WATER SOLUBLE SOLDER PASTE, WET BEHIND THE EARS OR WAVE OF THE FUTURE?

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ABSTRACT
Water soluble lead-free solder paste is widely used in today's SMT processes, but the industry is slowly moving away from water soluble solder pastes in favor of no-clean solder pastes. This shift in usage of solder paste is driven by an effort to eliminate the water wash process. Some components cannot tolerate water wash and elimination of water washing streamlines the SMT process. Despite this shift, certain applications lend themselves to the use of water soluble solder paste. High-reliability applications require removal of flux residues and it is much easier to remove water soluble flux residues than no-clean flux residues. Because of this reality, water soluble solder pastes will be used for the foreseeable future.

Due to industry movement away from water soluble solder pastes, research and development resources have been focused on no-clean technologies. Some water soluble solder pastes in use today were developed many years ago, possibly before the era of lead-free soldering. Because of the prevailing trend toward no-clean formulation efforts, water soluble solder paste technology has fallen behind no-clean technology, especially for use with lead-free solder alloys. However in order to meet today's requirements for certain applications, new high performance water soluble solder pastes are needed.

This paper details the research and development of a new water soluble lead-free solder paste which improves on the performance characteristics of existing technologies. The key attributes of this solder paste are as follows:

- Environmentally stable in a wide range of conditions
- Long stencil life
- Excellent print characteristics
- Nominal wetting especially on hard to wet surfaces
- Very low solder balling and graping
- Easily removable flux residues

Challenging test methods were used to develop this solder paste and the results are detailed in this paper. Testing on this new water soluble solder paste is compared and contrasted to existing solder paste products. This development work created a new water soluble lead-free solder paste that meets the current and future needs of the industry.

Key words: water soluble solder paste, environmental stability, stencil life, printing, wetting, solder ball, graping, water wash ability

INTRODUCTION
A brand new water soluble solder paste might be considered "wet behind the ears" until there is some history of success in the field. Before a solder paste is released to the market, testing is conducted to simulate real-world processes and validate performance in a laboratory. Such was the case with this new water soluble lead-free solder paste formulation. The details of the development process are detailed in this paper. The results of testing the new water soluble solder paste are compared to the results from existing products which have been used in the market for several years. The objective of the research and development project was to deliver a new water soluble lead-free solder paste that meets current requirements yet delivers on future performance needs of high-reliability applications. This new water soluble, lead-free solder paste could become the "wave of the future".

METHODOLOGY
The research and development process for a solder paste is fairly straight-forward and the basic development process is listed below:

1. Set process and performance objectives for the material.
2. Develop formulations for evaluation.
3. Produce small batches of multiple formulations.
4. Conduct testing to measure the performance objectives for the material.

5. Compare the results to existing, well-known commercialized products.
6. Repeat steps 2 through 5 until the new solder paste meets the desired objectives.

The process and performance objectives for the new high performance water soluble lead-free solder paste are shown below (Table 1).

Table 1 – Objectives and Detailed Goals for a High Performance Water Soluble Solder Paste

Objectives for a New Water Soluble Solder Paste	Detailed Goals
Environmentally stable in a wide range of conditions	• In high humidity environments, the solder paste should not absorb moisture or become "soupy" during use over an 8-hour work day. • In low humidity environments, the solder paste should not dry out during use over an 8-hour work day. • Storage at room temperature should not cause thickening or loss of activity of the solder paste.
Long stencil life	• The solder paste should be printable for at least 8 hours on the stencil, and respond well to pauses in printing.
Excellent print characteristics	• The solder paste should be printable over a range of print speeds and give good transfer efficiency and printed "brick" definition.
Nominal wetting especially on hard to wet surfaces	• The solder paste should generate excellent wetting on easy to wet surfaces like the electroless nickel immersion gold (ENIG) surface finish. • Wetting on hard to wet surfaces like the Organic Solderability Preservative (OSP) finish should be comparable to existing products.
Very low solder balling and graping	• The solder paste should generate very low solder balling and very low graping.
Easily removable flux residues	• The solder paste must generate flux residues that are easy to wash off of the circuit board with de-ionized water.

The test methods used in this project to measure performance are detailed by objective below. Many of these test methods were taken from previous work [1]. In some cases, existing test methods did not challenge the solder pastes and new methods were created.

