

Reliability Assessment of No-clean and Water-soluble Solder Pastes Part I

Emmanuelle Gu  n  , Steven Teh

INVENTEC Performance Chemicals

Bry sur Marne (France), Selangor (Malaysia)

Abstract

Looking back twenty-five years ago, the solder pastes residues had to be cleaned after reflow due to their corrosive nature: two ways of cleaning were possible, either with solvent or by using water, with or without detergent. Now the assembly world is mainly no-clean: paste formulation is safer in terms of chemical reliability and process costs are reduced without cleaning. However, some applications, i.e. military, aerospace, high frequency, semiconductor require a perfect elimination of the residue after reflow. There are several options to achieve this result: the use of a no-clean paste which residue can be removed with the most suitable cleaning method or the use of a paste designed to be cleaned, as a water-soluble solder paste.

The water-soluble solder pastes generally show great wettability because of their strong activation but they are also known to have shorter stencil life and to be more sensitive to working conditions as temperature and humidity, compared to the no-clean pastes. Additionally, with the components stand-off getting smaller and smaller, washing residues with water only is more and more challenging due to its high surface tension: the addition of detergent becomes often necessary.

The purpose of this paper is to highlight the differences between these two families of solder pastes to guide users in their choice. This will be achieved through the comparison of several recent water-soluble and no-clean formulations as far as reliability is concerned. First the printing quality will be evaluated (viscosity, tack, cold slump, printing speed according to pressure, stencil life, idle time, printing consistency). Then the reflow properties will be compared (hot slump, solderballing, reflow process window, wetting ability on different finishes). Finally the residue cleanability will be assessed. The IPC SIR test (method IPC TM 650 2.6.3.7) will be also done to conclude the study. Both standardized tests and production tests will be used to evaluate the performance of these two kinds of solder pastes.

Introduction

Solder paste is a compound that typically consists of a fusible alloy and some type of deoxidizing flux. Different pastes can have a variety of compositions, though a typical formula consists of powdered solder mixed in with a gel-like flux material. According to standard J-STD-004 "Requirements for Soldering Fluxes", solder pastes are classified into three types based on the flux types: (1) rosin based, (2) water-soluble and (3) no-clean. In the past, solder pastes were cleanable. There are generally two different types of cleanable pastes, water cleanable type (water-soluble paste) and chemical cleanable type (cleaned by solvent or detergent).

With the increased of package density, combined with the complete ban of CFCs by year 2000 (Montreal Protocol), the electronics industry was strongly driven to implement water cleanable process and no-clean processes. Furthermore, as the workability and reliability requirements of the process are becoming more strict and precise, water-soluble solder paste and no-clean solder pastes have been developed accordingly. As the name implies, flux residues from the water-soluble solder paste are designed to be cleaned using water. For example, for radio frequency (RF) circuits and high speed circuits, for performance reasons it is usually essential that assemblies have no flux residue after reflow. Many electronics manufacturers with a wide variety of products also prefer clean assemblies, such as medical equipment and military assemblies.

With the challenges of current miniaturization technology of SMT components, narrower spacing between components and substrates, lower stand-off and the higher temperatures used for lead-free applications, solder paste residue becomes more difficult to clean. Water-soluble pastes are also commonly used in hard-to-solder applications when solvent cleaning is not feasible or in applications where no-clean residues may pose cosmetic issues. Water cleaning is an easy process to control, and the equipment is relatively easy to maintain, though the cost effectiveness issue comparing to solvent base cleaning, becomes one of the hot debate topic in recent times.

From the application point of view, the obvious advantage of converting to water-soluble solder paste is the elimination of CFC's from printed circuit board cleaning processes. However, this solder paste technology is more sensitive to normal processing variables. Water-soluble materials often exhibit production sensitivity to moisture: moisture which enters the paste can degrade printability and promote solder balling. It has also been noted that water-soluble pastes typically have reduced tack times and may be less compatible with long reflow profiles. The lower level of activation associated with no-clean pastes may reduce the process window for full solder wetting of components.

The properties of six recent lead-free solder pastes will be described: three of them are water-soluble and three of them are no-clean. The characteristics of each paste will be reviewed. Then, printing performances will be evaluated through standardized laboratory tests such as viscosity, tackiness and slump and through tests in a printing machine. The reflow properties will be investigated through both standardized and production tests (hot slump, solderballing, wettability, reflow process window, graping ability). Finally, the cleaning ability will be assessed.

