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BENCHMARK STUDY: pH-NEUTRAL VS. ALKALINE CLEANING AGENTS

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ABSTRACT

In recent years, significant changes in solder paste formulations and assembly processes have occurred. Post reflow residues of tin-lead and newer lead-free soldering materials are more difficult to remove due to increases in component density, larger component packages, higher lead counts, finer lead spacing and lower standoff distances. While modern aqueous alkaline cleaning agents effectively remove these flux residues, achieving satisfactory results often requires an increase in temperature, exposure time, chemical concentration, and mechanical energy. This often presents a new set of challenges in the area of material compatibility.

Key words: pH-neutral defluxing, low standoff components, material compatibility, PCB defluxing, cleaning agent performance

INTRODUCTION

With the emergence of pH-neutral defluxing technologies in early 2009, pH-neutral formulations promised to set a new standard for material compatibility, while proving valuable to those who worked toward environmentally sound processes. As a result, potential users are very interested in assessing the differences between alkaline cleaning agents and the newer pH-neutral products, with regard to both, cleaning performance and material compatibility. One area of particular interest is the cleaning agent impact on sensitive metals.

Material compatibility issues between sensitive metals and cleaning solution arise when corrosion, i.e. the electrochemical deterioration of a metal due to the reaction with its environment, takes place. To prevent corrosion caused by the very cleaning solution that is meant to safeguard the assembly from corroding in-field and potentially fail, inhibitors come into play. In general, corrosion inhibitors are chemicals that form coordinative chemical bonds with metallic surfaces (adsorption), thereby developing a thin protective layer. They are normally distributed through a solution or by dispersion. Inhibitors slow corrosion processes by either increasing the anodic or cathodic polarization behavior, by reducing the movement or diffusion of ions to the metallic surface or by increasing the electrical resistance of the metal’s surface. Corrosion inhibitors can be classified as either inorganic or organic, with the latter being more prevalent due to solubility advantages, performance, and fewer environmental concerns. Examples of typical corrosion inhibitors are silicates, borates, alkanolamines, naphthalenesulfonic acid, triazoles, carboxylic acids, molybdates, polyols, and phosphate [1].

If the respective cleaning media do not work as intended, several types of corrosion can commonly occur on electronic assemblies, such as gas phase, uniform, pitting, electrolytic metal migration, and galvanic [2]. Fortunately, this has been an area of much research and electronics manufacturers today have a variety of cleaning choices to prevent such issues with the newer and more effective aqueous alkaline chemistries strongly preferred over solvents or traditional surfactants. Recently, however, the choices of aqueous products available for defluxing have expanded significantly with the introduction of pH neutral formulations.

For all aqueous solutions to do a superior job without affecting sensitive metal substrates, i.e. corrosion control, manufacturers have to add inhibitors. Studies have shown that choosing the correct type and amount of inhibition chemistry is critically important. Otherwise, the inhibitors themselves can present several problems in the SMT production process.

First, the solubility of certain inhibitors in concentrate chemistry is sometimes low and only a small percentage of the inhibitor can be added to the cleaning product formulation. Therefore, to achieve proper protection of sensitive metals using such problematic inhibitors, a higher recommended operating concentration is often required in the wash tank, which leads to unnecessary chemistry consumption. On the other hand, lowering the concentration leads to a lower amount of inhibitor available to protect sensitive metals. Second, these organic additives can have detrimental effects on the cleaning process as they also interact with any residue as well as the environment and inhibit the dissolution of such residue into the cleaning fluid. Finally and most importantly, certain inappropriate inhibitors are tightly bound to the metal surface and are more difficult or impossible to rinse from the substrate's surface and under components, where they linger insidiously, causing a host of problems over time. This contamination can adversely increase the electrical resistance of the contaminated areas, lead to conformal coating issues and cause unpredictable failures, thereby threatening the long-term reliability of the assembly.

The type and amount of inhibitors selected is also a function of the pH conditions in the process. Some inhibitors that work well at a certain pH will not function as well or at all if the pH is outside of this range. Therefore, pH-neutral cleaning agents offer distinct advantages. They require very small amounts of inhibitors because at this pH range (7 +/- 0.5), a unique and customized set of corrosion inhibitors is very effective, thereby solving the problems mentioned above. Due to their lower surface tension (less than 30 mN/m vs. 72 mN/m for water), pH-neutral solutions can penetrate the tiny spaces in and around components, do their job of removing contamination even at low concentrations and can be easily rinsed and dried [3]. Furthermore, pH-neutral cleaners are more environmentally friendly and eliminate waste water neutralization processes. Most importantly, however, using pH-neutral agents has been shown to eliminate material compatibility concerns in cases where alkaline agents have failed, thereby offering users a solution that previously did not exist.

ARTICLE SUMMARY

This collaborative study was conducted to compare the material compatibility and cleaning effectiveness of pH-neutral and alkaline technologies at low operating concentrations. In the first part of the assessment, material compatibility effects were examined. Particularly sensitive materials were chosen for exposure under worst case conditions. They included but were not limited to anodized aluminum, copper and certain nickel alloy substrates.

For the cleaning performance testing, the study employed the use of IPC approved B52 test boards [4]. While the most challenging component geometries were chosen, the authors also determined the need to quantify cleanliness to provide data that was not included in previous publications related to this topic. Extensive SIR, Ion Chromatography and analytical test data were accumulated to validate the visual residue analysis.