Environmental Stability

The environments in which solder pastes are used vary widely. Temperature and relative humidity vary based on geographic location and change seasonally. In a typical SMT process, a common temperature range is 18 – 24 ºC (65 – 75 ºF) and a common range for relative humidity is 15 – 55 %RH. The environment affects and changes solder paste over time, especially when the material is open to the air which can produce undesirable alterations. In low relatively humidity environments, solvents can evaporate out of the solder paste causing a drying effect. In high humidity environments, solder pastes can absorb water from the air which can cause causing a thinning effect. Reactions can take place in the solder paste causing a loss of activity and sometimes a thickening effect, especially when oxygen is present. As temperature increases these reaction rates increase, which shortens the usable life of a solder paste.

A few methods were used to measure the environmental stability of the new water soluble solder paste. Water soluble solder pastes tend to be hygroscopic (water absorbing) and fairly reactive. Ideally a solder paste can tolerate a wide range of environmental conditions and maintain a long stencil life and shelf life. These environmental test methods show significant differences in the performance of water soluble solder pastes.

The first method is a simple measurement of mass change when the solder paste is stored with exposure to the air over time. For this analysis, the solder paste is weighed initially and then periodically weighed at different time intervals and the percentage of mass change is calculated. This test is conducted in both low and high humidity environments. With this test method, water soluble solder pastes typically gain mass at a fairly high rate.

The second method is a measurement of tack force as it changes over time. Tack force is measured initially and then again after air-exposed storage for several hours. The tack force of water soluble solder pastes tends to decrease significantly over time and in some cases the solder paste surface hardens causing a complete loss of tack force [2].

Finally, an evaluation for environmental stability measures the reactivity of the solder paste. This test involves mixing the solder paste continuously for 6 hours while exposed to the air. The paste is then sealed in a container and stored overnight, following which the viscosity is measured and compared to the initial viscosity. A significant increase in viscosity indicates that some type of reaction has occurred. Print and reflow performance can also be evaluated before and after the test. Degradation in the print and reflow characteristics indicate reactivity / instability in the solder paste.

Stencil Life

Some water soluble solder pastes have a relatively short stencil life and their print performance can degrade significantly within a normal 8-hour work shift. If the relative humidity levels around the printer are high then some water soluble solder pastes might only be usable for a couple of hours. The best way to test stencil life is to run long-term tests on a printer [3, 4]. This method involves a combination of testing the solder paste's open time and response to pause on the printer. Solder paste is printed through small apertures with 0.50 area ratio and volume is measured using a solder paste inspection system (SPI). The solder paste sits idle on the printer for a period of time and is then printed and solder paste volume is measured again. This is repeated over an 8-hour time period. The process for testing stencil life is detailed below (Figure 1).

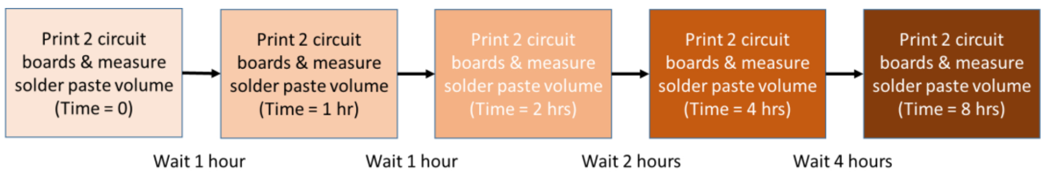


Figure 1 – Process for the 8-Hour Stencil Life Test

The volume data is used to calculate the mean and standard deviation of transfer efficiency which is compared for each elapsed time. Normally there is a decrease in the mean transfer efficiency over time and this occurs more quickly for some solder pastes than others. Ideally a solder paste should maintain a stable transfer efficiency over an 8-hour time period.

Print Characteristics

A high performance solder paste can be used with a wide range of print speeds (20 mm/sec to 100 mm/sec), and not surprisingly some solder pastes print better at higher speeds than others. As print speed is increased or decreased the solder paste deposit definition (which should be brick-like) should not degrade. This test is simply a measurement of the mean and standard deviation of transfer efficiency at various print speeds which are typically varied at low, medium and high speeds. Solder paste brick definition is evaluated for each speed but this is generally analyzed by qualitative visual inspection.

Wetting

To produce robust solder joints, solder pastes should fully wet and spread to the edges of the pad and wet the component leads. This is not always the case as some circuit board finishes are more difficult to wet than others. In general, solder paste spreads farther during reflow on the Electroless Nickel Immersion Gold (ENIG) finish than on the Organic Solderability Preservative (OSP) finish. Component leads can also be difficult to wet depending upon the finish, oxide growth, component age and storage conditions. This method for evaluation of wetting utilizes a designed circuit board pattern [5] as shown in Figure 2.

