Presented at IPC Printed Circuits Expo®
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Designers Summit 04

Lead-Free Soldering: DOE Study to Understand its Affect on Electronic Assembly Defluxing

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Abstract

Lead-free alloys under consideration have physical properties, which may directly impact industry standard electronic assembly cleaning processes. The purpose of this study is to evaluate how the use of nitrogen versus non-nitrogen reflow atmospheres affect the cleanability of flux residue from RMA, synthetic and water-soluble surface mount solder paste residues.

The designed experiment evaluated commercially available lead-free solder paste products and industry standard cleaning materials. The cleaning evaluations were conducted in a controlled application lab while using thermally profiled reflow conditions and cleaning equipment. The response variables used will be qualitative visual inspection of white residue and solder bump appearance.

Introduction

Lead-free soldering requires new process material consideration. Assemblers rely on material and equipment suppliers for research, development, reliability testing, and process knowledge. Hwang (2003, Nov) states, "many consider the fundamental principles and production-floor practices developed around eutectic Sn63/Pb36 solder will be equally valid for Pb-free assembly. [1]" The SAC NEMI approved alloy composition poses several processing challenges, two of which affect cleaning: flux composition and reflow temperature.

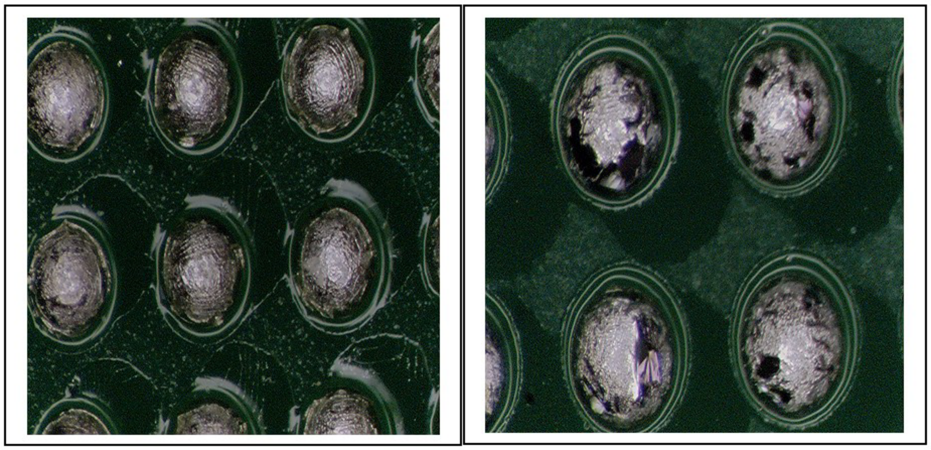
It is widely reported that the solderability of SAC lead-free alloy is poorer than eutectic Sn/Pb. Lee & Brooks [2](2003, Oct) report the following:

- To maintain wetting that is identical to Sn/Pb, an increase of about 50ºC to the soldering temperature may be needed.
- Pb-free solderability becomes significantly poorer with weaker no-clean and pure rosin fluxes in comparison to Sn/Pb solder.
- Pb-free alloys do not wet as well too lead-free terminations.

To improve wettability, flux compositions may require higher activation. High solid flux formulations may leave more residue, which may require cleaning. It is well known that a higher processing temperature increases cleaning difficulty. This study evaluates the cleanability of water soluble, rosin, and synthetic flux residue that was reflowed in air as compared to nitrogen using commercial cleaning equipment and cleaning chemistry.

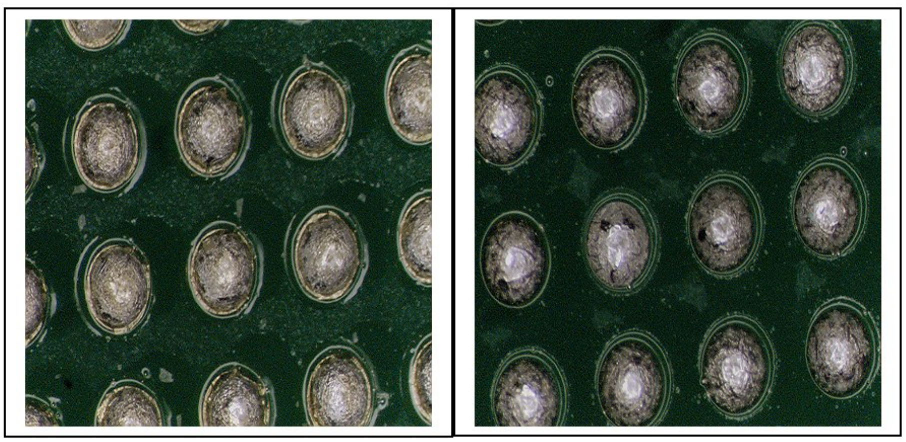
Why Nitrogen Reflow

It is common knowledge that nitrogen inerted soldering improves wetting and reduces oxidation. At higher lead-free ambient soldering conditions, the flux residue may oxidize and char. When soldering in a nitrogen inerted environment, it is theorized that wetting will improve flux residue will be transparent and easier to clean. If this theory holds true, this could support the thought that lead-free cleaning will be more challenging. Figures 1 and 2 show examples of two separate fluxes that were soldered in air as compared to nitrogen reflow. The level and appearance of the residue is clearer and less for boards soldered in a nitrogen environment.



(a) (b)

Figure 1 – (a) Ambient Soldering Environment (b) Nitrogen Inerted Environment



(a) (b)

Figure 2 - (a) Ambient Soldering Environment (b)Nitrogen Inerted Environment

Design of Experiment

Premise:

- NEMI Chosen Lead-Free Alloy
  - ◊ 95.5 Sn/3.9Ag/0.6Cu (SAC)
  - ◊ 217ºC liquidus
- Higher processing temperatures increases oxidation of flux residue, which may increase cleaning difficulty
- Nitrogen inerted atmosphere reduces oxidation of flux residue, which may improve cleanability

Hypothesis:

- Lead free residue is harder to clean due to higher reflow temperatures and complex flux formulations
- Boards reflowed in a nitrogen environment will clean easier than those soldered in an air environment

Experimental Design:

Cleaning electronic assemblies is a common industry standard. Three electronic cleaning processes are common practice: (1) aqueous, (2) semi-aqueous, and (3) vapor phase. Commercial cleaning equipment designs are available for each of these processes.

