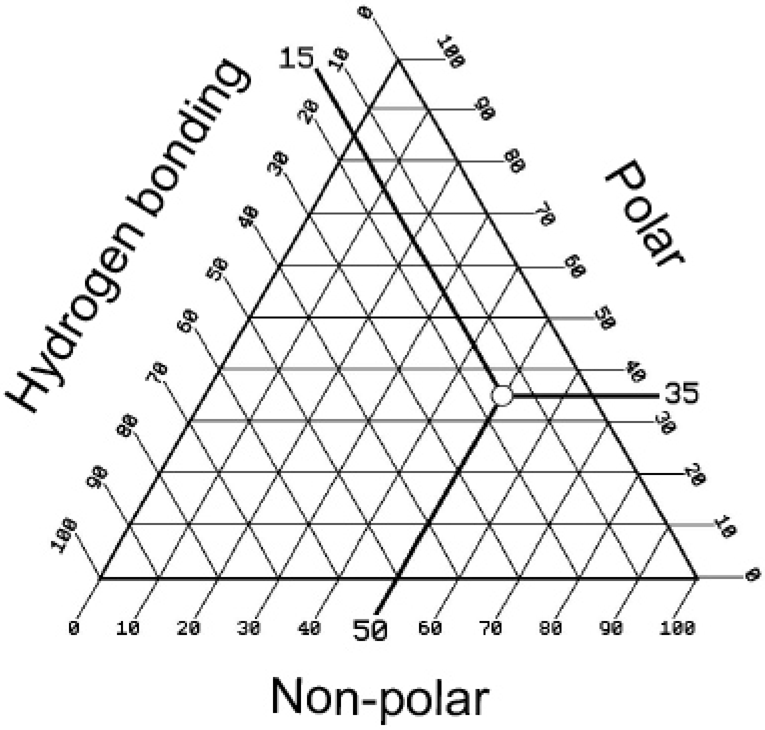


Figure 3: Teas Diagram (from J. Burke, "The Handbook for Critical Cleaning, CRC Press, 2001)

The Hildebrand solubility parameter provides a numerical estimate of the degree of interaction between materials, and can be a good indication of solubility, particularly for nonpolar materials.[6] Building from the Hildebrand solubility work, Hansen developed Hansen Solubility Parameters to predict if one material will dissolve in particular solvent or cleaning material.[7]

Hildebrand and Hansen theorems postulate that solvents will clean soils will dispersive, polarity and hydrogen solubility forces near the solvent used to clean a particular soil. When cleaning electronic flux residues, the soil is typically a combination of ingredients that have different solubility parameters. The challenge is engineering a solvent cleaning agent that provides a balance of the three forces within the range of the soils being targeted (Figure 4).

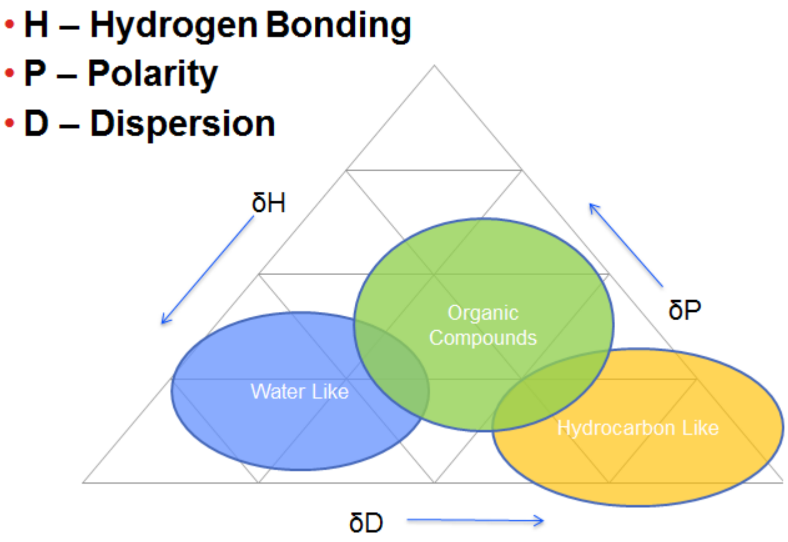


Figure 4: Solubility Forces Plotted within the Teas Chart

Experimental data of several common solvents with known solubility parameters can be used to determine the solubility parameters of flux residues by product name. The data findings can be used to calculate a solubility parameter for the each soil tested. Figure 5 illustrates the position on the Teas Chart for a number of soils from Solder Pastes tested.

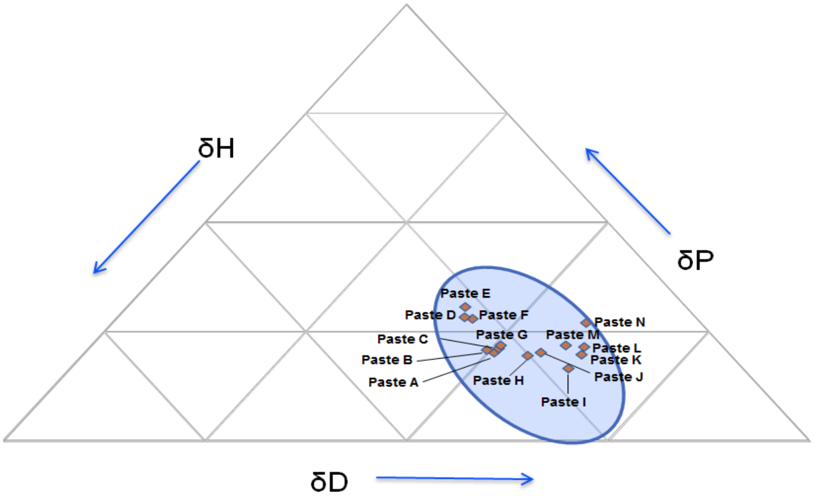


Figure 5: Solder Paste Flux Residues Position on the Teas Chart

Flux residues from a multitude of soldering materials are not a single point on the Teas chart. The flux residue for each material tested is distributed to a larger away from its calculated area due to the different materials contained within the residue. Flux residues, being multi-component soils, require an engineered cleaning solvent to remove the soil.