Core Objectives:

1. **Material Compatibility:** The material compatibility of sensitive metals such as aluminum alloys, nickel, copper, etc was tested using visual inspection with an Olympus SZ 40 microscope with up to 60x magnification.

2. **Cleaning Performance:** The performance of pH-neutral cleaning agents was compared with alkaline cleaning solutions containing varying degrees of inhibition. To inspect the cleaning performance, several different analytical methods were used such as visual inspection, Ion Chromatography and third party SIR analysis.

METHODOLOGY

The research design compared the material compatibility of two alkaline cleaning agents with varying degrees of inhibition and a pH-neutral cleaning agent with sensitive metals. For this part of the study, various types of sensitive metals were exposed to the same alkaline and pH-neutral cleaning agents as well as DI-water. A visual inspection was performed after 15 minutes and 24 hours exposure as well as after three weeks of storage under normal environmental conditions. These data were subsequently used to determine the methodology in the second part of the study.

While conducting several extensive preliminary cleaning trials to define the process settings for further and more detailed analyses in the second phase of the cleaning performance testing, ten most commonly used leaded and lead-free no-clean and water-soluble solder pastes were applied to the boards and reflowed in a 10-stage oven [5]. Tables 1 and 2 show the reflow profiles. Subsequently, the boards were cleaned applying the process settings outlined in Table 7 and visually inspected. In the second phase of the cleaning trials, a fewer number of test boards and only 2 solder pastes were chosen. After subjecting the boards to the same reflow parameters, they were cleaned with both agents and inspected via SIR Analysis and Ion Chromatography.

All results were recorded and analyzed before drawing final conclusions.

Table 1: Actual reflow profile as used during the cleaning trials for lead-free solder pastes

	Preheat Zones							Reflow Zones			Cooling
	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	Zone 10	
TOP	100°C	120°C	150°C	180°C	190°C	210°C	225°C	235°C	245°C	225°C	4 Zones
BOTTOM	100°C	120°C	150°C	180°C	190°C	210°C	225°C	235°C	245°C	225°C	4 Zones

Table 2: Reflow profile as used during the cleaning trials for leaded solder pastes

	Preheat Zones							Reflow Zones			Cooling
	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	Zone 10	
TOP	90°C	100°C	130°C	160°C	170°C	190°C	210°C	220°C	230°C	210°C	4 Zones
BOTTOM	90°C	100°C	130°C	160°C	170°C	190°C	210°C	220°C	230°C	210°C	4 Zones

PART 1 – MATERIAL COMPATIBILITY

Methodology: Part 1 (material compatibility) of this study was divided into three phases. The object was to compare the material compatibility of several different cleaning agents with sensitive metals. The materials tested were anodized coating, alodine coating, iridite coating, electroless nickel plating, aluminum and copper. All parts were exposed to a pH-neutral cleaning agent, two competitor alkaline products with different inhibitor types and amounts as well as pure DI-water for 15 minutes which is 6 times the typical process exposure and 24 hours (576 times the typical process exposure). It is important to point out that these exposure times are extraordinary when compared to production floor conditions. During an inline cleaning process, the usual exposure time is approximately only 2 to 3 minutes. All parts were rinsed with 140°F DI-water. Additionally, all substrates were examined after 3 weeks of storage under "real world" conditions, i.e. exposed to oxygen, ambient temperatures and other environmental factors. All substrates were inspected for material changes via 40x magnification. The process parameters for the material compatibility tests (phases 1 and 2) can be summarized as follows:

Table 3: Process parameters for material compatibility tests – phase 1 and phase 2

Cleaning Agents	Equipment	Substrates Tested
pH-neutral, alkaline, DI-water	Beaker, continuously stirred	Sensitive metals, coatings, platings
Concentration	**Temperature**	**Exposure Time**
10%, 100% (DI-water)	150°F	Short-term: 15 min. Long-term: 24 hrs.

Results – Phase 1: The short-term test results (15 minute exposure = 6x normal process exposure) show that the pH-neutral cleaning agent, the competitor alkaline product A, and DI-water are fully compatible with all substrates tested as no change was observed. Competitor alkaline product B was deemed compatible with only 4 out of the 6 substrates tested since no change of the substrate was noted. Only iridite coating and aluminum experienced some discoloration (Table 4).

Table 4: Short-term exposure – 15 minutes

Short-term exposure - 10%, 150°F, 15 min.				
	pH-neutral	Competitor alkaline product A	Competitor alkaline product B	DI-water
Anodize coating	+	+	+	+
Alodine coating	+	+	+	+
Iridite coating	+	+	0	+
Electroless nickel plating	+	+	+	+
Aluminum	+	+	0	+
Copper	+	+	+	+

\+ no change
0 some discoloration
– discoloration & corrosion
\- - significant discoloration & corrosion

Results – Phase 2: The long-term test results (24 hour exposure = 576x normal process exposure) demonstrate that the pH-neutral cleaning agent and the competitor alkaline product A are still the leaders of the pack with the latter performing better as no change was observed with any of the substrates. The pH-neutral cleaning agent did very slightly discolor and corrode only copper. The competitor alkaline product B, on the other hand, was only compatible with 50% of the substrates tested as it discolored and corroded anodize coating, iridite coating and aluminum. It is interesting to note that, after 24 hours, even DI-water was no longer fully compatible with all tested materials as some discoloration affected aluminum. Furthermore, some very slight hazing was observed on the copper substrate. The authors, however, felt that this was not enough of a material change to warrant a rating adjustment (Table 5).

