ABSTRACT
Since the demise of CFCs as a cleaning option in the 1970s (1), no-clean fluxing technology has become increasingly popular in electronics assembly (2). The benefits include a reduced number of process steps, simpler qualification with no need to specify cleaning detail, and reduced cost.

For customers requiring the extra confidence that cleaning brings, the option of water wash has remained, with many products available. This approach allows the use of highly activated materials ideal for components with poor solderability and/or high thermal demand with no risk of failure in service.

The clear demarcation between these two strategies has blurred slightly over recent years, with some manufacturers seeking to combine the convenience of no-clean fluxing with the confidence of water wash by cleaning no-clean flux residue.

This paper assesses the wisdom of such an approach.

Key words: Solder paste, cleaning.

1. INTRODUCTION

1.1. Water Wash and No-clean Products

(In addition to fluxing capability,) the key requirement of a water wash fluxing medium is that afterward, soldering residues must be removed by water wash, preferably without chemical additives. It is not necessary for all flux components to be water soluble, so long as this is conferred by the soldering process. A typical medium is based on water soluble resin activated by amine hydrohalides and organic acids, with suitable solvents and rheology modifiers.

A typical no-clean fluxing medium comprises rosin (often modified to improve color and reduce the likelihood of oxidation), other components to complement activity (some of these may be similar to those in the water wash medium), corrosion inhibitors, solvents and gelling agents. The central element is rosin. Its physicochemical properties are ideal.

During the reflow process, a viscous liquid is formed that acts as a robust activator. When reflow is complete, it solidifies, encapsulating products from the fluxing process and un-reacted flux components. Because it is a water insoluble dielectric, rosin becomes an in-situ conformal coating that protects underlying circuitry such as from high humidity.

In contrast with water wash fluxing mediums, there is no requirement that all flux residues are soluble in a particular solvent. In fact, given the wide range of materials used, from water soluble dicarboxylic acids and amine hydrohalides to water insoluble organic halogenated compounds and rosin, as well as various metal salts, oxides and hydroxides formed during the soldering process, this is highly demanding. No-clean products are formulated to be no-clean. Product validation (e.g. SIR and electrochemical migration) is performed based on this understanding.

1.2 Cleaning Options

Saponification is a ubiquitous and long-standing cleaning method. A saponifier is an alkaline material that reacts with the acidic functionality in contaminants to form a soap that is soluble, or at least dispersible, in water. In this form it is removed from the substrate. Outside the world of electronics, saponifiers form the basis of many household and industrial cleaning systems such as dishwasher detergent. The primary target in electronics is rosinous flux residue where the saponifier reacts with the acidic moiety to form rosin soap. A similar mechanism will remove un-reacted carboxylic acid. As the saponifier is delivered in the form of an aqueous solution, water soluble flux residue is vulnerable too. However, depending on the rigour of the cleaning process, water insoluble and non-saponifiable contamination may remain.

There are many glycol ether cleaning solvents on the market. These, too, are generally good solvents for rosin. However, they have less propensity to other flux contamination, especially more polar (low molecular weight) carboxylic acids. When applied as a semi-aqueous process, in which it is mixed with water and/or a water rinse follows, the range of contaminants removed increases.
Cleaning with pure water (without saponifier) will remove water soluble contamination only, unless there is significant physical force and/or high temperature, in which case a physical “scrubbing” action will operate. This can be effective, but it may risk PCB integrity.

2. FEASIBILITY OF CLEANING A “NO-CLEAN” PASTE

2.1 Experiment
Although there are many reasons not to clean a “no-clean” solder paste, there is increased interest in doing so. “No-clean” solder paste exploits a flux chemistry that is designed to encapsulate activators that remain on the board after soldering. It is not meant to be cleaned after soldering; therefore, the residues are harder to remove from a printed circuit assembly.

The residue that remains after soldering contains activators, gelling agents and resins. The amount depends on the composition of the solder paste and the process conditions (e.g. reflow temperatures) to which the assembly was exposed.