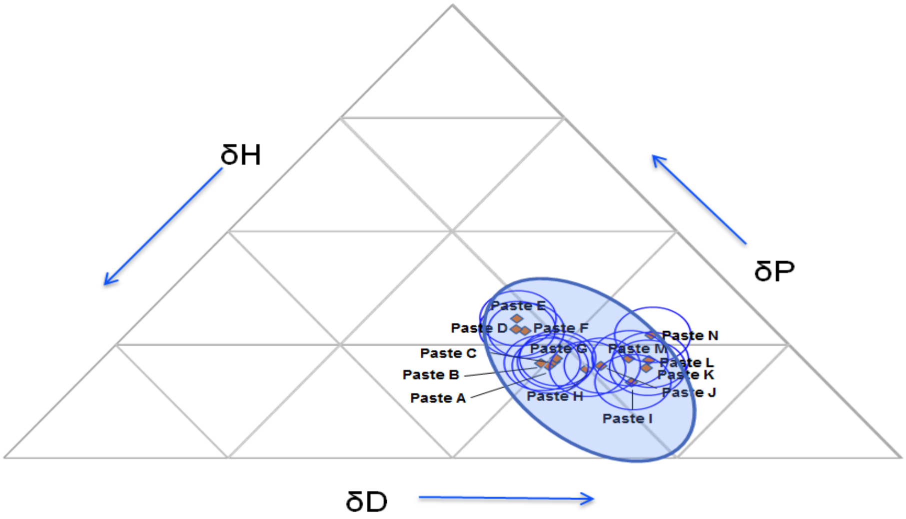


Figure 6: Flux Residue Distributed in a Larger Area Represented by the Circles

A partial list of solvents with "like" solubility parameters to the flux residue soils in question are listed in Figure 7.

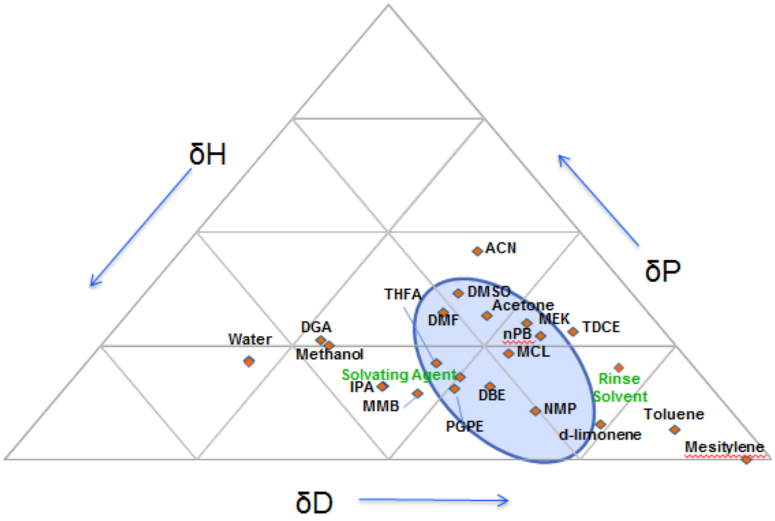


Figure 7: Solvents Solubility Position on the Teas Chart

Removal of solvents with high order of toxicity narrows possible candidates as shown in Figure 8.

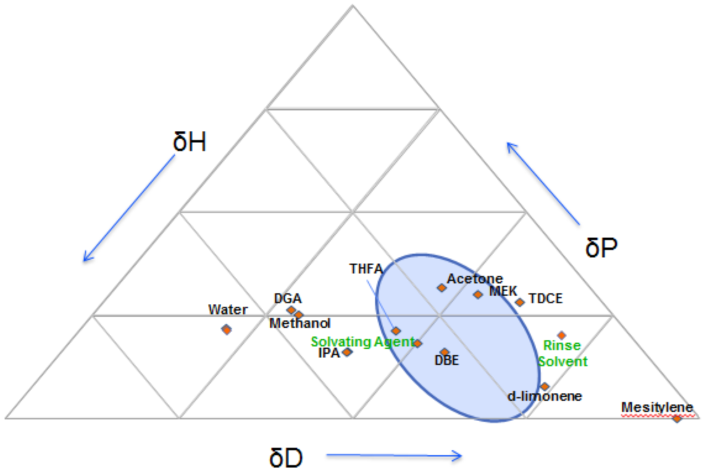


Figure 8: Solvent with Lower Levels of Toxicity

Removal of flammable solvents narrows the list of candidates as shown in Figure 9.