Table 5: Long-term exposure – 24 hours

Long-term exposure - 10%, 150°F, 24 hrs.				
	pH-neutral	Competitor alkaline product A	Competitor alkaline product B	DI-water
Anodize coating	+	+	-	+
Alodine coating	+	+	+	+
Iridite coating	+	+	-	+
Electroless nickel plating	+	+	+	+
Aluminum	+	+	-	0
Copper	-	+	+	+

\+ no change
0 some discoloration
– discoloration & corrosion
-- significant discoloration & corrosion

Results – Phase 3: After completing the last phase of the compatibility trials, i.e. 3 weeks storage at ambient temperatures and exposure to environmental factors, the authors also inspected the untreated substrates to establish a baseline for comparison and examined all the treated metals for material changes. No changes were observed for the controls. Upon examination, DI-water and the pH-neutral agent showed the best results as no changes occurred during the 3-week period. For DI-water only the same minor compatibility issues were found with aluminum (some discoloration) which had also been observed at the 24 hour mark. The pH-neutral cleaning agent demonstrated the best chemistry outcome as no material change was noted after 3 weeks. Next, the competitor alkaline product A demonstrated full compatibility with only 4 out of the 6 substrates, also failing with copper as it showed a significant amount of corrosion and discoloration. Furthermore, some discoloration was noted on the electroless nickel plating as well. Both of these metals had been in perfect shape after 24 hours of exposure. Lastly, competitor alkaline product B’s compatibility further deteriorated within the 3-week period as it proved to have a negative impact on all but one substrate. Alodine coating and copper exhibited some discoloration, whereas the anodize coating, iridite coating and aluminum experienced discoloration and corrosion. Only the electroless nickel plating was left unchanged (Table 6).

Table 6: Long-term exposure – 3 weeks after cleaning

Long-term exposure - 3 weeks after cleaning					
	pH-neutral product	Competitor alkaline product A	Competitor alkaline product B	DI-water	Untreated
Anodize coating	+	+	-	+	+
Alodine coating	+	+	0	+	+
Iridite coating	+	+	-	+	+
Electroless nickel plating	+	0	+	+	+
Aluminum	+	+	-	0	+
Copper	-	--	0	+	+

\+ no change
0 some discoloration
– discoloration & corrosion
\- - significant discoloration & corrosion

To further analyze and exemplify the long-term environmental exposure effects after cleaning with the above agents, the authors chose to examine the impact on copper.

With its wide range of applications in the electronics manufacturing industry, copper is usually deemed resistant toward environmental and chemical influences. It is, however, known that in aggressive media, this metal is particularly susceptible to corrosion [6].

Close-up views of the copper lead frames under 40x magnification demonstrate the changes observed after three weeks of environmental exposure. Figure 1 shows the untreated control substrate with no changes. The copper is still shiny without any discoloration or corrosion.

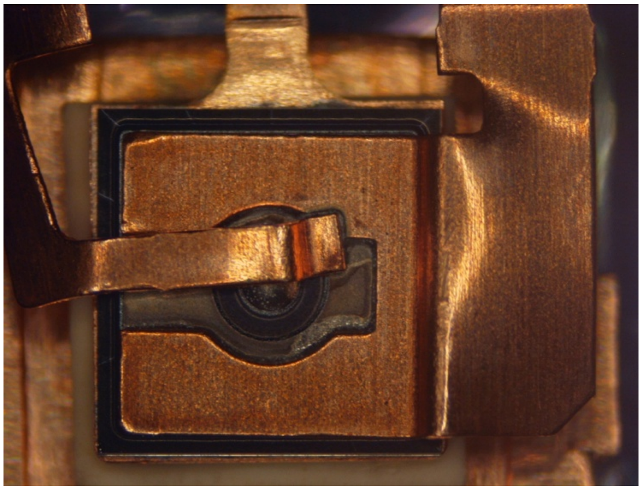

Figure 1: Close-up view of copper lead frame, untreated – after 3 weeks of environmental exposure

The lead frame cleaned with the pH-neutral cleaning agent experienced no change after having been exposed to the environment for three weeks. In other words, the substrate looked just like it did after having been exposed to the pH-neutral solution for 24 hours. Minor discoloration specs and lines had also been noted at that time (Figure 2).

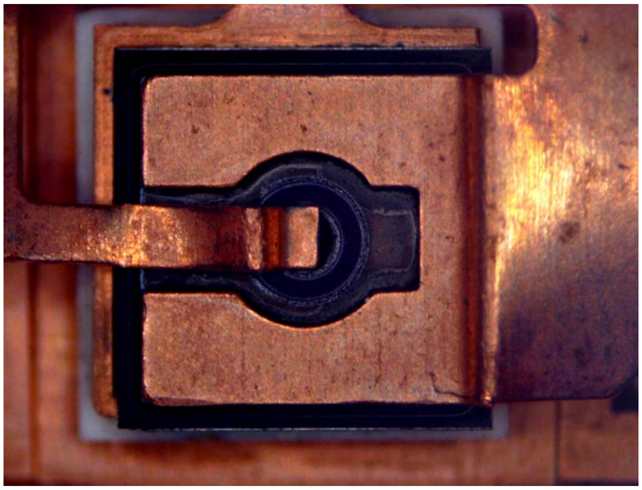

Figure 2: Close-up view of copper lead frame cleaned with pH-neutral cleaning agent – 3 weeks after cleaning and environmental exposure

The lead frame cleaned with the competitor alkaline cleaning product A, on the other hand, became significantly discolored and corroded after 3 weeks of environmental exposure, which constitutes a major transformation as the substrate was perfect after 24 hours of exposure. The copper lead frame showed a tremendous amount of corrosion in the difficult to rinse areas as well as on the flat surfaces. Major discoloration, i.e. significant lines, was noted throughout the substrate’s surface (Figure 3).