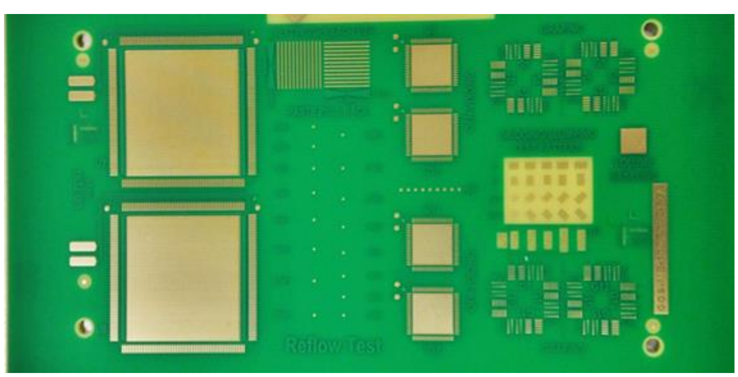


Figure 2 – F2A Reflow Test Circuit Board [5]

This circuit board has a wetting pattern made up of 12 vertical and 12 horizontal circuit lines. 15 solder paste deposits ("bricks") are printed along each line with a pitch varying from 0.4 mm at the edges to 0.1 mm near the center (Figure 3). This test pattern is similar to one used by Guene [6].

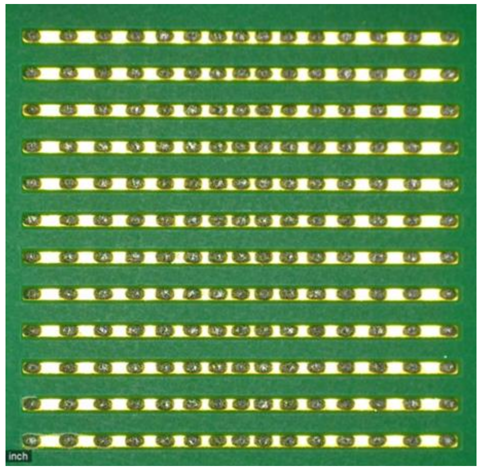


Figure 3 – F2A Wetting Pattern before Reflow

During reflow the solder paste flows together down the line (Figure 4) and afterwards the percentage (%) of spread / wetting is calculated.

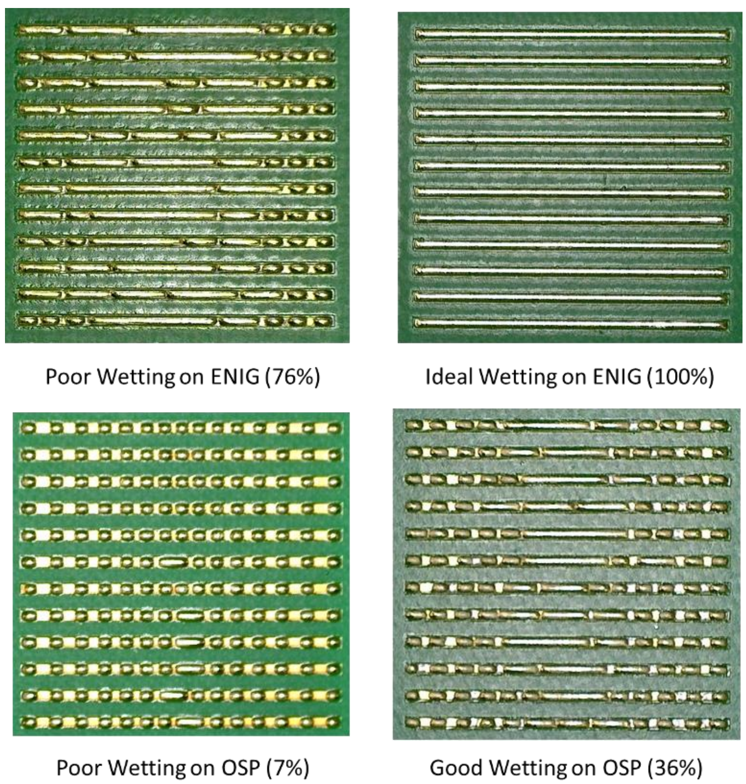


Figure 4 – F2A Wetting Pattern after Reflow for ENIG and OSP Finishes

This test is run on both ENIG and OSP surface finishes. In general, wetting on the ENIG surface is typically greater than 90% and wetting on the OSP surface typically ranges from 15% to 30%.

Solder Balling and Graping

Well formulated solder pastes produce no solder balling or graping. The water soluble lead-free solder pastes on the market today tend to produce more solder balling and graping than their no-clean counterparts. The same F2A reflow circuit board (Figure 2) is used to evaluate both the solder balling and graping attributes. The pullback pattern has a range of overprint areas (Figure 5) which is used to measure the potential for solder balling. The data is summarized as the largest overprint percentage (%) with fewer than 5 solder balls, and the largest overprint percentage (%) with fewer than 10 solder balls.