The first experiment was a study to identify the possibility of cleaning a “no-clean” solder paste and to define the impact of the different parameters on cleaning performance. A full factorial design of experiment was run with the following parameters and levels:

<table>
<thead>
<tr>
<th>Factor</th>
<th>Unit</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning</td>
<td>ºC</td>
<td>35</td>
<td>50</td>
<td>65</td>
</tr>
<tr>
<td>temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cleaning time</td>
<td>Min</td>
<td>5</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Concentration</td>
<td>%</td>
<td>DI-water only</td>
<td>DI-water + 10% detergent</td>
<td>DI-water + 20% detergent</td>
</tr>
<tr>
<td>saponifier</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Layout of the Design of Experiment

The experiment was done using a small lab scale washing device. Solder paste was printed on copper samples (stencil 107 x 76 x 0.2 mm with three round holes or 6.5 mm diameter aperture).

The samples were reflowed in a convection oven using a typical three minute tin-lead reflow profile with a peak temperature of 215 ºC. The reflowed samples were washed using different saponifier concentrations, temperatures and times. The amount of residues removed was weighed using a four figure balance.

The average amount of solder paste applied on the samples was 0.070 gram. After soldering, 51 percent of the flux remained. The other 49 percent evaporated as a result of the reflow process.

2.2 Data analysis
All factors in the experiment – temperature, concentration and cleaning time – significantly impacted on the cleaning result. DI-water only was unable to clean a “no-clean” solder paste. No-clean solder paste contains non-polar water insoluble residues. These can only be cleaned by the additives in water such as saponifiers.

Figure 1. Removed amount of flux from the solder paste. Data are the means of the parameter levels.

The concentration of the cleaning agent and the cleaning time had the highest impact. Figure 2 shows the relation between both factors.

Figure 2. Board cleanliness as a function of cleaning time and concentration saponifier.
2.3 Further cleaning tests
These data formed the basis of two cleaning processes for a test board that was soldered with three different no-clean solder pastes.
- Spray in air
- Ultrasonic
The test boards were soldered, cleaned and tested for cleanliness by means of visual inspection and using an Ionic Contamination measuring device.

The maximum levels of flux residues left on the assembly are defined in IPC J-STD-001E:
- Class 1 assemblies less than 200 mg/cm²
- Class 2 assemblies less than 100 mg/cm²
- Class 3 assemblies less than 40 mg/cm²

The spray in air test was conducted in a batch washing machine using an aqueous cleaner and the following parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saponifier detergent</td>
<td>20%</td>
</tr>
<tr>
<td>Cleaning time</td>
<td>12 minutes</td>
</tr>
<tr>
<td>Cleaning temperature</td>
<td>60 °C</td>
</tr>
<tr>
<td>Rinses</td>
<td>6 rinses with Di-water</td>
</tr>
<tr>
<td>Dry time</td>
<td>12 minutes</td>
</tr>
<tr>
<td>Dry temperature</td>
<td>65 °C</td>
</tr>
</tbody>
</table>

Table 2. Cleaning conditions batch washer

Ultrasonic cleaning of printed circuit assemblies has been under discussion for 50 years. According to IPC-STD 001E, ultrasonic cleaning is permissible:
1. On bare boards or assemblies, provided only terminals or connectors without internal electronics are present.
2. On electronic assemblies with electrical components, provided the manufacturer has documentation available for review showing that the use of ultrasonic does not damage the mechanical or electrical performance of the product or components being cleaned. (3)

Modern ultrasonic cleaners have variable frequencies to prevent the build up of potentially damaging harmonics. The bare test board was cleaned in a single tank ultrasonic cleaning system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saponifier detergent</td>
<td>20%</td>
</tr>
<tr>
<td>Cleaning time</td>
<td>12 minutes</td>
</tr>
<tr>
<td>Cleaning temperature</td>
<td>60 °C</td>
</tr>
<tr>
<td>Frequency</td>
<td>30 kHz</td>
</tr>
<tr>
<td>Rinses</td>
<td>4 rinses with Di-water</td>
</tr>
<tr>
<td>Dry time</td>
<td>8 minutes</td>
</tr>
<tr>
<td>Dry temperature</td>
<td>65 °C</td>
</tr>
</tbody>
</table>

Table 3. Ultrasonic cleaning conditions

Visual inspection of the boards after cleaning showed that all flux residues were removed and the solder joints appeared cosmetically clean.