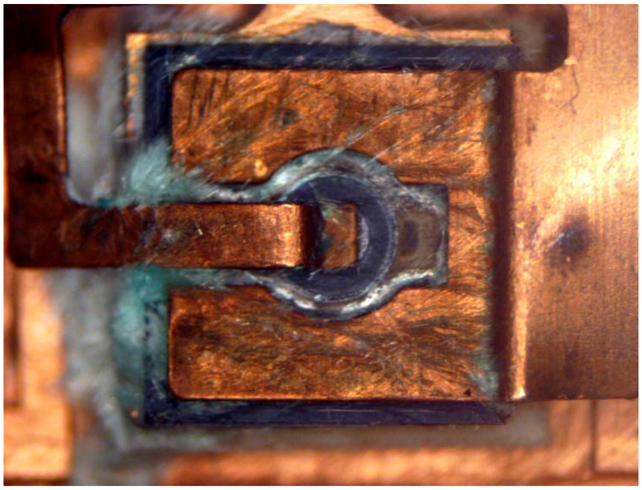

Figure 3: Close-up view of copper lead frame cleaned with competitor alkaline product A – 3 weeks after cleaning and environmental exposure

Figure 4 demonstrates that there was some material change observed after 3 weeks of environmental exposure. This lead frame had been subjected to competitor alkaline cleaning agent B. After 24 hours of exposure, the copper substrate was still perfect. After 3 weeks of environmental exposure, however, the substrate's surface appeared hazy and showed some discolored specs and lines (Figure 4).

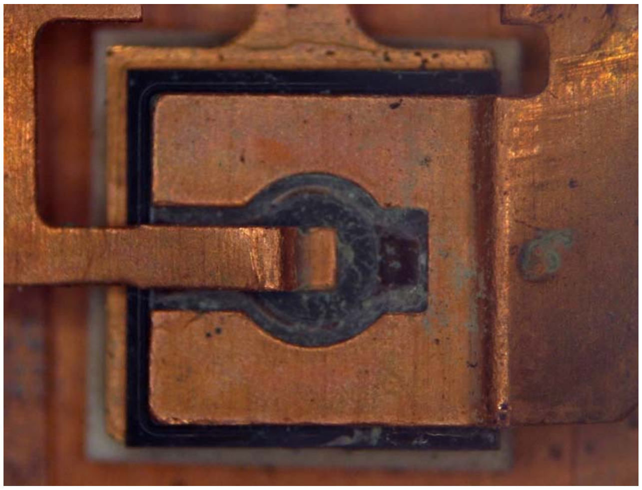

Figure 4: Close-up view of copper lead frame cleaned with competitor alkaline product B – 3 weeks after cleaning and environmental exposure

Lastly, the authors inspected the copper lead frame that had been exposed to DI-water only. The image shows that after 3 weeks of storage in the environment no change was observed (Figure 5).

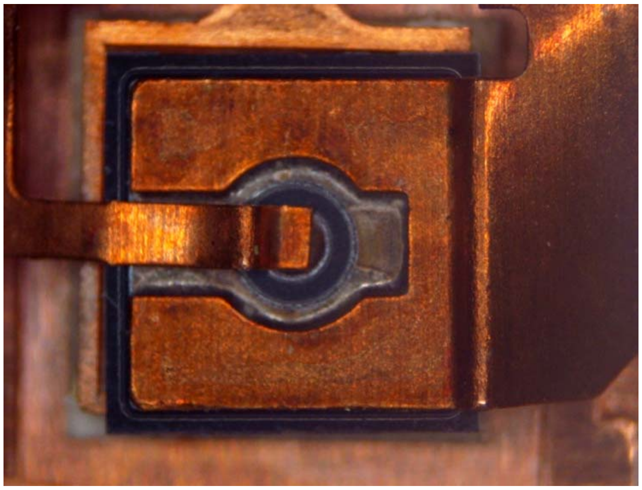

Figure 5: Close-up view of copper lead frame cleaned with pure DI-water - 3 weeks after cleaning and environmental exposure

CONCLUSIONS PART 1 - MATERIAL COMPATIBILITY

The above material compatibility tests clearly demonstrate that while short-term exposure to aqueous cleaning solutions may not have any influence on material compatibility, the long-term effects also need to be examined.

First, the authors are not surprised that slight hazing developed on the copper substrate after exposure to DI-water. Dionized water over time becomes inherently acidic via CO_2 absorption and copper, dust, etc. rapidly supply ions, thus re-ionizing deionized water. Therefore, as outlined in the introduction of this paper, the addition of inhibitors in all media is important to prevent corrosion especially if users are concerned about the long-term reliability of their product.