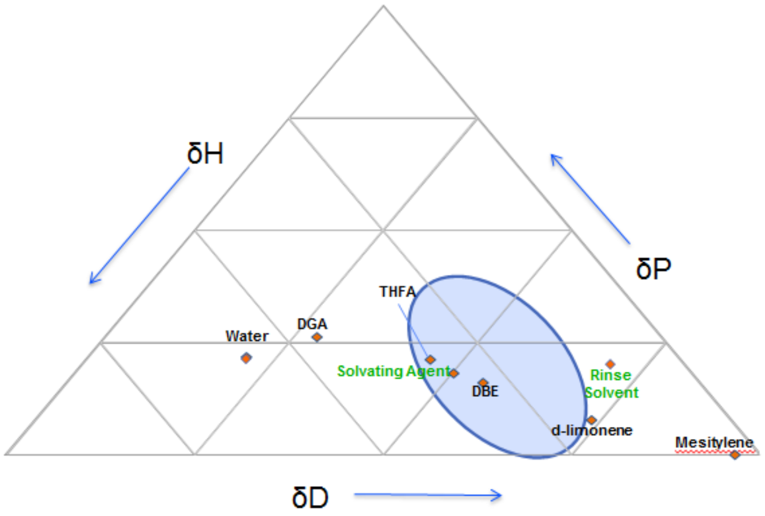


Figure 9: Solvent Candidates with Low Levels of Flammability

The key to cleaning any soil is the ability to engineer a cleaning material that has “like” properties to the soil. Engineering the three forces into the cleaning material formulation allows for the ability to dissolve the targeted soil. The dispersive property targets the soil nonpolar material set, in this case the resin flux structure. The polarity property creates the attractive and repulsive forces needed to dissolve the polar molecules within the flux composition. Hydrogen bonds create an electrostatic attraction between polar molecules. An engineered material that combines these attractive forces will be more successful in cleaning a multitude of flux residues with different properties.

Cleaning Machine

Duo-Solvent cleaning machines contain two stages. Stage 1 is an immersion cleaning chamber charged with the engineered cleaning solvent. Multi-stage agitation and thermal heat provide the thermodynamic forces needed to displace and dissolve the flux residues from the surface and under bottom termination components. Stage 2 is designed to rinse the assemblies free of the solvating agent and ionic residues.

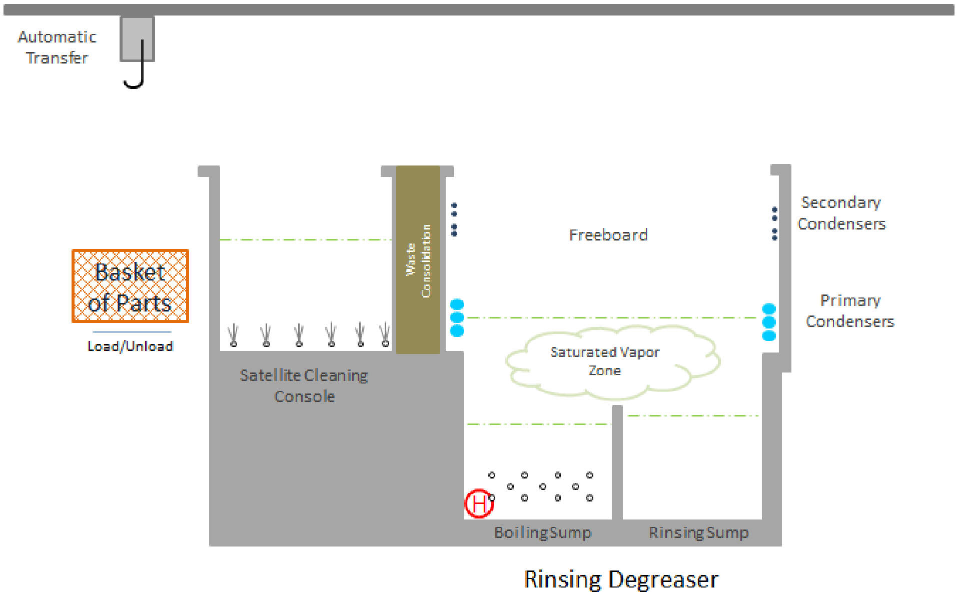


Figure 10: Cleaning Machine Designed for the Duo-Solvent Process

The cleaning machine has an engineered solvent separation system designed to continuously, in real time, remove the engineered solvent and flux soils carried from Stage 1 into Stage 2 (Figure 11). The vapor pressure of the rinse solvent is higher than engineered solvating agent. The solvent separation system extracts the cleaning solvent from the rinse solvent. Purification and recovery of the rinse solvent real time provides a high level of reproducibility with time.

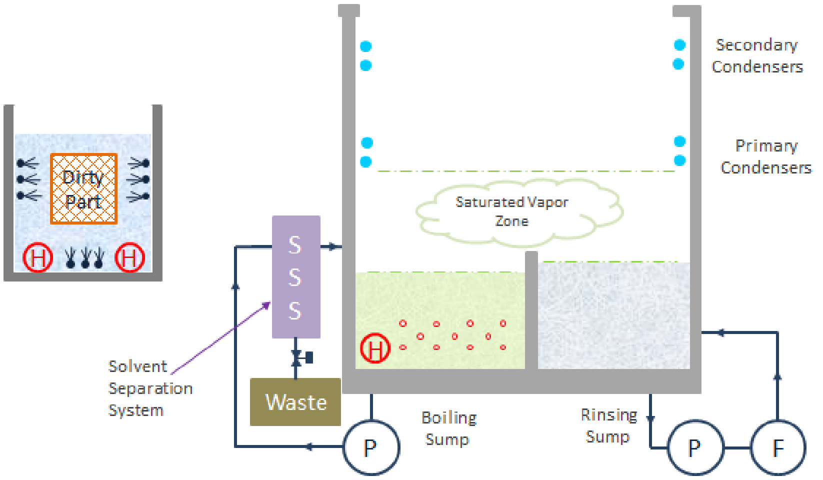


Figure 11: Solvent Separation Systems Continuously Purifies the Rinse Solvent

Experimental

The IPC PCB052-ENIG / CRET test vehicle was selected to run cleanliness on an industry accepted Lead-Free solder paste (Figure 12). The boards were assembled by a defense contractor. Following assembly, the boards were sent for cleaning using the Duo-Solvent cleaning process.