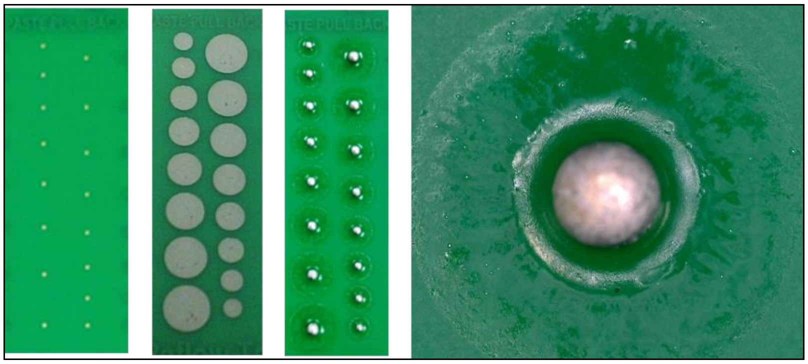


Figure 5 – F2A Solder Balling Before and After Reflow

The graping potential of a solder paste is measured using a specially designed pattern (Figure 6). Graping is counted as the number of solder deposits showing graping out of a total possible and is summarized as a graping percentage.

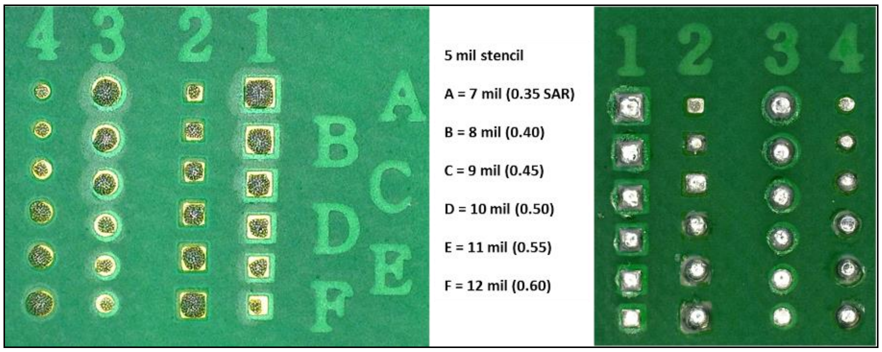


Figure 6 – F2A Graping Before and After Reflow

Solder balling and graping can be measured for different types of reflow profiles and alloys. A high performance solder paste should produce low solder balling and low graping with a variety of reflow profile conditions.

<u>Water Washability</u>

Water soluble solder pastes are often mis-named. Many water soluble solder pastes generate flux residues that are not truly soluble in water (Figure 7). The beaker on the left contains flux residue that is not completely soluble in water while the beaker on the right contains a flux residue that is completely soluble.

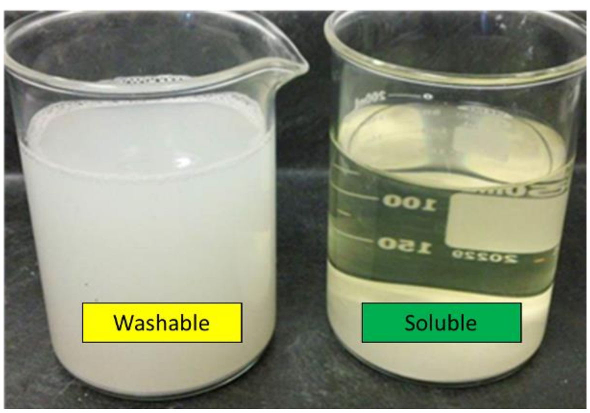


Figure 7 – Water Washable (Left) vs. Water Soluble (Right)

The flux residues that are not truly soluble in water can still be washed from the circuit board but it is easier to remove residues that are completely water soluble. Ideally solder paste flux residues can dissolve easily in DI water without the need to use cleaning agents. Washability is evaluated after reflow using a wash process with low pressure tap water, followed by inspection for residues. This is a worst-case type of washing that will show issues with washability if they exist.

<u>Reflow Profile Information</u>

The reflow profile used in these test methods was a standard linear ramp type profile for SAC305 alloy. The details for the reflow profile are shown below (Table 2).