Second, the fact that some material changes (discoloration) were observed on the lead frame that had been exposed to competitor cleaning agent B is noteworthy. More importantly, though, the fact that competitor cleaning agent A caused a significant amount of post rinse degradation is quite worrisome. The authors hypothesize that any deterioration of the substrate's surface may have been caused by a possible lack of rinsability of the corrosion inhibitor in this particular cleaning medium. As outlined in the introductory section of this paper, oftentimes the amount and type of inhibitor added to the cleaning solution can impact its rinsability. Additionally, any environmental effects on the inhibitor residue may have also caused the degradation over time.

It is important for users to realize that even if substrates are deemed perfectly clean and compatible with their cleaning solution soon after exposure, the long-term study results (3 weeks after cleaning and environmental exposure) indicate that material changes may happen later in the field, which can cause reliability problems in the long run.

PART 2 - CLEANING PERFORMANCE

PHASE 1: Preliminary Cleaning Trials

Methodology: All cleaning trials were conducted immediately after the 24 hour material compatibility testing. After carefully examining the compatibility results, the authors chose to only perform cleaning trials with the most compatible alkaline product (competitor alkaline product A at the 24 hr. exposure mark) and the same pH-neutral agent. In the preliminary cleaning trials, current ZESTRON test boards populated with 0603, 0805, 1206 and SOT23 components (classified as "low standoff' with less than 1 mil of spacing) using 10 of the most common leaded and lead-free solder pastes were reflowed according to the above profiles (Tables 1 and 2) and cleaned with a pH-neutral cleaning agent and the competitor alkaline product A at 10% concentration, 150ºF and with a belt speed of 0.6 ft./min. Table 7 summarizes the process settings. The surface cleanliness as well as the areas under the components were visually inspected.

Table 7: Process settings for cleaning performance tests

Cleaning Agents	Equipment	Paste Tested
pH-neutral, alkaline	AS 200, Inline	NO-Clean LF/leaded
Concentration	**Temperature**	**Wash Cycle**
10%	150°F	0.6 ft./min

Results: The surface cleanliness results of these preliminary cleaning trials indicate that both cleaning agents performed equally well. All surfaces were perfectly clean (Table 8).

Table 8: Surface cleanliness results

Surface cleanliness		
Solder Paste	**pH-neutral**	**Competitor alkaline product A**
Solder paste 1: Leaded, NO-clean	+	+
Solder paste 2: Leaded, NO-clean	+	+
Solder paste 3: Leaded, NO-clean	+	+
Solder paste 4: Leaded, NO-clean	+	+
Solder paste 5: Leaded, NO-clean	+	+
Solder paste 6: Lead-free, NO-clean	+	+
Solder paste 7: Lead-free, NO-clean	+	+
Solder paste 8: Lead-free, water-soluble	+	+
Solder paste 9: Lead-free, NO-clean	+	+
Solder paste 10: Lead-free, NO-clean	+	+

The under-component cleanliness results, however, were quite different. For solder pastes 1, 3, 4, 6 and 8, no under-component residue was found at all when the boards were cleaned with the pH-neutral solution. For solder pastes 2, 5, 7, 9 and 10, minor residues were detected under one of the four low standoff components only. In summary, the pH-neutral product was able to clean most of the flux residues with residual wetness found only under one of the four types of low standoff components (1206) on 50% of the boards.

The competitor alkaline product A, however, left a few more problems. The product failed to clean solder pastes 1, 2, 3, 5, 6, 7, 9 and 10 from underneath several of the four low standoff component varieties. Only solder pastes 4 and 8 were completely cleaned. In summary, wetness was found underneath several different types of components (1206, 0805, SOT23) affecting the majority (80%) of the boards. The results are summarized in Table 9.

Table 9: Under-component cleanliness results

Under Components		
Solder Paste	**pH-neutral**	**Competitor alkaline product A**
Solder paste 1: Leaded, NO-clean	+	-
Solder paste 2: Leaded, NO-clean	-	-*
Solder paste 3: Leaded, NO-clean	+	-
Solder paste 4: Leaded, NO-clean	+	+
Solder paste 5: Leaded, NO-clean	-	-*
Solder paste 6: Lead-free, NO-clean	+	-
Solder paste 7: Lead-free, NO-clean	-	-*
Solder paste 8: Lead-free, water-soluble	+	+
Solder paste 9: Lead-free, NO-clean	-	-
Solder paste 10: Lead-free, NO-clean	-	-

\+ Clean
\- Wetness/residue detected under one component
-* Wetness/residue detected under several components

Conclusion

The results indicate that since obvious differences in surface and under-component cleanliness levels do exist, the pH-neutral agent clearly outperformed the competitor alkaline cleaning agent A. A board that is perfectly clean on the surface can fail when the spaces underneath the components are examined. The authors conclude that there are several potential reasons for these results. First, any lack of performance could be related to concentration, i.e. 10% may be too low of an effective concentration to clean these challenging boards properly, especially for the alkaline product. Second, the observed cleanliness issues may be due to the inhibition packages (type and amount) that the cleaning agents contain. Third, cleaning product formulations and mechanisms also play an important role. Finally, the residues found may be a result of inhibitors bonding with the very contamination the cleaning agent was intended to remove thereby preventing the dissolution of the residue.