The test boards were tested for ionic residues. Results for the three different alloys and two washing methods are listed in the Figure 4.

Figure 3. No-clean solder paste test boards before and after cleaning.

Figure 4. Ionic residues levels: All are well below the maximum of 40 mg/cm².
3. SMALL COMPONENTS WITH LOW STAND-OFF

3.1 Potential risk of contamination

Electrochemical migration may occur between adjacent conductors under an applied electric field in a humid environment. Metal at the anode dissolves and the resulting metal ions (cat ions) migrate towards the cathode where they are reduced, forming a dendrite structure that grows back towards the anode, ultimately risking short circuit. Even when this does not occur, the electrochemical cell that is formed between the conductors will exhibit reduced surface insulation resistance. Both phenomena are potentially detrimental to circuit integrity, especially fine-pitch.

In particular, reliability concerns result from highly active organic acid and/or halide/halogenated flux residues trapped under low stand-off components and not removed during post-soldering cleaning.

Currently, there are insufficient process control and quality assurance methods for detecting flux residue trapped in this way. (5)

If a water wash flux is used, all residues must be removed from the assembly. If not, they are a potential risk (e.g. dendrite growth). A more serious issue arises with the recent trend of cleaning a “no-clean” solder paste using DI-water with a (small) concentration of the cleaning agent. As with water wash paste, if the flux residues are not completely removed from the assembly, they also are a potential risk for failure, since the protective properties of the rosins have been damaged by the cleaning attempt.

Miniaturization is one of the major trends in electronic assembly. Components become smaller and smaller. As a result, pick-and-place machines and printers need to be more accurate and solder paste powders may require a powder type 4 or 5 instead of type 3. These smaller powder sizes require a review of the solder paste flux system. The fine powder has more metal surface and therefore may require more flux or a modified activation system. More flux in the paste means more flux residues after soldering underneath small components.

Another phenomenon that occurs with fine-pitch components is solder graping – poor coalescence. Solder graping refers to poor solder wetting: where the solder paste has partially melted, but has not coalesced or flowed completely. Solder powder (oxidation, contamination of the metal) may impact graping, but the flux system also requires a stronger activator or materials that give it more thermal stability.

Graping should not be considered a defect if only the outer solder spheres are joint to melting and remain part of the molten bulk of solder, and they do not violate the minimum electrical clearance.
Miniaturization introduces some challenges for cleaning processes. Distances between the pads reduce dramatically from 3.5 mm for 2010 to 0.1 mm for 01005 components. The risk of bridging, electro-migration, etc. increases and the stand-off height of components reduces. This requires a cleaning chemistry with a low surface tension and sufficient capillary force to penetrate below these small components.

After cleaning the “no-clean” flux, residues are gone, including the entrapped solder spheres.

Figure 8. Component dimensions and stand-off.

After removing the soldered chip components, it was clear that the entire volume underneath components that are smaller than 0603 was completely filled with solder paste flux residues, blocking the ingress of the cleaning agent.

To verify the clean ability of small components with low stand-off an assembly was cleaned using the lab device from the previous design of experiment (DoE). Using the same cleaning agent (20% concentration) at a temperature of 50 °C, the boards were cleaned with varied cleaning times. Components were removed to visually inspect the presence of flux residues.

Table 4. 0 = all residues gone, - = some residues left, X = residues still there

<table>
<thead>
<tr>
<th>Components</th>
<th>Cleaning time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 min</td>
</tr>
<tr>
<td>MELF</td>
<td>-</td>
</tr>
<tr>
<td>0402</td>
<td>X</td>
</tr>
<tr>
<td>0603</td>
<td>X</td>
</tr>
<tr>
<td>1206</td>
<td>X</td>
</tr>
</tbody>
</table>

4. REFLOW PROFILES AND IMPACT ON RESIDUES

The reflow profile will impact the solder and cleaning performance of the solder paste. The heating profile also will affect wetting, the amount of flux residue and the hardness/clean-ability of the residue.