Lead-free soldering elevates the peak reflow temperature 40-50ºC higher than eutectic Sn/Pb soldering. In addition, lead-free alloys exhibit poorer wetting. Solder flux performs a number of important functions: (1) thermal transfer to the area of the solder joint, (2) wetting of the solder on the base metal, and (3) prevents oxidation of the metal surface at soldering temperatures.[3]

Cleaning ease is a function of the soil (flux composition), thermal excursions, component standoff, and board density. Water soluble flux compositions, for eutectic Sn/Pb, are successfully removed with hot DI water and mechanical energy. Successful lead-free water soluble flux cleaning may require DI water plus an additive. Rosin and synthetic (no-clean) flux residues are commonly removed with chemical additives added to water, semi-aqueous and vapor degreasing. Increased thermal excursions may require higher cleaning chemistry concentration, longer process time, and higher processing temperatures.

The experiment investigates the cleaning effectiveness of flux residue after the reflow soldering process.

The test boards were processed at a standard condition. If residue remained from the standard condition, increased time was applied to evaluate cleaning efficacy at longer exposure time. If no residue remained from the standard condition, decreased time was applied to evaluate cleaning efficacy at shorter exposure time.

Conditions

- 35 SAC lead-free materials were tested
  - ◊ 7 – water soluble
  - ◊ 3- RMA
  - ◊ 25 – low residue no-clean
- Test board was unpopulated. The board finish was HASL Sn/Pb. Solder paste was stencil printed onto the board.
- Electrovert Omniflow 10E reflow oven
- Nitrogen inerted atmosphere was below 100 ppm oxygen
- Reflow profile (Figure 3)

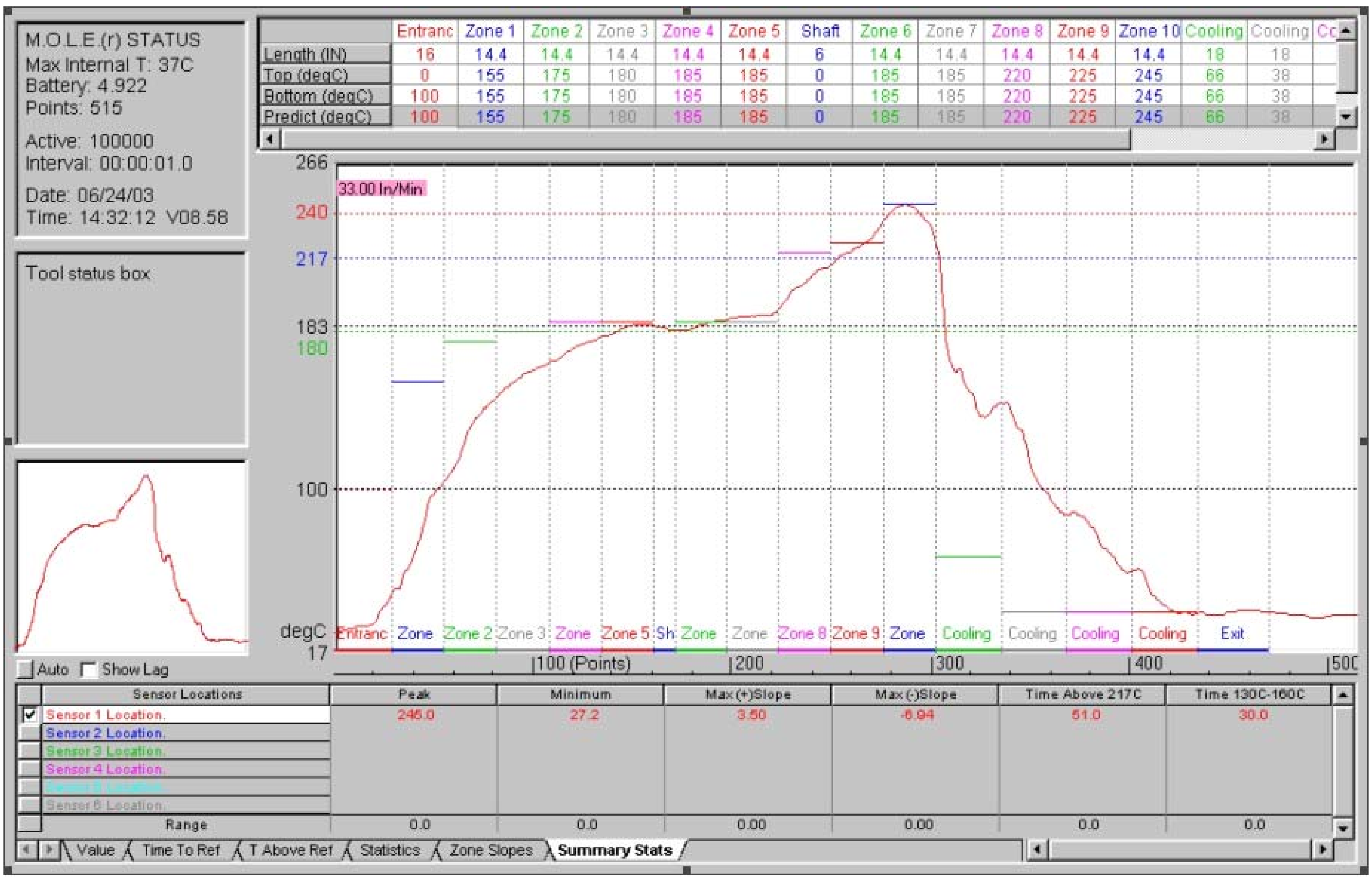


Figure 3 – Reflow Profile

- Boards were cleaned using:
  - ◊ Cleaning Equipment
    - ❍ Commercial aqueous inline cleaning machine
    - ❍ Centrifugal semi-aqueous batch cleaner
    - ❍ 2 – Sump Vapor Degreaser
  - ◊ Cleaning Chemistries
    - ❍ Aqueous
      - ❣ DI-water without additives: Cleaner A

        - ❣ DI-water with solvency, wetting and mild reactivity (10% concentration) # 1: Cleaner B
        - ❣ DI-water with solvency, wetting and mild reactivity (30% concentration) #2: Cleaner C
        - ❣ DI-water with solvency, wetting and mild reactivity (20% concentration) #3: Cleaner D
    - ❍ Semi-Aqueous
        - ❣ Semi-aqueous polar organic solvent composition: Cleaner E
    - ❍ Vapor Phase
        - ❣ Vapor phase solvent azeotrope: Cleaner F
- Response Variables
    - ❍ Qualitative
        - ❣ Visual inspection of residue
        - ❣ Assign percent cleanliness for inspected boards
    - ❍ Quanitative
        - ❣ Ionograph (not reported in this document)
- Factorial Experiment
    - ❍ Factor A : Flux Type
    - ❍ Factor B: Cleaning Material