In order to further quantify and qualify these findings, several additional test vehicles were chosen, reflowed, and cleaned with both solutions. Subsequently, the boards were subjected to SIR and Ion Chromatography analyses.

PHASE 2: SIR and Ion Chromatography Analyses

Methodology: The next phase of the cleaning performance testing, added SIR and Ion Chromatography analyses in order to further evaluate what lies beneath and more precisely gauge the assemblies' cleanliness. Previous studies have shown that relying on visual inspections only may not always be best practice [7].

SIR Analysis

Methodology: The goal of performing an additional SIR Analysis was to further compare the cleaning performance of a pH-neutral and the competitor alkaline cleaning agent, i.e. going beyond visual analysis. SIR (Surface Insulation Resistance) testing evaluates the propensity for assembly failure caused by shorts or current leakage between metal conductors. It is an electrical test that measures a change in current over time and is typically performed at elevated temperatures and humidity levels [8].

Based on the preliminary cleaning trial results, 8 IPC-B52 test boards (Figure 6) were reflowed after the application of a previously tested no-clean, leaded solder paste according to the above profiles (Tables 1 and 2). 4 boards (1 bare control board, 3 test boards populated with QFP160 components) were cleaned with the competitor alkaline cleaning agent A and 4 boards (1 bare control board, 3 test boards populated with QFP160 components) were cleaned with the pH-neutral solution according to the following process parameters:

Table 10: Cleaning Process Parameters for SIR Testing

Cleaning Agents	Equipment	Paste Tested
pH-neutral, alkaline	AS 200, Inline	NO-Clean leaded
Concentration	**Temperature**	**Wash Cycle**
10%	150°F	0.6 ft./min

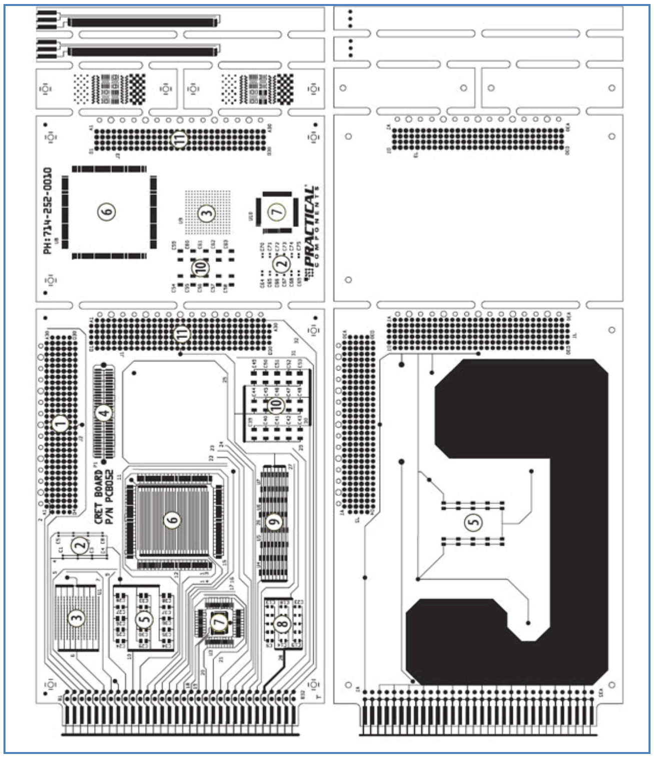

Figure 6: IPC-B52 Test Board

Cleanliness testing for conductivity was done via third party SIR testing according to IPC-TM-650, method 2.6.3.7 by Trace Laboratories in Hunt Valley, MD [9].

Results: The findings showed that all boards passed SIR testing. After close examination of the results, however, one should note that the pH-neutral cleaning agent performed slightly better (1/2 a decade). A representative example of the test results is shown the graph below (Figure 7).

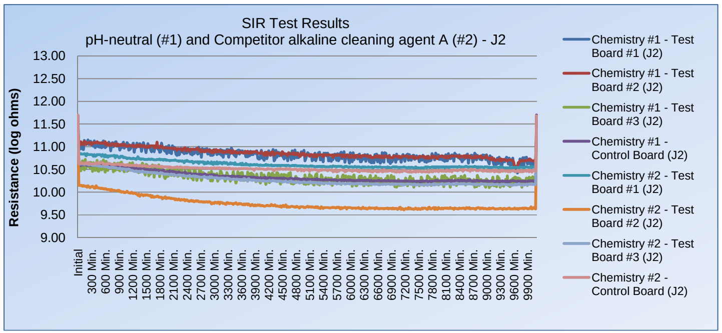

Figure 7: SIR Test Results

Conclusion

While both chemistries passed the SIR testing and can be deemed viable options for cleaning assemblies, the pH-neutral chemistry slightly outperformed the competitive alkaline cleaning agent A. This may surprise some readers as earlier generations of pH-neutral formulations required much higher concentrations and/or temperatures to compete with alkaline agents.

Ion Chromatography Analysis

Methodology: The object of performing additional Ion Chromatography testing according to IPC-TM-650 method 2.3.28 was to move beyond visual inspection and conduct a more detailed cleaning performance comparison of a pH-neutral and the competitor alkaline cleaning agent A [9]. Ion Chromatography is a test for ionic cleanliness that determines if contaminants are present on electronic assemblies and bare boards. Such contaminants, when mixed with moisture and an applied voltage, often contribute to electrochemical failures [10].