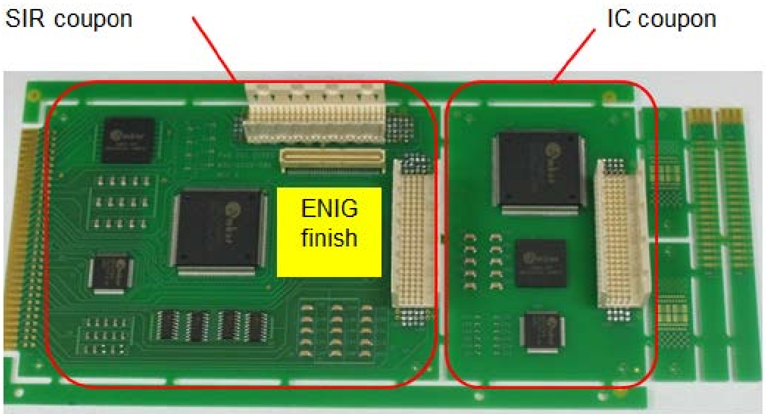


Figure 12: IPC B-52 Test Vehicle

Table 2 provides an overview of the DOE matrix.

RunOrder	Test Board	Solder Paste	Cleaning	Testing Main Board	IC Break Out Board
1	B-52	No Solder Paste	Not Cleaned	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28
2	B-52	No Solder Paste	Not Cleaned	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28
3	B-52	Lead Free No-Clean	Lead Free NC ~ Not Cleaned	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28
4	B-52	Lead Free No-Clean	Lead Free NC ~ Not Cleaned	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28
5	B-52	Lead Free No-Clean	Partially Cleaned with Rinse Solvent	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28
6	B-52	Lead Free No-Clean	Partially Cleaned with Rinse Solvent	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28
7	B-52	Lead Free No-Clean	Totally Cleaned Solvent Process	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28
8	B-52	Lead Free No-Clean	Totally Cleaned Solvent Process	SIR 2.6.3.7 for 7 & 14 days	IC 2.3.28

Data Findings

Figure 13 provides an example of the Lead-Free no clean flux residues after soldering.

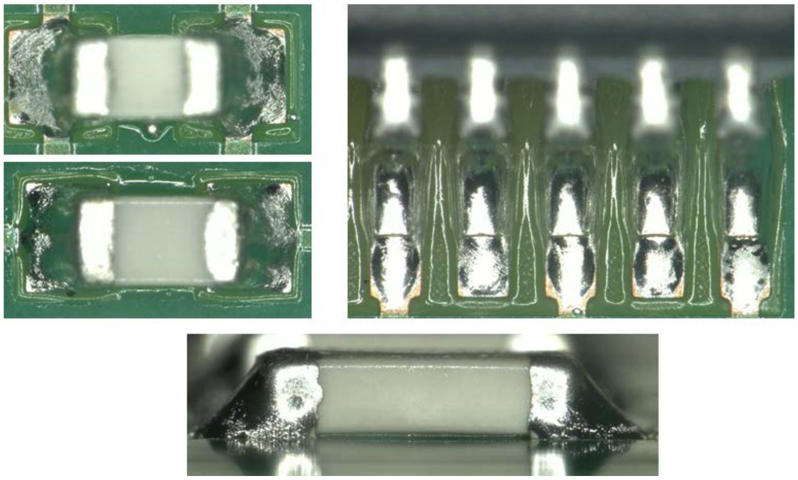


Figure 13: Flux Residue Examples after Solder

To achieve a partially cleaned condition, the assemblies to meet this condition within the DOE were cleaned with the Rinse Solvent only. Figure 14 provides an example of the Partially Cleaned test boards.

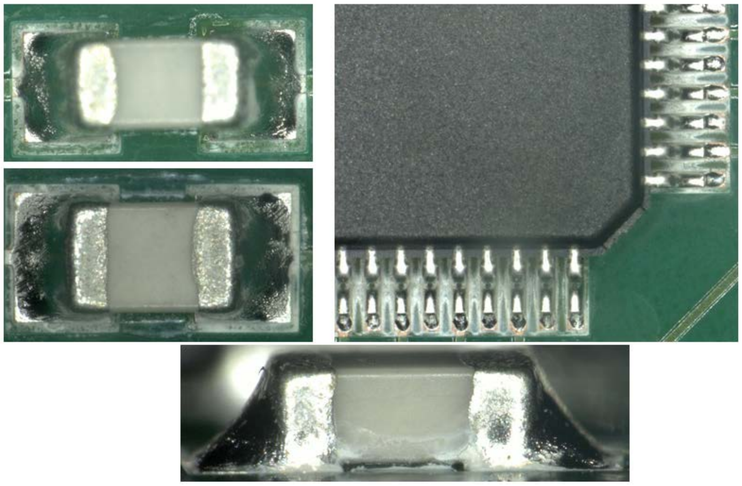


Figure 14: Partially Cleaned Test Board Images

Test boards cleaned with the Duo-Solvent process were free of visible white residues (Figure 15).