Data Analysis

- Water Soluble Flux Cleaned with DI water only (Figure 4)
- Rosin Flux (Figure 5)
- Synthetic low residue (no-clean) flux: (Figure 6)

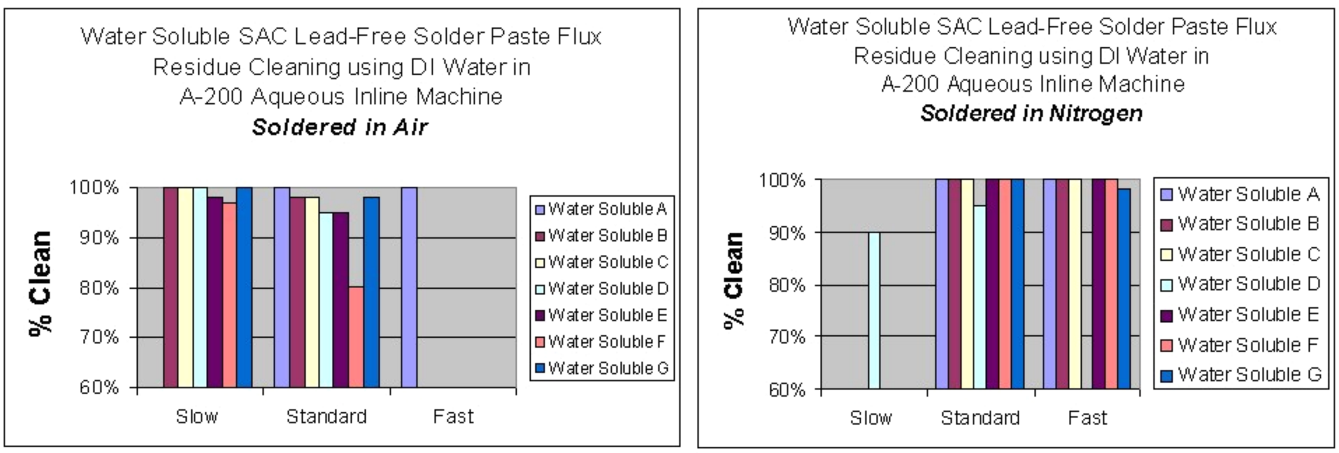


Figure 4 - Water Soluble Flux Cleaned with DI Water Only

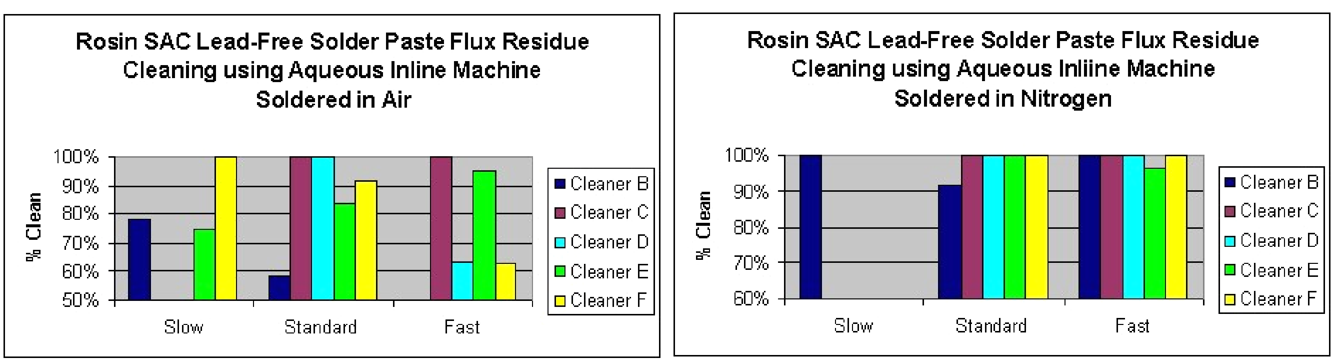
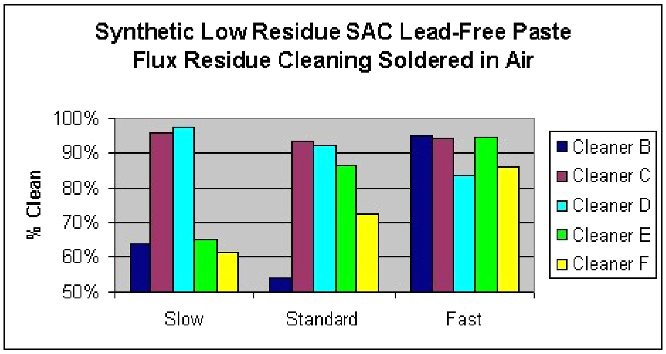


Figure 5 - Rosin Flux



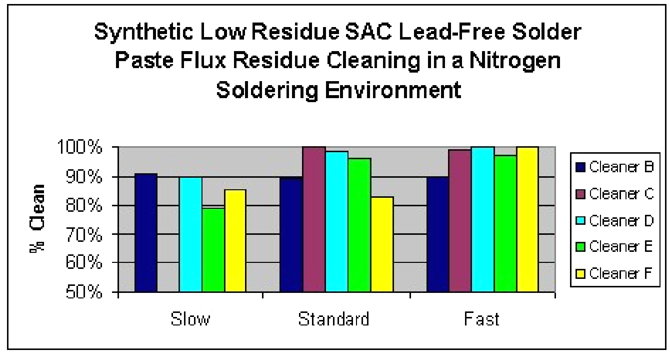


Figure 6 - Synthetic Low Residue (no-clean) Flux

The results represent the mean values of all fluxes cleaned, with DI water only, which are in the matrix. Only one of the water-soluble fluxes was 100% clean when using DI water only at standard processing conditions. This data point supports the hypothesis that lead-free flux residue is harder to clean. Conversely, water-soluble flux soldered in a nitrogen inerted-soldering environment, cleaned well at both standard and fast processing speeds. There was a unique anomaly; water-soluble D cleaned less effectively when soldered in nitrogen verse air.

The results represent the mean values of all the fluxes cleaned with the aqueous, semi-aqueous, and vapor phase chemistries. Cleaner B is an aqueous chemistry (solvency, wetting, and mild reactivity) that was run at 10% concentration, 135ºF. This cleaning material is highly effective on eutectic Pb/Sn rosin solder paste residue. The data indicates poor cleaning performance at standard, slow and fast processing speeds. This data point supports the hypothesis that cleaning is more difficult but improves for boards that are soldered in a nitrogen environment.

Cleaner C is an aqueous chemistry (solvency, wetting, and mild reactivity) that was run at 30% concentration, 145ºF. Two process variables were increased, concentration (increase of 20%) and temperature (increase of 10ºF). These parameters increased cleaning effectiveness. As seen by the data, both cleaning was highly effective in both air and nitrogen soldering environments. This data point nullifies the hypothesis but points to the need of more aggressive cleaning process parameters.