Based on the assessment during the preliminary cleaning trials, 8 ZESTRON test boards (Figure 8) were used. These particular test boards have been specifically designed for the cleaning agent to fail as they are populated with the most challenging low standoff components and sensitive substrate types. 4 each of the ZESTRON test boards were reflowed after applying a no-clean, leaded solder paste as well as 4 each were reflowed after the application of a no-clean, lead-free solder paste according to the aforementioned profiles (Tables 1 and 2). Subsequently, they were cleaned with the following process parameter settings:

Table 11: Cleaning Process Parameters for Ion Chromatography Testing (IPC-TM-650, method 2.3.28)

Cleaning Agents	Equipment	Paste Tested
pH-neutral, alkaline	AS200, Inline	NO-Clean leaded
Concentration	**Temperature**	**Wash Cycle**
10%	150°F	0.6 ft./min

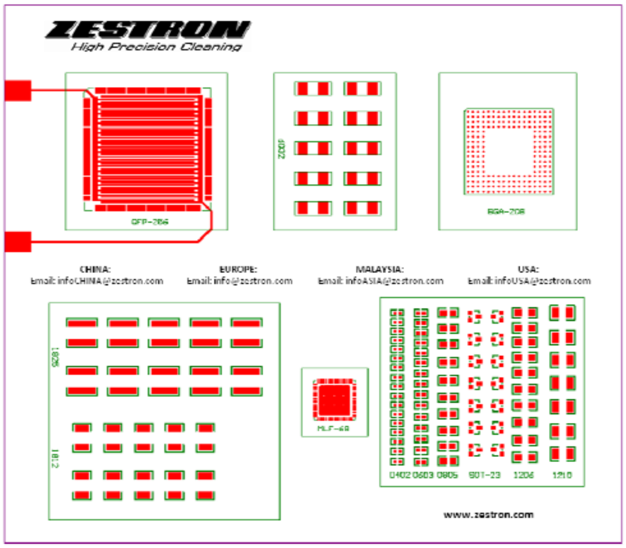

Figure 8: ZESTRON test board

The cleanliness of all 8 boards was analyzed via Ion Chromatography according to IPC-TM-650, method 2.3.28.

Results for Ion Chromatography Analysis: All boards passed the Ion Chromatography Analysis for both, the pH-neutral and the competitor alkaline cleaning agent A with the exception of some minor fluoride residues on two test vehicles. In fact, in 70% of the possible cases, no ionic residue species were detected after cleaning with the pH-neutral product. Respectively, in 69% of the possible cases, no ionic residue species were detected after cleaning with the competitor alkaline cleaning agent A. The anion analysis values for fluoride exceeded the maximum contamination level of 3 µg/in^2 by 0.2 on one of the boards that had been cleaned with the pH-neutral cleaning agent. Similarly, the anion analysis results for fluoride exceeded the maximum contamination level of 3 µg/in^2 by 0.1 on one of the boards that had been cleaned with the competitor alkaline cleaning agent A. Please refer to tables 12 and 13 for detailed cleanliness results for solder pastes 1 and 2 (no-clean, leaded) and both cleaning agent applications.

Table 12: Ion Chromatography Test Results for solder paste 1, no-clean, leaded

<table>
<tr><th colspan="6">Ion Chromatography Test Results</th></tr>
<tr><th colspan="6">Anion Species always tested for</th></tr>
<tr><th>Ionic Species</th><th>Maximum Contamination Levels</th><th>Board # 1-1</th><th>Board # 1-2</th><th>Board # 3-1</th><th>Board # 3-2</th></tr>
<tr><td>Fluoride (F$^-$)</td><td>3</td><td>ND</td><td>3.2</td><td>ND</td><td>2.9</td></tr>
<tr><td>Acetate ($C_2H_2O_2^-$)</td><td>3</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>Formate ($CH_2O_2^-$)</td><td>3</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>Chloride (Cl$^-$)</td><td>4</td><td>0.78</td><td>0.69</td><td>1.47</td><td>1.41</td></tr>
<tr><td>Nitrite (NO_2^-)</td><td>3</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>Bromide (Br$^-$)</td><td>10</td><td>0.18</td><td>ND</td><td>0.40</td><td>0.34</td></tr>
<tr><td>Nitrate (NO_3^-)</td><td>3</td><td>ND</td><td>ND</td><td>1.78</td><td>ND</td></tr>
<tr><td>Phosphate (PO_4^{2-})</td><td>3</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>Sulfate (SO_4^{2-})</td><td>3</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>WOA (Weak Organic Acid)</td><td>25</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><th colspan="6">Cation Species always tested for</th></tr>
<tr><td>Lithium (Li$^+$)</td><td>3</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>Sodium (Na$^+$)</td><td>3</td><td>0.2</td><td>0.4</td><td>0.3</td><td>0.4</td></tr>
<tr><td>Ammonium (NH_4^+)</td><td>3</td><td>0.4</td><td>0.4</td><td>0.4</td><td>0.4</td></tr>
<tr><td>Potassium (K$^+$)</td><td>3</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>Magnesium (Mg^{2+})</td><td>1</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
<tr><td>Calcium (Ca^{2+})</td><td>1</td><td>ND</td><td>ND</td><td>ND</td><td>ND</td></tr>
</table>