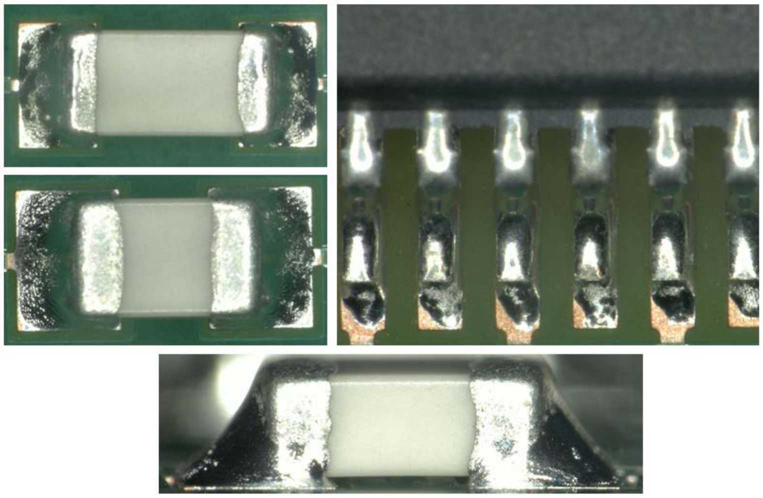
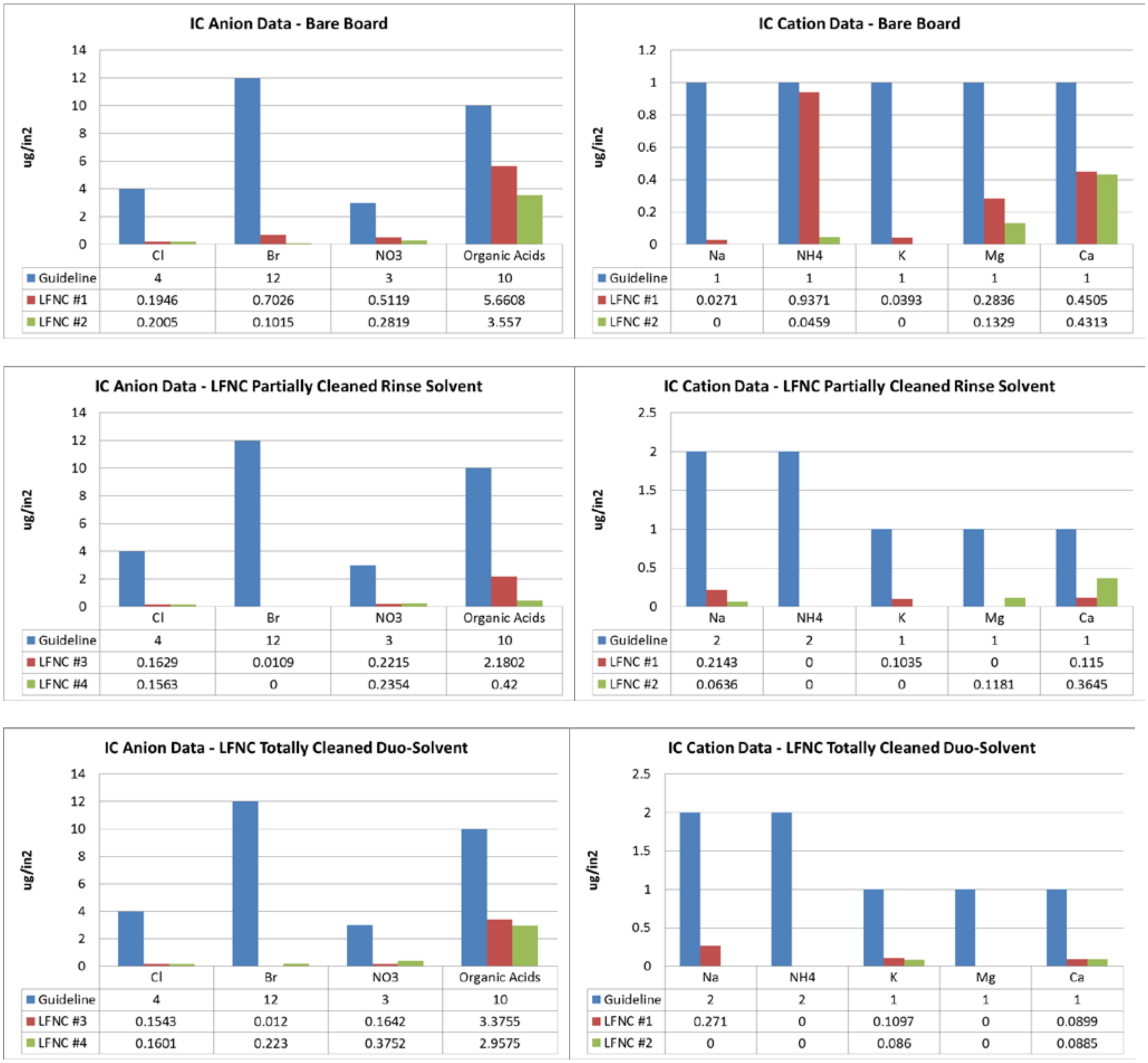


Figure 15: Clean Test Board Images

Ion Chromatography was performed per IPC TM-650 2.3.28. Boards were extracted with 20 ml of 75% IPA / 25% DI at 80˚C for 1 hour. Samples were split for detection of anions and cations. The data from the IC was used to calculate micrograms per square inch.



IC Anion Data - Bare Board

	Cl	Br	NO3	Organic Acids
🟦 Guideline	4	12	3	10
🟥 LFNC #1	0.1946	0.7026	0.5119	5.6608
🟩 LFNC #2	0.2005	0.1015	0.2819	3.557

IC Cation Data - Bare Board

	Na	NH4	K	Mg	Ca
🟦 Guideline	1	1	1	1	1
🟥 LFNC #1	0.0271	0.9371	0.0393	0.2836	0.4505
🟩 LFNC #2	0	0.0459	0	0.1329	0.4313

IC Anion Data - LFNC Partially Cleaned Rinse Solvent

	Cl	Br	NO3	Organic Acids
🟦 Guideline	4	12	3	10
🟥 LFNC #3	0.1629	0.0109	0.2215	2.1802
🟩 LFNC #4	0.1563	0	0.2354	0.42

IC Cation Data - LFNC Partially Cleaned Rinse Solvent

	Na	NH4	K	Mg	Ca
🟦 Guideline	2	2	1	1	1
🟥 LFNC #1	0.2143	0	0.1035	0	0.115
🟩 LFNC #2	0.0636	0	0	0.1181	0.3645