Cleaner D is an aqueous chemistry (solvency, wetting, and mild reactivity) that was run at 20% concentration, 135ºF. One process variable was increased from Chemistry B, which was concentration by 10%. Under standard processing conditions, cleaning was good. For fast process conditions, cleaning fell off for boards reflowed in air but was good for boards reflowed in nitrogen. This further supports the hypothesis that is lead-free cleaning is more difficult but improves when soldered in a nitrogen environment.

Cleaner E is a semi-aqueous chemistry (polar organic solvent composition) that was run at 100%, concentration, 140ºF, and processed in the centrifugal cleaning machine. Boards reflowed in air, cleaning at standard processing conditions was fair but improved to good for boards slow processing. Conversely, boards that were soldered in nitrogen cleaned good for standard and fast processing conditions, which further supports the hypothesis.

Cleaner E is a vapor phase azeotrope composition based on fluorinated/chlorinated/alcohol composition. The boiling point of the composition is in the range of 108-112ºF. As with Cleaner D, cleaning at standard processing conditions was fair but improved to good for boards soldered in nitrogen. This further supports the hypothesis.

The results represent the mean values of all the fluxes cleaned with the aqueous, semi-aqueous, and vapor phase chemistries.

Cleaner B performed poorly on boards that were soldered in air. The reason for the good score at the fast processing speed, there were a few fluxes that cleaned at the standard processing conditions that were run at fast conditions. Those few fluxes exhibited good cleaning. Boards soldered in nitrogen improved the cleaning but was still below acceptability.

Cleaner C, which performed very well on rosin fluxes, performed fair for boards that were soldered in air. For boards soldered in nitrogen cleaning was much improved but there were a few fluxes that did not totally clean.

Cleaner D cleaning performance was similar to cleaner C. Both cleaner C & D cleaned a number of the materials in air but cleaning improved when soldering in nitrogen. This further indicates the importance of high cleaning concentration and temperature.

Cleaner E performed well on many of the materials but did poorly on others. Cleaning did improve on boards that were soldered in nitrogen. This highlights the differences in flux formulations, especially these synthetic low residue materials.

Cleaner F did poor on many of the fluxes that were soldered in air but improved for those soldered in nitrogen. When using a vapor degreasing process, the data points to the importance of flux compatibility.

Interpretation of data

- Does it support the hypotheses?

  The data supports the hypotheses that cleaning will be more difficult for lead-free assemblies. The inferences indicate the following:

  - Water-soluble fluxes may require a small level of cleaning agent to fully remove the residue for assemblies soldered in air. It is believe that the flux vehicle volatilizes and in turn leaves a metal salt. This salt requires an additive with DI water to clean.
  - Rosin fluxes are harder to clean at higher processing temperature. The data indicates that the cleaning materials require higher solvency and temperature. For assemblies soldered in nitrogen, these process parameters can be relaxed.
  - Synthetic low residue (no-clean) fluxes exhibit the most cleaning difficulty. The data indicates that nitrogen improves cleaning but, there are many flux compositions that exhibit poor cleanability. Therefore, if cleaning is a requirement, flux selection becomes an important criterion.

References

1. Hwang, J.S. (2003, Nov). Lead-free implementation – Two Approaches. *SMT.*
2. Brooks, R. & Lee, N.C. (2003, Oct). *Challenges in Implementing Pb-Free Assembly*. Indium Corporation of America.
3. Lee, N.C. (2002). *Reflow soldering processes and troubleshooting SMT, BGA, CSP and Flip Chip Technologies.* Butterworth-Heinemann. ISBN0-7506-7218-8.

Lead-Free Soldering: DOE Study to understand its affect on Electronic Assembly Defluxing

APEX 2004: Cleaning

2-26-2004

By:

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Introduction

- Lead-free soldering requires new process material consideration
- Hwang (2003, Nov) *"many consider the fundamental principles and production-floor practices developed around eutectic Sn63/Pb36 solder will be equally valid for Pb-free assembly"*
- The SAC NEMI approved alloy pose several processing challenges: two which affect cleaning
  - flux composition
  - reflow temperature

Solderabililty of SAC Pb-free Alloy

- Lee & Brooks (2003, Oct)
  - *To maintain wetting that is identical to Sn/Pb, and increase of 50°C to the soldering temperature is needed*
  - *Pb-free solderability is significantly poorer with weaker no-clean and pure rosin fluxes*
  - *Pb-free alloys do not wet as well too lead-free terminations*