Table 2 – Reflow Profile for SAC305 Alloy (Linear Ramp)

Profile Length (45 ºC to Peak Temperature)	4.0 to 4.5 minutes
Ramp Rate	1.0 to 1.5 ºC/second
Time Above Liquidus (217 ºC)	50 to 70 seconds (60 seconds nominal)
Peak Temperature	240 to 250 ºC (245 ºC nominal)

RESULTS AND DISCUSSION

The results of the development work on the new solder paste are separated by objective below. The new solder paste was compared to two existing products which are called Solder paste A and Solder paste B. Solder paste A and solder paste B are both water soluble lead-free solder pastes that have been in the market for many years. The new solder paste is named New SP in the results below. All of these solder pastes were made with SAC305 IPC Type 3 (25 to 45 µm) sized solder powder. The results of testing each of these solder pastes are compared and contrasted.

Environmental Stability

The mass change of the solder pastes was evaluated over 24-hours at 20% RH and 55% RH. The mass change results are shown below (Table 3).

Table 3 – Mass Change with 24-Hour Storage Open to Air

Relative Humidity	Solder Paste A	Solder Paste B	New SP
20%	Loss of 0.01% wt	Loss of 0.03% wt	Gain of 0.05% wt
55%	Gain of 0.22% wt	Gain of 0.40% wt	Gain of 0.31% wt

After storage at 20% RH all three solder pastes displayed negligible mass change. Mass change of less than 0.1% by weight over a 24-hour period indicates good environmental stability. After storage at 55% RH all three solder pastes gained a significant amount of mass. Solder paste B gained roughly double the mass of solder paste A. This indicates that solder paste B is much more hygroscopic (water absorbing) than solder paste A. The new solder paste improved upon the performance of solder paste B at 55% RH.

Tack force of each solder paste was measured over time as they were stored open to the air. The tack force coupons were stored at room temperature and 55% RH over a 72-hour period and tack force was measured after every 24-hours (Figure 8).

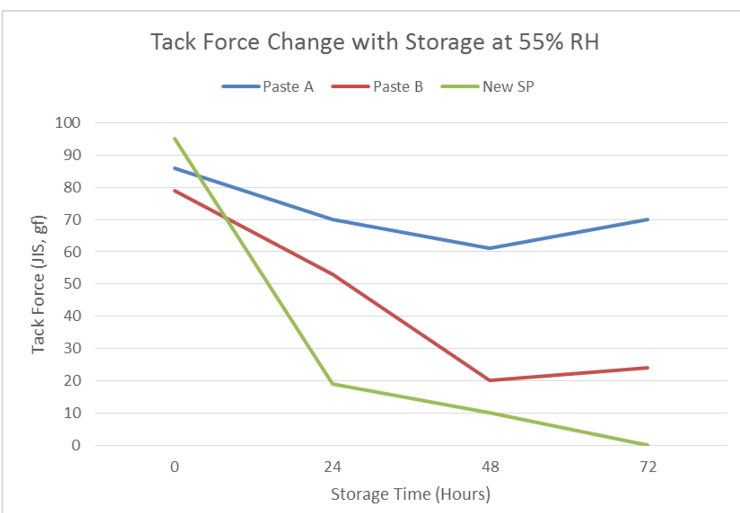


Figure 8 – Tack Force Change with 72-Hour Storage Open to Air

Solder paste A (blue) was the most stable in this test showing the least tack force change. Solder paste B (red) showed a large drop in tack force after 24-hours and another drop after 48-hours. The new solder paste (green) showed the largest drop after 24-hours and had essentially no tack left after 48-hours. In this test, solder paste A showed the best environmental stability.

This tack force test was repeated over an 8-hour time period. The tack force test coupons were printed and placed into a chamber at room temperature and 55% RH. The tack force was measured every hour for 8 hours and the data is shown below (Figure 9).

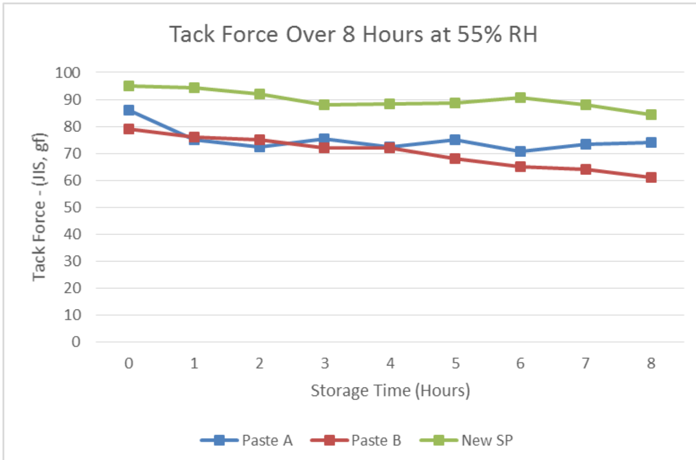


Figure 9 – Tack Force Change with 8-Hour Storage Open to Air

Over an 8-hour time period, all three solder pastes (A, B, and New) showed a slight decrease in tack force. The new solder paste (green) and solder paste A (blue) gave less of a drop in tack force than solder paste B (red). The new solder paste displays better performance than solder paste B in this test.