IC Anion Data - LFNC Totally Cleaned Duo-Solvent

	Cl	Br	NO3	Organic Acids
🟦 Guideline	4	12	3	10
🟥 LFNC #3	0.1543	0.012	0.1642	3.3755
🟩 LFNC #4	0.1601	0.223	0.3752	2.9575

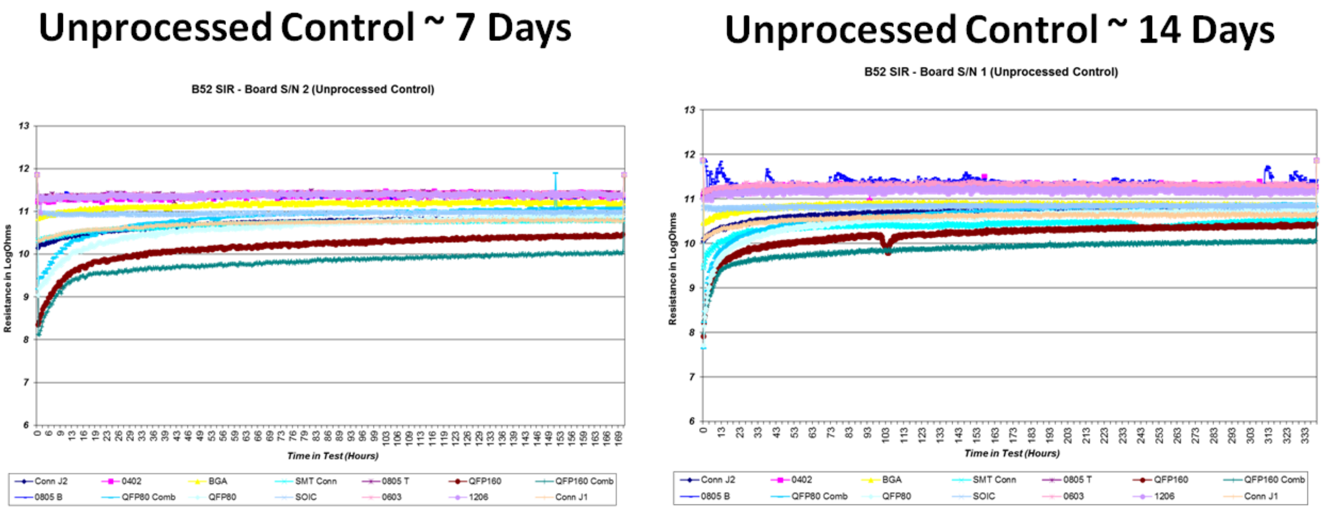
IC Cation Data - LFNC Totally Cleaned Duo-Solvent

	Na	NH4	K	Mg	Ca
🟦 Guideline	2	2	1	1	1
🟥 LFNC #1	0.271	0	0.1097	0	0.0899
🟩 LFNC #2	0	0	0.086	0	0.0885

Figure 16: IC Data Findings

Surface Insulation Resistance is used to determine the propensity of a material and how the material is processed that may lead to an electrochemical event (Ex. Corrosion, dendrites or leakage). For this evaluation the test was performed using IPC-TM-650, method 2.6.3.7 with a slight modification. The boards were analyzed at 40˚C/90% RH; 5 VDC bias; 7 Day test and 14 Day test with 20 minute measurement intervals. Two sets of test conditions are represented in the data findings. One set was run from the traditional 7 days and other for 14 days.

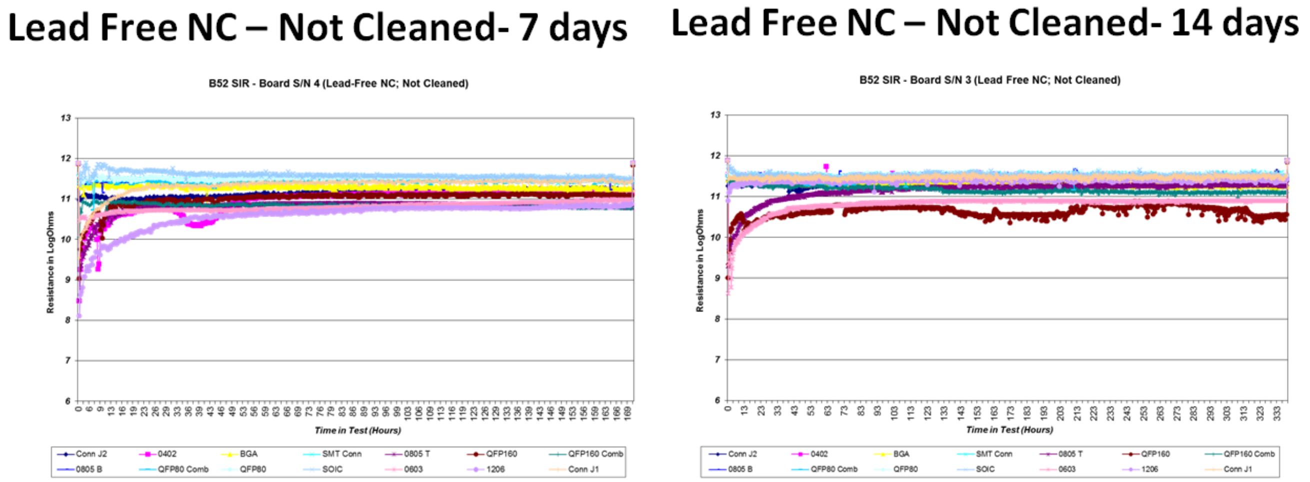
Surface Insulation Resistance is important test in determining electrical reliability impacted by flux residues / ionic contaminants, conductive / corrosive nature of residues, and the potential formation of dendrites and/or leakage issues. Measurements exceeding 100 MΩ (1.0E+08 Ohms or 8.0 LogOhms) for processed test boards and measurements exceeding 1000 M Ω (1.0E+09 Ohms or 9.0 LogOhms) for unprocessed control boards are required to pass.