A Taguchi DoE was performed to define the best wetting conditions for the solder paste and the amount of residue remaining on the assembly after soldering.

The factors in the experiment cover the three critical heating phases in the reflow process: preheat, soak and peak temperatures. The fourth factor is the atmosphere (air vs. nitrogen).

A thermogravimetric analyzer (TGA) was used to reflow the solder paste that was printed on the copper coupons. A solder paste deposit of 1.5 mm diameter was printed with a 100 µm stencil. During soldering the weight loss was monitored and the amount of residue could be defined. Under a microscope, the wetting diameter was measured. After cross sectioning the joint, solder height and solder angle could be defined (the smaller the wetting angle the better the wetting of the solder).

Figure 9. Mean effects of parameters on wetting. The smaller the wetting angle, - the better.
For tin-lead alloys, the best spreading was achieved using a fast ramp up in the preheat part with a peak temperature of 215 °C in a nitrogen atmosphere.

The water wash paste has stronger activators, which result in better wetting. The average wetting angle for water wash was 1 ° smaller than the "no-clean" score.

5. LEAD VS. LEAD-FREE

Lead-free soldering introduces numerous additional challenges to the cleaning process. Water wash is an attractive option for lead-free soldering because higher activated flux systems can be used. However, due to the higher soldering temperatures, the residues become harder, making cleaning more difficult.

The flux residue is more difficult to clean because of a higher molecular weight, more complicated ingredients structure, and more side reaction products in flux residue. (4)

The surface tension of lead-free alloys is approximately 20 percent higher than the SnPb. This affects the wetting properties. The result can be found when measuring the wetting angle of the solder joint.

For each solder paste, the optimal settings were defined with the Taguchi approach. Afterwards, confirmation runs with the best settings showed the following data:

<table>
<thead>
<tr>
<th>Wetting angle [°]</th>
<th>Remaining flux [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No-clean Water wash</td>
<td>No-clean Water wash</td>
</tr>
<tr>
<td>SAC 305</td>
<td>19.2</td>
</tr>
<tr>
<td>SN100C</td>
<td>17.9</td>
</tr>
<tr>
<td>SnPb</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Table 5. Wetting angle for the different solder pastes on Copper coupons soldered under best reflow conditions with nitrogen atmosphere.

The TGA defines, the remaining flux amount after soldering. For lead-free solders, there are less flux residues because the thermal profile has higher temperatures than a SnPb reflow profile.

The water wash flux system is completely different from the “no-clean.” By weight, there are more residues left on the printed circuit board (PCB). These residues have a completely different composition. They are hydroscopic, and active, but can be easily removed even with DI-water.

6. CONCLUSION

Cleaning agents have been improved and cleaning has become a value-added production step in soldering processes where reliability in the field is critical of corrosion and current leakage.

DI-water alone may not be sufficient to remove flux residues under small SMD components. It is limited to removing non-ionic residues from the surface of a PCB. Due to its high surface tension, DI-water is not able to penetrate underneath low stand-off devices.

“No-clean” solder paste can be cleaned, but DI-water alone is not able remove the hard residues that emit water instead of dissolve in water. A saponifier is required to remove all the resins.

When washed off completely a water wash solder paste is preferred, because it is easy to clean, has stronger activators and is safe after cleaning. There is the risk that if not completely washed off (miniaturization increases the risk due to low stand-off height, high population, and finer conductor widths and spaces), reliability becomes critical.
REFERENCES:


(3) IPC J-STD-001E “Requirements for Soldered Electrical and Electronic Assemblies,” p43


(5) Dr. Mike Bixenman, “OA Flux Cleaning Studies on Highly Dense Advanced Packages Parameters.”