Reactivity testing was done using the 6 hour mix method. Solder paste A and the new solder paste were mixed continuously for 6 hours open to the air. They were placed in sealed jars and stored overnight at room temperature. The viscosity was measured and compared to the initial viscosity which are shown below (Table 4).

Table 4 – Viscosity Before and After 6 Hour Mix Reactivity Testing

Solder Paste	Viscosity Initial (Production Spiral Pump Viscometer, Kcps)	Viscosity Final (Production Spiral Pump Viscometer, Kcps)	Viscosity Change (%)
Solder Paste A	630	680	7.9% increase
New Solder Paste	760	690	9.2% decrease

A change in viscosity of more than 20% typically indicates that some type of reaction occurred during the 6 hour mix test. An increase in viscosity indicates that the solder paste flux reacted with the solder powder and air creating oxidation by-products of the solder paste. Increases in viscosity can also be caused by evaporation of solvents from the solder paste resulting in a drying effect. A decrease in viscosity is expected due to aggressive shear thinning of the solder paste. If a decrease in viscosity of more than 20% is observed then that indicates some type of instability in the solder paste or possibly moisture absorption from the air caused a thinning effect. Solder paste A and the new solder paste showed viscosity changes of less than 10% which indicates good stability.

<u>Stencil Life</u>

Stencil life was tested through an 8-hour print test. The solder paste was printed using a stencil with 0.4 mm pitch BGA arrays with an area ratio of 0.50. The stencil was made of laser cut, fine grain steel with 8 µm to 9 µm grain size. The stencil thickness was 127 µm (5 mil), the aperture sizes were 254 µm (10 mil) and the aperture shapes were rounded squares. Printed solder paste volumes were measured initially and after 1, 2, 4, and 8 hours on the printer. Mean transfer efficiencies were calculated and are charted below (Figure 9).

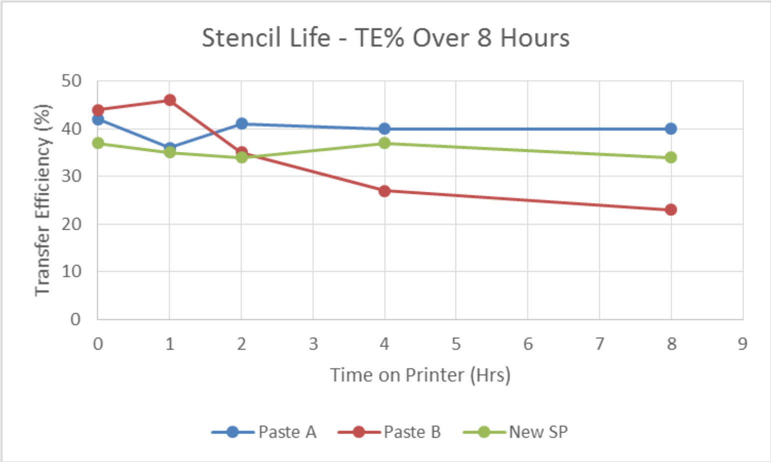


Figure 9 – Transfer Efficiency Changes over 8-Hours on the Printer

Solder paste A (blue) held fairly constant transfer efficiencies over the 8-hour time. Solder paste B (red) did not fare as well. There was a distinct drop in transfer efficiency after 4 and 8-hours on the printer. The new solder paste (green) showed very stable transfer efficiency over time. The new solder paste provides similar stencil life and response to pause as solder paste A and an improvement in stencil life and response to pause over solder paste B.

<u>Print Characteristics</u>

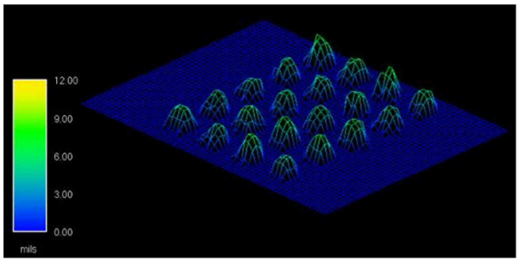
Print characteristics were tested by printing the solder pastes at 20, 50 and 100 mm/sec print speeds. The solder paste was printed using the same test stencil and aperture sizes as described in the Stencil Life section. The mean transfer efficiency was calculated for each solder paste at each print speed (Table 5).