Experiments

The pastes used for this evaluation were all made of SnAg3Cu0.5 (SAC305) alloy with type 3 (25/45 microns, -325/+500 mesh) particle size. The selected water-soluble pastes are named A, B and C and the no-clean pastes are named D, E and F. The flux designation according to J-STD-004A and the metal content are gathered in the Table 1.

We ensured that all the pastes used for the study were recently manufactured (four weeks to eight weeks). Before starting the evaluation, the aspect and the viscosity of the pastes were checked in order to ensure that they were compliant with the initial specifications.

Table 1: Solder pastes characteristics

Paste	A	B	C	D	E	F
Nature	Water-soluble	Water-soluble	Water-soluble	No-clean	No-clean	No-clean
Alloy	SnAg3Cu0.5					
Particle size	Type 3					
Flux type	ORH0	ORH1	ORH1	ROL0	ROL0	ROL1
Metal Content	88.0	89.0	89.5	88.0	88.5	88.5

Acid index, non volatile residue and viscosity

The metal contents of the solder pastes (**MC**, expressed in percentage) and their non-volatile residues (**NVR**, expressed in percentage of the total flux medium) were measured although the ability of a solder paste residue to be cleaned is more linked to its quality than to its quantity. The acid index (**Ia**) was determined by acid-base titration.

The dynamic viscosity was determined using two types of viscometers: Brookfield and Malcom (Figure 1). The viscosity was first measured with a spindle type viscometer Brookfield DVII at 5 rotations per minute (RPM) using a TF spindle. Measures were made without mixing, and after mixing, at 20°C and 25°C according to the test method described in IPC-TM-650 method 2.4.34. The viscosity with a spiral pump viscometer Malcom PC1-TL was determined at 10RPM and 25°C. The results are listed in Table 2. The viscosity data are given in Pascal.second (Pa.s).

All the results were found in accordance with the initial specifications. The highest viscosity was found for paste C, which also had the highest metal content. The acid indexes of the water-soluble solder pastes were low compared to the ones of the no-clean pastes: a value of 5 was even found for paste B. The non volatile residues were a bit higher for water-soluble solder pastes than for no-clean ones.

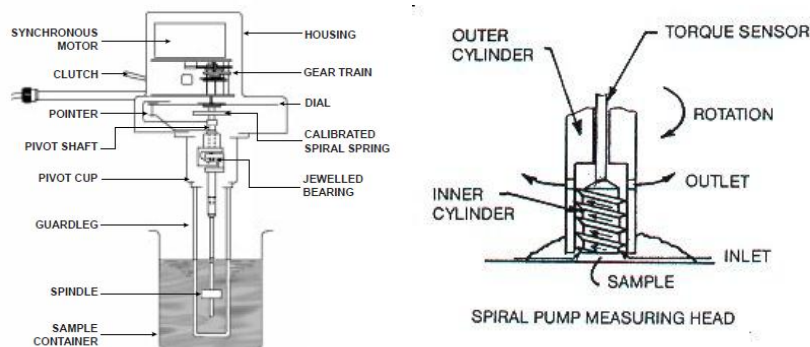


Figure 1. Schematic representation of a) Brookfield viscometer (source Brookfield) b) Malcom viscometer (source Malcomtech)

Table 2: Metal content, non volatile residue, acid index and viscosity measurements

Paste	A	B	C	D	E	F
MC measured	87.5	88.5	89.2	87.6	88.2	88.3
NVR (%)	61	72	86	53	66	63
Ia	55	5	67	105	112	130
Brookfield viscosity 20°C	1130 / 940	1010 / 920	1230 / 1160	950 / 880	1050 / 950	1060 / 930
Brookfield viscosity 25°C	1000 / 850	890 / 780	1120 / 1030	850 / 750	920 / 830	950 / 800
Malcom viscosity 25°C	205	165	180	150	175	170

Tackiness

The tackiness was assessed using our internal test which is designed to measure the tack force of a solder paste with an applied force of 1 g/mm² or 4g/mm²: low applied forces are more representative of the actual use of a solder paste at the pick and place step and allow a better tack force discrimination from one paste to another. The common standards measure the cohesion of a solder paste at higher forces, 15 g/mm² for IPC TM 650, method 2.4.44.