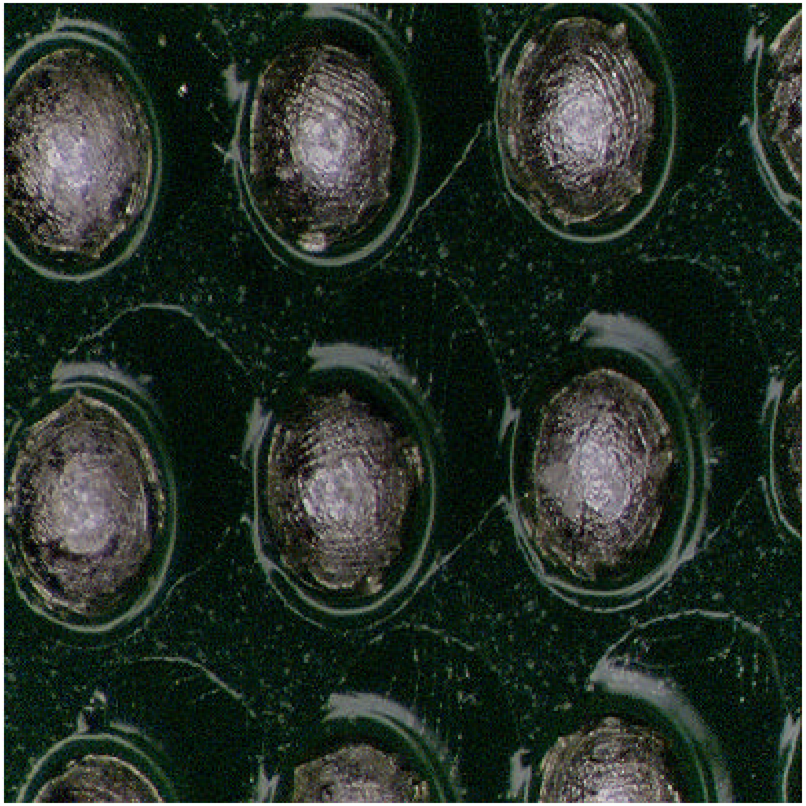
To improve wetting

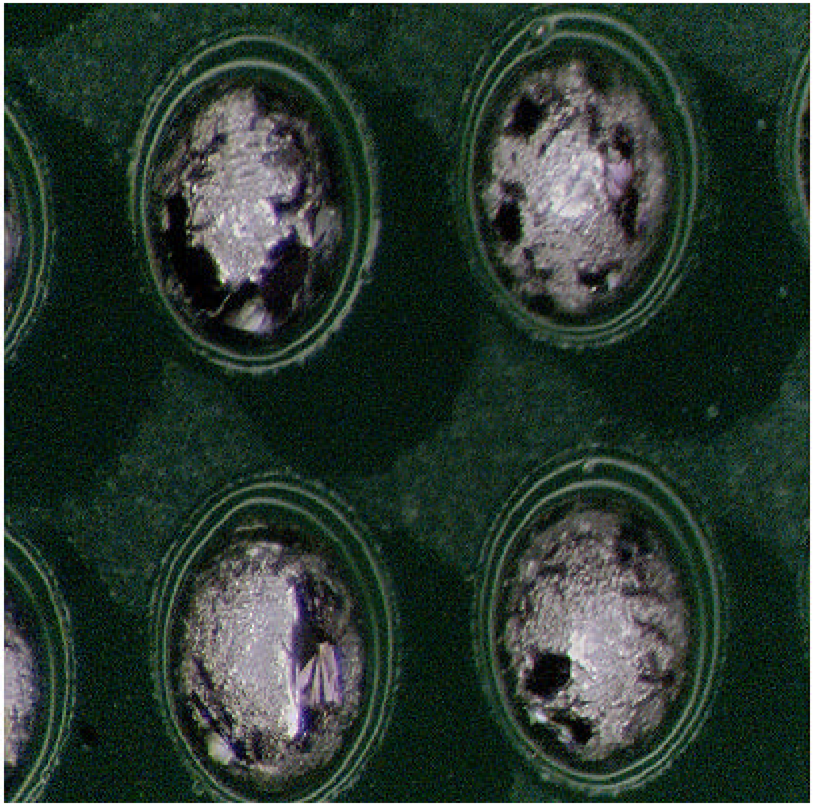
- Flux compositions
  - require higher activation
    - ionic residue that may affect reliability
  - flux solids increased to 20% of metal content
    - may leave more residue
  - higher processing temperatures
    - increase cleaning difficulty

Why Nitrogen Reflow?

- Nitrogen inerted soldering (hypothesis)
  - improves wetting and reduces oxidation
  - flux residue does not char
  - flux residue is transparent and easier to clean
- Solder in air (hypothesis)
  - higher activation needed
  - flux residue is harder
  - flux residue is more challenging to clean

Nitrogen vs. Air Soldering





Ambient Soldering

Nitrogen Soldering

Design of Experiment

- Premise
  - NEMI Lead Fee Alloy
    - 95.5Sn/3.9Ag/0.6Cu (SAC)
    - 217°C
  - Higher processing temperature increases oxidation of flux residue, which may increase cleaning difficulty
  - Nitrogen inerted atmosphere reduces oxidation of flux residue, which may improve cleanability

Design of Experiment

- Hypothesis
  - Lead free residue is harder to clean due to higher reflow temperatures and complex flux formulations
  - Boards reflowed in a nitrogen environment will clean easier than those soldered in an air environment

Design of Experiment

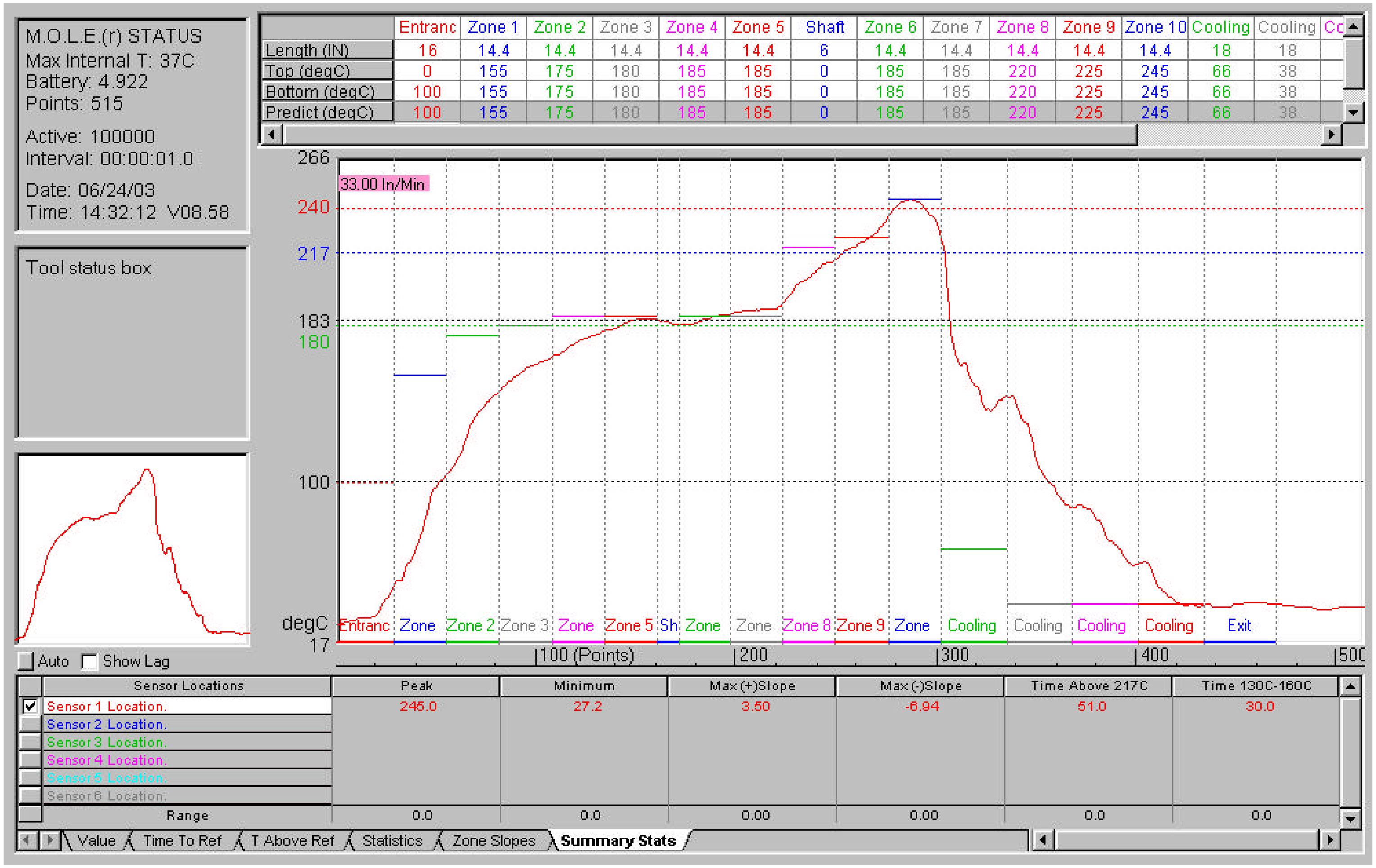
- Experimental Design
  - 3 cleaning processes evaluated
    - aqueous in-line
    - semi-aqueous centrifugal
    - vapor phase 2 sump degreaser
  - Solder pastes were obtained from leading suppliers
  - Standard test board
  - Boards were solder using a standard ambient and nitrogen reflow profile
  - Cleaning was judged qualitatively using 10-30x microscope