Table 5 – Transfer Efficiency at Various Speeds

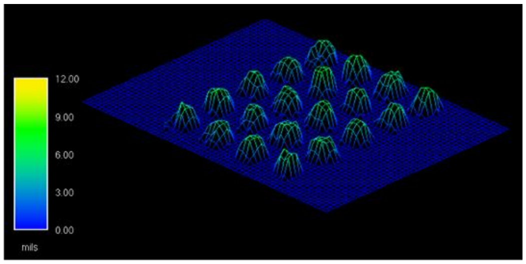
Print Speed (mm/sec)	**Solder Paste A (Mean TE %)**	**Solder Paste B (Mean TE %)**	**New SP (Mean TE %)**
20	42%	44%	37%
50	45%	44%	37%
100	44%	39%	31%

Solder paste A showed consistent transfer efficiency over this range of print speeds. Solder paste B showed consistent transfer efficiency at 20 mm/sec and 50 mm/sec print speeds, but there was some loss of transfer efficiency at 100 mm/sec. This reduction in transfer efficiency is fairly common when solder pastes are printed at high speeds. The new solder paste also gave consistent transfer efficiencies at the 20 mm/sec and 50 mm/sec print speeds but there was a slight loss of transfer efficiency at a speed of 100 mm/sec.

Images of the solder paste bricks show some difference in the print characteristics of these solder pastes (Figure 10). These images were taken from prints that were run at a print speed of 50 mm/sec.



Paste B Printed 3D Image



New Paste Printed 3D Image

Figure 10 – Images of Solder Paste Bricks for Solder Paste B and New SP (50 mm/sec)

Solder paste B tends to show some peaking of the solder paste bricks with higher spikes than the new solder paste. The New solder paste tends to create uniform rounded solder paste bricks which is a desirable quality.

Wetting

Wetting was tested for each solder paste using ENIG and OSP coated F2A reflow test boards (Figure 2). A standard linear reflow profile (Table 2) was used in this test. The wetting or spread percentages for each solder paste on each surface finish are shown below (Figure 11).

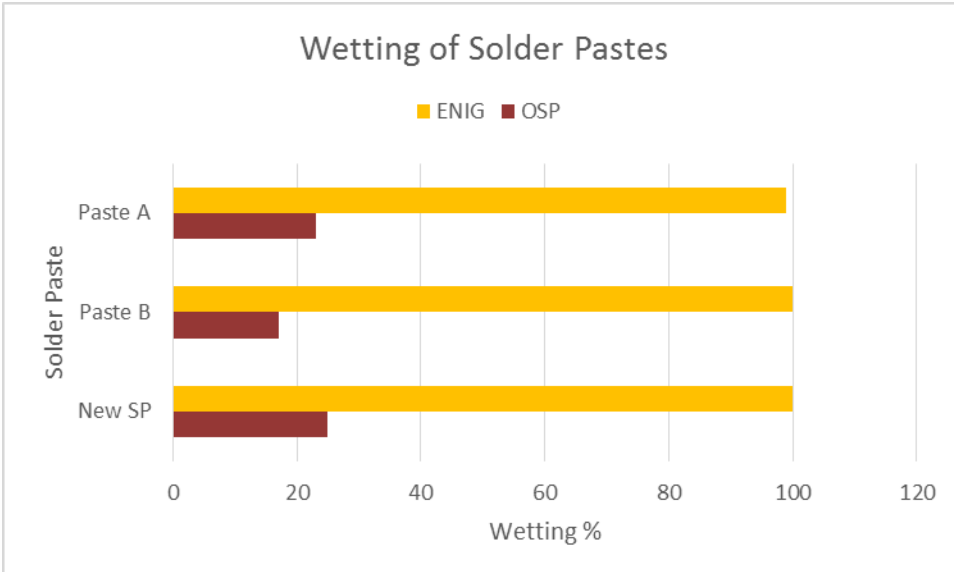


Figure 11 – Wetting / Spread Results on ENIG and OSP Surface Finishes

All three solder pastes spread very well on the ENIG surface finish (golden) and gave wetting percentages near 100%. This is an expected result as most pastes wet the ENIG surface very well. The OSP surface (dark red) shows much lower wetting overall. Solder paste A and the new solder paste wetted the OSP surface better than solder paste B (Figure 12). Guene [7] reported similar wetting results for ENIG and OSP surface finishes.