Unprocessed Control ~ 7 Days

Unprocessed Control ~ 14 Days

Figure 17: Unprocessed Controls

For the 7 day unprocessed control board, all test patterns maintained well above 1000 MΩ limit. For the 14 day unprocessed control board, the data grouping was tight and maintained well above the 1000 MΩ limit. The QFP160 data dropped approximately 101 hours into test, but recovered. A fiber was observed, but no other visual anomalies were noted. The 0805B (bottom side) showed erratic behavior throughout test. Again, a fiber was noted and was plated over. Additionally, solder mask over traces was discolored on one side of the pattern. No evidence of any water spotting, corrosion or dendritic activity.


Lead Free NC – Not Cleaned- 7 days

Lead Free NC – Not Cleaned- 14 days

Figure 18: Lead Free Not Cleaned Boards

The 7 day data findings for the Lead-Free not cleaned boards found all patterns maintained well above the 100 MΩ limit beyond 24-hour grace period. Data variability was observed during first few hours of test due to acclimation of the test board and material. This is common. Data was tightly grouped beyond 49 hours and very stable. For the 14 day data findings, the uncleaned NC board showed good SIR levels overall well above the 100 MΩ limit. The data was somewhat erratic, which is likely due to the presence of flux residues. The QFP160 was the lowest trending pattern on the board and also showed the most pronounced erratic behavior. There was no evidence of any water spotting, corrosion or dendritic activity noted.

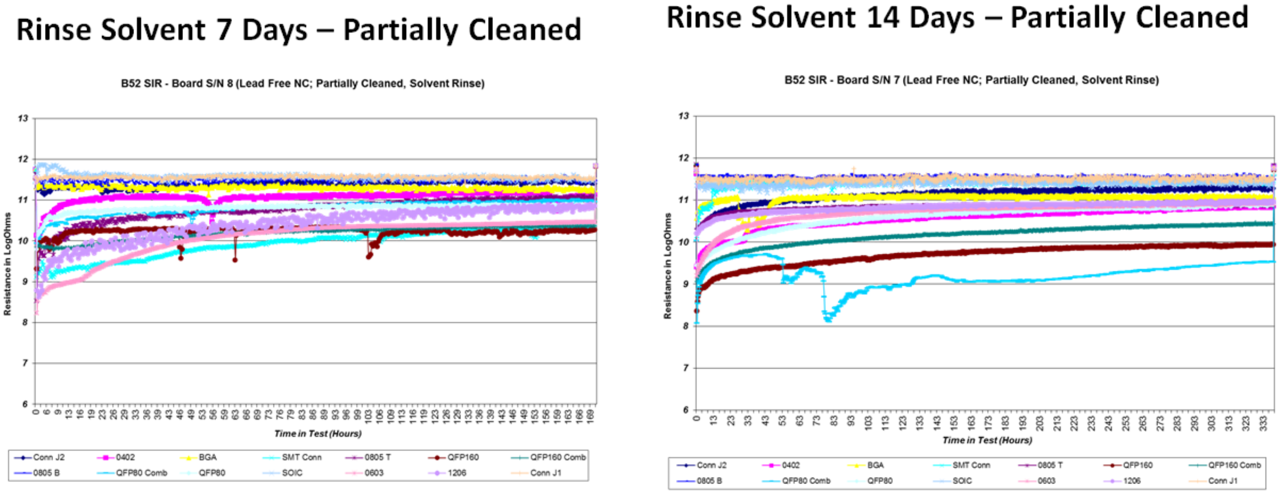
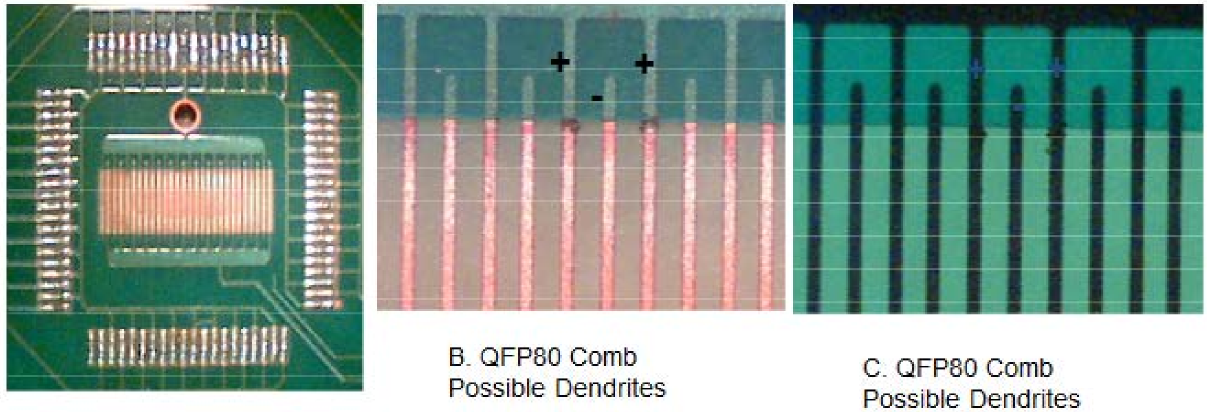


Figure 19: Rinse Solvent Cleaned Boards

The 7 day data findings for the Rinse Solvent, pattern data maintained above 100 MΩ limit. However, considerably more variability resulted. Patterns QFP160 comb, 1206 cap field and 0402 cap field showed more erratic performance. Since the parts were rinsed only in the solvent and not cleaned in solvating agent, more white residue remained. White residues contributed to erratic performance. The 14 day data findings for the Rinse Solvent, the board showed good SIR performance, except for the QFP80 comb.