Design of Experiment

- Conditions
  - 35 SAC lead-free materials were tested
    - 7 - Water-soluble
    - 3 - RMA
    - 25 - Low residue (no-clean)
  - Test boards were unpopulated
  - Electrovert Omniflow 10E reflow oven
  - Nitrogen inerted below 100 ppm

Design of Experiment

- Reflow Profile



Design of Experiment

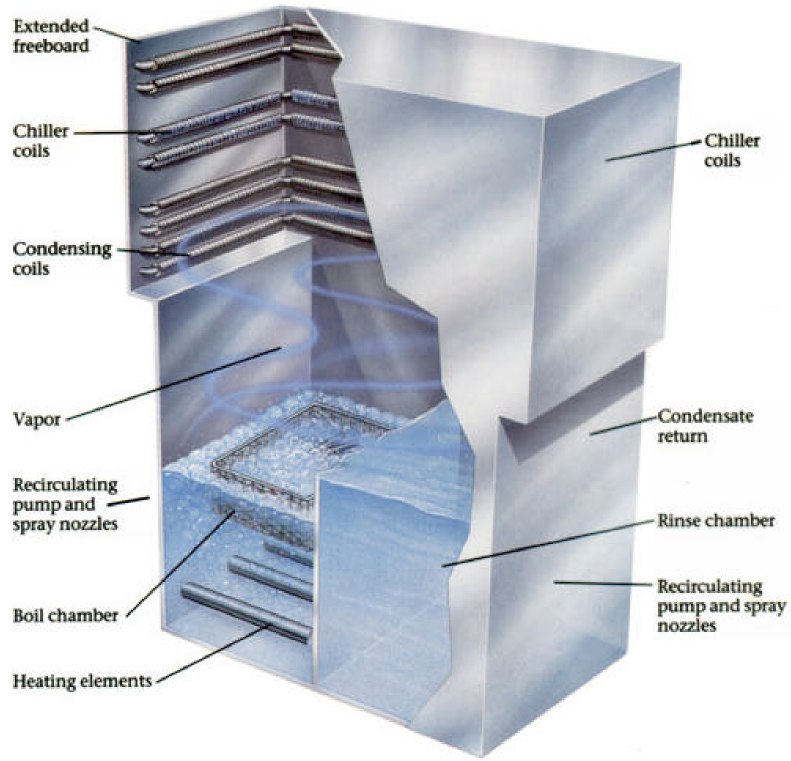
- Aqueous In-line

Design of Experiment

- Centrifugal

Design of Experiment

- 2 sump vapor degreaser



Design of Experiment

- Cleaning Chemistries
  - Aqueous, which were processed in the in-line
    - **Cleaner A**: DI-water without additives
    - **Cleaner B**: DI-water with solvency, wetting and mild reactivity @ 10% concentration
    - **Cleaner C**: DI-water with solvency, wetting and mild reactivity @ 30% concentration
    - **Cleaner D**: DI-water with solvency, wetting and mild reactivity @ 20% concentration

Design of Experiment

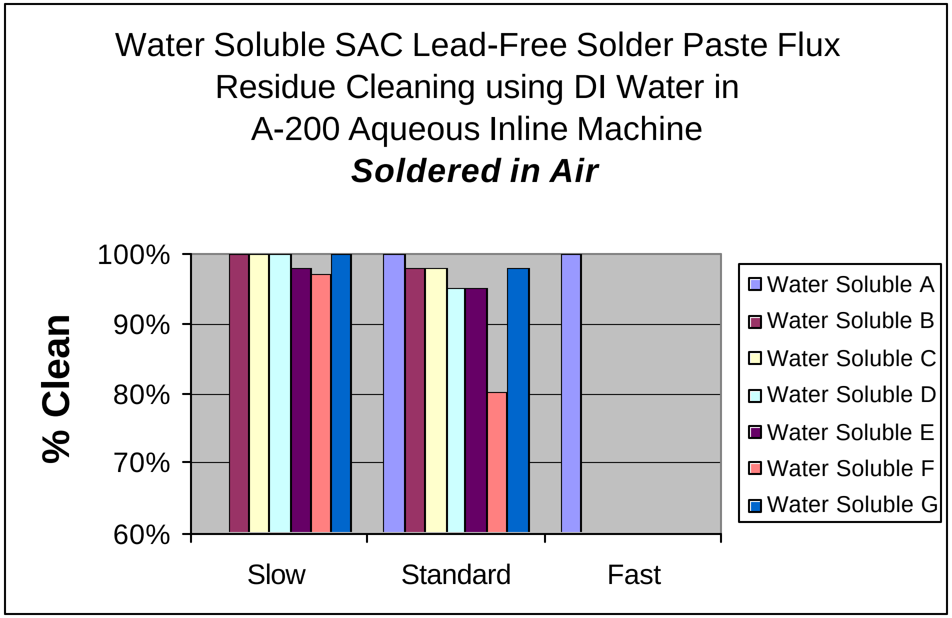
- Cleaning Chemistries
  - Semi-Aqueous, which was centrifugal processed
    - **Cleaner E:** semi-aqueous polar organic solvent composition
  - Vapor Phase, which was processed in vapor degreaser
    - **Cleaner F:** vapor phase solvent azeotrope