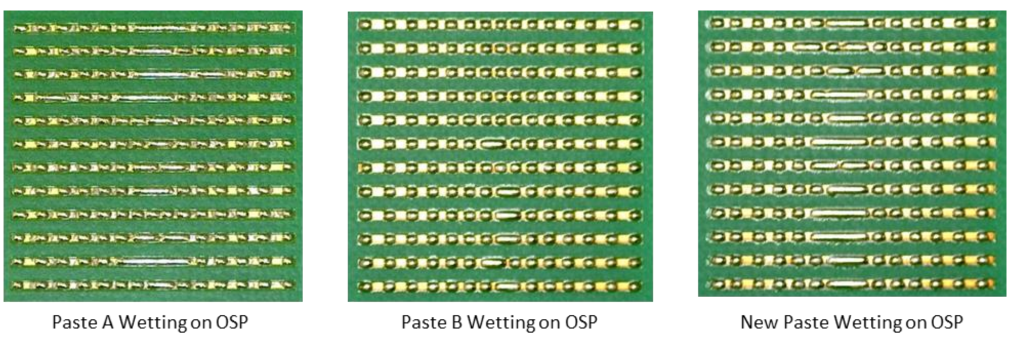


Figure 12 – Wetting / Spread on OSP

Solder Balling and Graping

Solder balling and graping were evaluated for each solder paste using the F2A reflow test board. A standard linear reflow profile (Table 2) was used and the results are shown below (Table 6).

Table 6 – Solder Balling and Graping Results

Test	Solder Paste A	Solder Paste B	New SP	Best Possible Result / Goal
Graping (%)	42%	9%	17%	**0%**
Solder Balling (<10 balls)	900% overprint	1250% overprint	1250% overprint	**1250%**
Solder Balling (<5 balls)	750% overprint	1100% overprint	1250% overprint	**1250%**

Graping is calculated by counting the number of deposits with graping and dividing by the total possible. Low graping percentages are desirable. Solder paste A generated a fairly high graping percentage. Solder paste B showed much better performance than solder paste A. The new solder paste generated a low graping percentage which was much better than the performance of solder paste A.

Solder balling is evaluated by inspecting the overprint areas of the F2A reflow test board. Larger overprint ratings are desirable in this test. Solder paste B generated less solder balling than solder paste A. The new solder paste generated the least overall solder balling and therefore had the best performance.

Water Washability

After reflow the circuit boards were washed using hot tap water with low flow / pressure and without any scrubbing. Pictures of the circuit boards after washing show some differences in solder paste performance (Figure 13).

Figure 13 – Flux Residues on Circuit Boards after Washing

In general, all three solder pastes washed very cleanly and left very little residue after washing. Solder paste B shows some slight residue around the solder deposits, while solder paste A and the new paste show very little residue.

The water from washing multiple circuit boards with each solder paste was captured. The appearance of the water gives some indication of the water solubility and water wash ability of each solder paste flux residue (Figure 14).

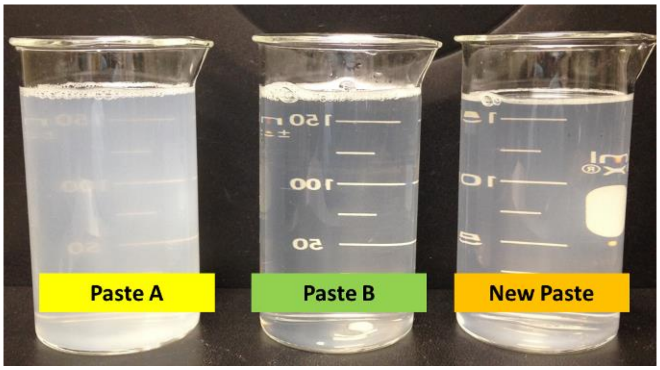


Figure 14 –Wash Water Containing Solder Paste Flux Residues

The flux residue from solder paste A is not completely soluble in water which is evidenced by the cloudiness of the water wash solution. The flux residues from solder paste B and the new solder paste create relatively clear water solutions. Based on the solubility of the flux residues in water, it would be easier to wash the residues from solder paste B and the new solder paste than solder paste A.

Summary of Results

All of the testing results on solder paste A, solder paste B, and the new solder paste are summarized below (Table 7). The performance of each solder paste is compared to the other solder pastes using a ranking system (0, +, -). A rank of (0) indicates the baseline or typical performance of solder paste. A rank of (+) indicates improved performance over the baseline solder paste. A rank of (-) indicates reduced performance as compared to the baseline solder paste.

Table 7 – Summary of Testing Results for Each Solder Paste

Test Method / Property	Solder Paste A	Solder Paste B	New Solder Paste
Environmental stability: Low relative humidity	0	0	0
Environmental stability: High relative humidity	+	-	0