Visually, there was evidence of white residue left under the part. Figure 20, photo A, shows and outline in the middle of the comb pattern. Visually, there appeared to be possible dendrites present. The direction of the growths further suggests dendritic activity (See photo’s B and C).



B. QFP80 Comb
Possible Dendrites

C. QFP80 Comb
Possible Dendrites
(Backlighting)

A. QFP80 Comb

Figure 20: Rinse Solvent Cleaned SIR Images

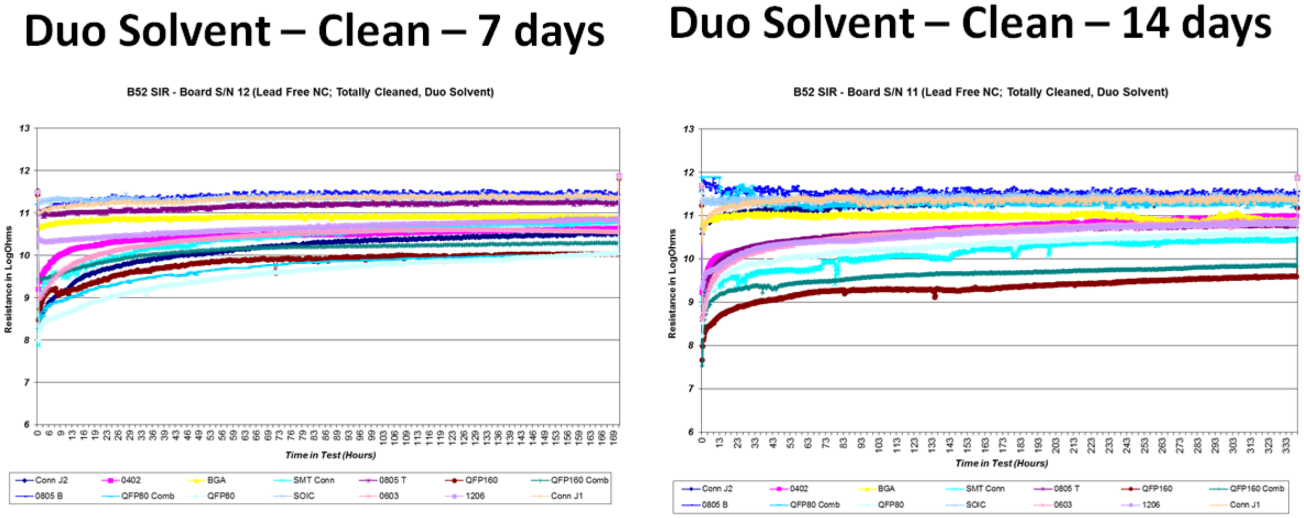


Figure 20: Duo-Solvent Cleaned Boards

Overall the data from the Duo-Solvent cleaned boards was good and maintained well above the 100 MΩ limit. Duo-Solvent S/N 12 showed better data stability. The variation observed in the two samples may be an indication of process / material variability. Starting board cleanliness may also be at work in the data. The SMT Connector on S/N 11 had some intervals where the data jumped around. Visually, the only item observed was some very mild process debris. There was no evidence of any water spotting, corrosion or dendritic growth.

Inferences from the Data Findings

Visual, IC and SIR results find that the Duo-Solvent cleaning process is effective for cleaning electronic assemblies soldered with no-clean solder pastes. A summary of the findings are as follows:

1. Unprocessed boards
   - Both were adequately clean
   - Met the minimum SIR requirements to pass the test.
2. Lead Free NC ~ not cleaned
   - Overall good electrical resistivity when left uncleaned. Some data variability observed, especially in the QFP160 location.
   - The second board (S/N 4) showed better overall SIR performance, less data variability. This suggests potential process variability.
   - Met the minimum SIR requirements to pass the test.
3. Duo-Solvent Rinse cleaned
   - The QFP80 comb of S/N7 saw some loss in resistivity but recovered
   - The cause appeared to be white residue next to component terminations. Possible dendritic activity led to lower resistance levels.
   - Most patterns met the minimum SIR requirements to pass the test.
4. Duo-Solvent Totally cleaned
   - Some data variability was observed across several components. The SMT Connector showed the most pronounced variability, but maintained above the defined limit.
   - QFP160 values passed but trended lower than other values
   - Met the minimum SIR requirements to pass the test.

Research Conclusions

The Duo-Solvent cleaning process is designed to remove flux from Printed Circuit boards using an engineered solvating cleaning composition. Following the cleaning process, the PCB is rinsed in a solvent to remove excess solvating agent and ionic residues. The process produces clean and dry PCBs in one machine with short cycle time, low energy usage and small footprint.

Flux compositions are multi compositional soils. Cleaning fluids designed for Duo-Solvent process require a combination of dispersive, polar and hydrogen bonding forces. Engineered cleaning fluids require the ability to clean multi-compositional flux residues and rinse with a high vapor pressure solvent composition. The high vapor pressure rinse solvent enables a waterless solvent-based process for cleaning printed circuit assemblies. The data found that the process is effective at *removing* no-clean Lead-free flux residues. The rinse fluid is effective at removing drag-out from wash process and ionic residues during the rinse process.

Properly designed cleaning equipment enables the process. The solvating agent is processed in a cleaning module external to the vapor degreaser. The rinse solvent requires a low surface tension and solubility with the cleaning solvent. The first rinse takes place in the boil sump with the rinse sump and vapor zones providing final rinses. A solvent separation system cleans and recovers the rinse solvent on a continuous basis. The process design provides a waterless cleaning design.

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