Boards 1-1 and 1-2 cleaned with pH-neutral product
Boards 3-1 and 3-2 cleaned with competitor alkaline product A
ND = no residues detected

Table 13: Ion Chromatography Test Results for solder paste 2, no-clean, leaded

Ion Chromatography Test Results					
Anion Species always tested for					
Ionic Species	Maximum Contamination Levels	Board # 2-1	Board # 2-2	Board # 4-1	Board # 4-2
Fluoride (F^-)	3	2.8	2.8	2.8	3.1
Acetate ($C_2H_2O_2^-$)	3	ND	ND	ND	ND
Formate ($CH_2O_2^-$)	3	ND	ND	ND	ND
Chloride (Cl^-)	4	0.75	0.70	0.90	1.24
Nitrite (NO_2^-)	3	ND	ND	ND	ND
Bromide (Br^-)	10	0.18	0.11	0.30	0.28
Nitrate (NO_3^-)	3	0.05	ND	ND	ND
Phosphate (PO_4^{2-})	3	ND	ND	ND	ND
Sulfate (SO_4^{2-})	3	ND	ND	ND	ND
WOA (Weak Organic Acid)	25	ND	ND	ND	ND
Cation Species always tested for					
Lithium (Li^+)	3	ND	ND	ND	ND
Sodium (Na^+)	3	0.3	0.3	0.4	0.4
Ammonium (NH_4^+)	3	0.5	0.4	0.4	0.3
Potassium (K^+)	3	ND	ND	ND	ND
Magnesium (Mg^{2+})	1	ND	ND	ND	ND
Calcium (Ca^{2+})	1	ND	ND	ND	ND

Boards 2-1 and 2-2 cleaned with pH-neutral product
Boards 4-1 and 4-2 cleaned with competitor alkaline product A
ND = no residues detected

Conclusion

The overall results show that both chemistries cleaned almost equally well, with the pH-neutral cleaning agent performing just slightly better.

CONCLUSIONS
PART 2 - CLEANING PERFORMANCE

In summary, after conducting extensive testing and analyses, the above results indicate that when it comes to cleaning performance, the pH-neutral product and the competitor alkaline cleaning agent A are both very viable solutions. Both chemistries were able to provide a clean surface. In the under-component cleanliness visual examination, the pH-neutral cleaning agent performed significantly better overall. Both solutions left some residues behind. After examining the SIR test results, the pH-neutral agent finished slightly ahead of its counterpart. The ion chromatography values also confirmed these findings, as again, the pH-neutral chemistry did a slightly better job of removing ionic residues.

In order to fully understand the implications of the findings, the authors drew their final conclusions after carefully examining both parts of this study: material compatibility and cleaning performance.

FINAL CONCLUSIONS

This comprehensive and collaborative study was conducted to assess the material compatibility and cleaning performance of a pH-neutral precision cleaning product and two competitor alkaline chemistries. The purpose of this paper has been to merely benchmark a pH-neutral formulation against alkaline cleaning agents and to explore the differences without invalidating the performance and effectiveness of either technology.

Alkaline cleaning agents are widely used throughout the electronics manufacturing industry. These proven chemistries replaced solvents some time ago and perform extremely well at low temperatures and low concentrations as well as short contact times. In fact, the future is bright for alkaline cleaning as current products continue to meet today's challenges and new products are being developed to fulfill future requirements. Without a doubt, this technology will remain the cornerstone of the precision cleaning industry in the near future.

Overall, the study results are quite encouraging with regard to cleanliness. This study proved that pH-neutral cleaning agents can compete with alkaline products. In fact, in this particular case, the pH-neutral product outperformed the alkaline product. Both can definitely do a superior job of removing all residues from the board's surface, whereas, in this case, the pH-neutral chemistry took the lead in cleaning residues from the tight spaces underneath the components.

There are, however, some distinct differences with regard to material compatibility. As noted in the first part of this study, it is important for users to realize that even if substrates are deemed perfectly clean and compatible with their cleaning solution soon after exposure, long-term product related effects can compromise the reliability of the assembly. This study proved that the pH-neutral cleaning agent was far superior in the area of material compatibility as both alkaline products experienced significant problems during the different test phases.

Whether choosing a pH-neutral or an alkaline product, all aqueous precision cleaners in the electronics manufacturing industry must contain some sort of inhibiting additive in order to avoid corrosion affecting sensitive metal substrates. The question of how much and what kind of inhibitor to use depends on the cleaning agent, as this study clearly suggests that differences do exist. Unfortunately, there is no universal solution for protecting sensitive metals as finding the proper combination of specific inhibitors is a complex function of numerous significant parameters.

It is important to note, that there are some distinct differences between alkaline and pH-neutral cleaning agents that may influence the user's choice. pH-neutral chemistries offer an unprecedented level of environmental friendliness, thereby reducing worker safety and government regulation compliance concerns as well as the need for costly waste water neutralization processes. They are also easy to rinse and gentle on precision cleaning equipment.

This research paper is the 6th in a series written by ZESTRON on optimizing precision cleaning processes for electronics manufacturing industry. These studies have been presented at the industry's known conferences SMTAI and IPC/APEX. Based on our findings, key market developments have been initiated, thereby addressing the current shortcomings observed in the industry.

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