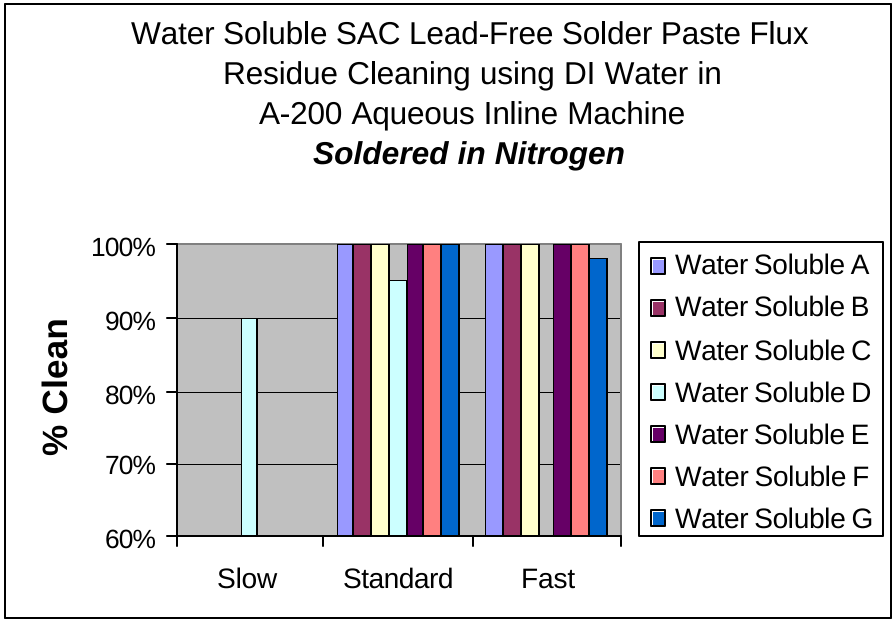
Design of Experiment

- Response Variables
  - Qualitative
    - Visual inspection of residue
    - Assign Percent cleanliness for inspection boards
  - Quantitative
    - Ionograph
  - Factorial Experiment
    - Factor A: Flux type
    - Factor B: Cleaning material

Data Analysis

- **Cleaner A:** DI water with no additives



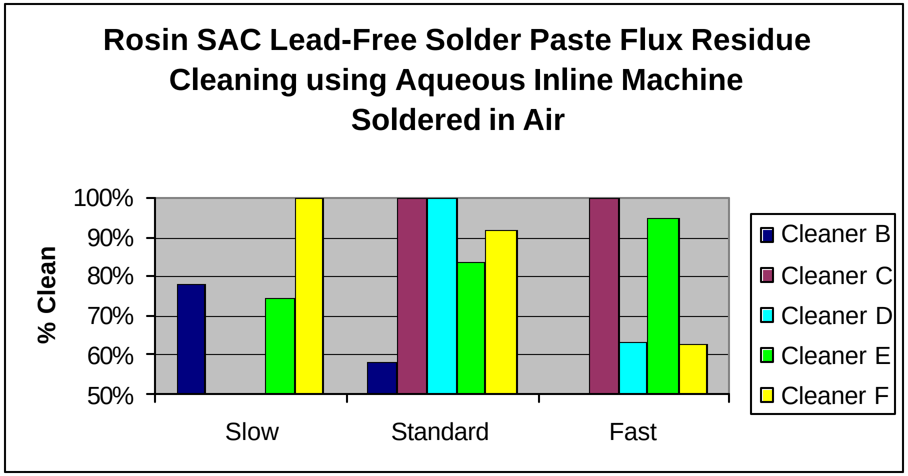


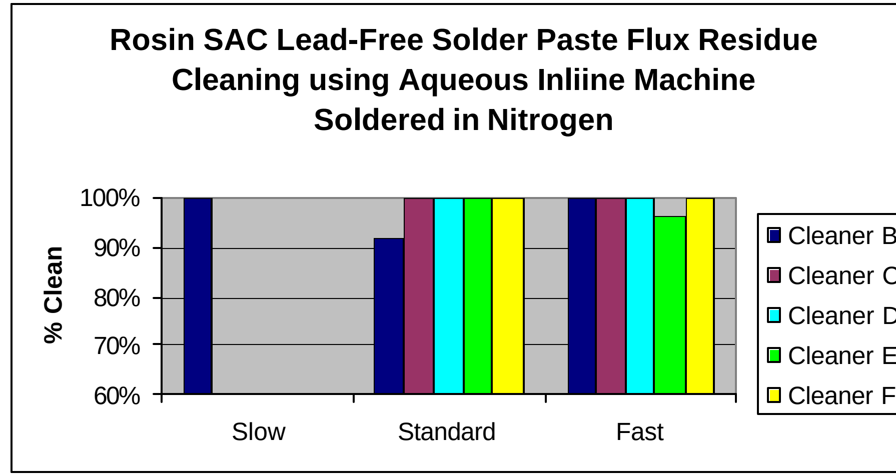
- Mean values of all fluxes clean
- Ambient: only 1 water-soluble cleaned
- Supports hypothesis
- Cleaning may require an additive with water

Data Analysis

- **Rosin Flux**
  - **Cleaner B**: DI-water with solvency, wetting and mild reactivity @ 10% concentration
  - **Cleaner C**: DI-water with solvency, wetting and mild reactivity @ 30% concentration
  - **Cleaner D**: DI-water with solvency, wetting and mild reactivity @ 20% concentration
  - **Cleaner E:** semi-aqueous polar organic solvent composition
  - **Cleaner F:** vapor phase solvent azeotrope

Rosin Flux





- Results represent the mean values of all fluxes cleaned
- Supports hypothesis
- Further explanation on the next few slides

Rosin Flux

- **Cleaner B**: DI-water with solvency, wetting and mild reactivity @ 10% concentration (135°F)
  - Material is highly effective on eutectic Pb/Sn rosin flux residue
  - Ambient: poor cleaning performance at standard, slow and fast processing speeds
  - Nitrogen: Good cleaning on all but one paste
  - Data point supports the hypothesis that cleaning is more difficult but improves for boards that are soldered in a nitrogen environment

Rosin Flux

- **Cleaner C**: DI-water with solvency, wetting and mild reactivity @ 30% concentration, (145°F)
  - Two process variables increased
    - concentration (increase of 20%)
    - temperature (increase of 10°F)
  - Cleaning was highly effective in both air and nitrogen
  - Nullifies the hypothesis but points to the need for more aggressive cleaning process parameters

Rosin Flux

- **Cleaner D**: DI-water with solvency, wetting and mild reactivity @ 20% concentration
  - One process variable increased
    - Concentration (increase of 10%)
  - Under standard processing conditions, cleaning was good for both ambient and nitrogen
  - For fast processing conditions, cleaning fell off for ambient but was good for nitrogen
  - Supports the hypothesis that Pb-free cleaning is more difficult but improves when soldering in nitrogen

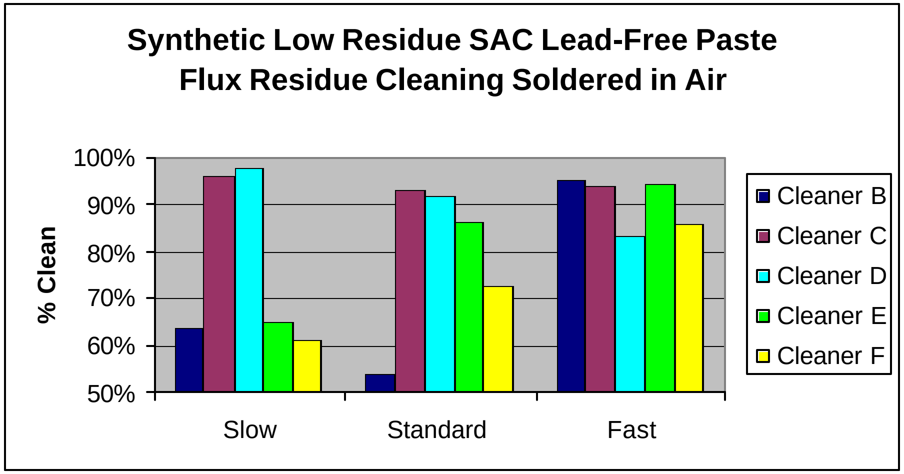
Rosin Flux

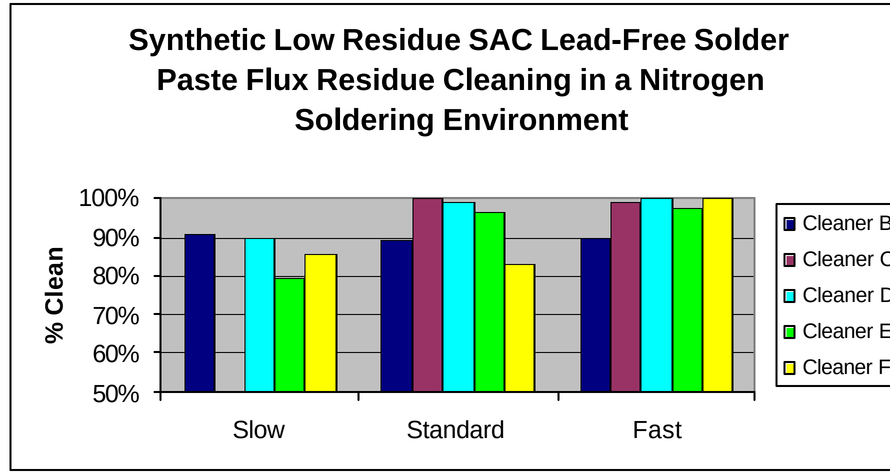
- **Cleaner E:** semi-aqueous polar organic solvent composition, 100%, 140°F
  - Ambient: Cleaning at standard process parameters was fair but improved to good for boards processed at slow speeds
  - Nitrogen: Boards that were solder in nitrogen cleaned good at both standard and fast processing conditions
  - Supports the hypothesis that Pb-free cleaning is more difficult but improves when soldering in nitrogen

Rosin Flux

- **Cleaner F:** vapor phase solvent azeotrope
  - Azeotrope composition based on fluorinated/halogenated/alcohol composition
  - Boiling Point 108-112°F
  - Ambient: Cleaning at standard parameters, board were fair.
  - Nitrogen reflowed boards cleaned good
  - Further supports the hypothesis that Pb-Free cleaning is more difficult but improves when soldered in nitrogen

Synthetic low residue (no-clean)





- Results represent the mean values of all fluxes cleaned
- Supports hypothesis
- Further explanation on the next few slides

Synthetic low residue (no-clean)

- **Cleaner B**: DI-water with solvency, wetting and mild reactivity @ 10% concentration (135°F)
  - Material is highly effective on eutectic Pb/Sn rosin flux residue
  - Ambient: poor cleaning performance
  - Nitrogen: Improved cleaning but still below acceptability
  - Data point supports the hypothesis that cleaning is more difficult but improves for boards that are soldered in a nitrogen environment

Synthetic low residue (no-clean)

- **Cleaner C**: DI-water with solvency, wetting and mild reactivity @ 30% concentration, (145°F)
  - Two process variables increased
    - concentration (increase of 20%)
    - temperature (increase of 10°F)
  - Ambient: Cleaning performance was fair
  - Nitrogen: Cleaning performance was much improved
  - Data point supports the hypothesis that cleaning is more difficult but improves for boards that are soldered in a nitrogen environment

Synthetic low residue (no-clean)

- **Cleaner D**: DI-water with solvency, wetting and mild reactivity @ 20% concentration
  - One process variable increased
    - Concentration (increase of 10%)
  - Ambient: Cleaning performance was fair
  - Nitrogen: Cleaning performance was much improved:
  - Supports the hypothesis that Pb-free cleaning is more difficult but improves when soldering in nitrogen

Synthetic low residue (no-clean)

- **Cleaner E:** semi-aqueous polar organic solvent composition, 100%, 140°F
  - Ambient: Performed well on many of the materials but did poorly on others.
  - Nitrogen: Good performance all but a few pastes
  - Supports the hypothesis that Pb-free cleaning is more difficult but improves when soldering in nitrogen

Synthetic low residue (no-clean)

- **Cleaner F:** vapor phase solvent azeotrope
  - Azeotrope composition based on fluorinated/halogenated/alcohol composition
  - Boiling Point 108-112°F
  - Ambient: Cleaning was poor
  - Nitrogen: Cleaning improved on many but there were others that did poorly.
  - Further supports the hypothesis that Pb-Free cleaning is more difficult but improves when soldered in nitrogen

Interpretation of Data

- Data supports the hypothesis that cleaning is more difficult for Pb-Free assemblies
- Water soluble solder paste soldered in air:
  - May require a small level of aqueous cleaning agent to fully remove residue for assemblies soldered in air
  - It is believe that the flux vehicle volatizes and in turn leaves a metal salt
  - The salt requires an additive with DI water to clean

Interpretation of Data

- Rosin solder paste soldered in air:
  - Boards soldered in air were harder to clean
  - The data indicates that the cleaning materials require higher solvency and temperature
  - For assemblies soldered in nitrogen, these process parameters can be relaxed

Interpretation of Data

- Synthetic Low Residue (no-clean)
  - Most difficult too clean
  - Some of the fluxes soldered in air were very difficult to clean.
    - Aggressive process parameters required
  - Boards soldered in nitrogen clean must better
  - If cleaning is a requirement, flux selection should be considered

For More Information

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