The measurements were performed at room temperature (21°C +/-3°C) and (50% +/-10%) relative humidity. The first measure was done after printing and the evolution of the tackiness was followed. The follow-up of tackiness with an applied force of 1 g/mm² according to time is presented as a graph and table attached in Figure 2. The low limit is 1 g/mm² (equal to the force applied). The pastes exhibit initial values between 1.2 (paste A) and 1.6 (paste F). All the pastes keep a tackiness above the limit for 24 hours except the paste C which adhesion starts to decrease between 8 and 18 hours. Internally, we have correlated the tackiness with the abandon time (idle time) on the stencil during printing: if a solder paste does not lose its tackiness for 24 hours during this test, the abandon time on the stencil is about 4 hours for 0.4mm pitch and 120µm stencil thickness at room temperature.

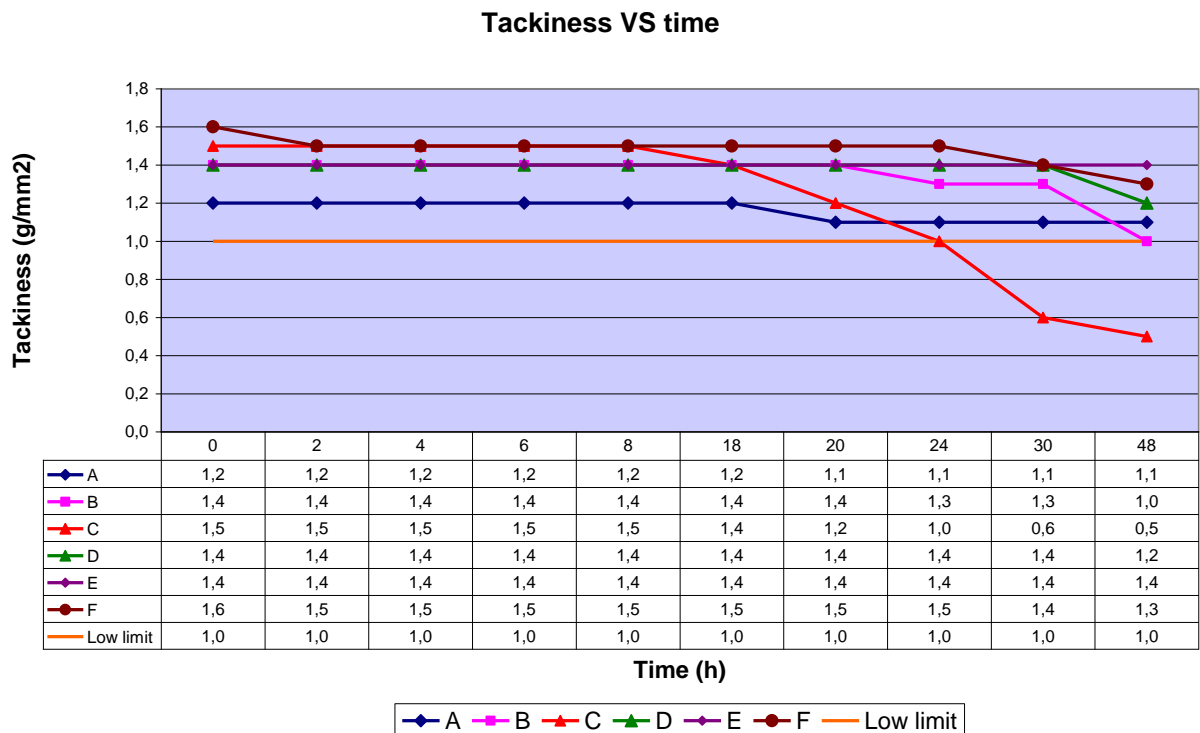


Figure 2. Tackiness versus time

Slump

The slump was tested according to IPC-TM-650 method 2.4.35. The pastes were printed on alumina substrates through the IPC-A21 0.2mm thick stencil (Figure 3).

For cold slump the substrates were observed after 10 to 20 minutes at ambient conditions (25 +/-5°C and 50+/-10% relative humidity): the minimum spacing at which the bridges are formed is noted. The paste shall show no evidence of bridging when spacing is 0.56mm or greater (for 0.63x2.03 pad size) and 0.25mm or greater (for 0.33x2.03 pad size) to conform to J-STD-005 paragraph 3.6.1.

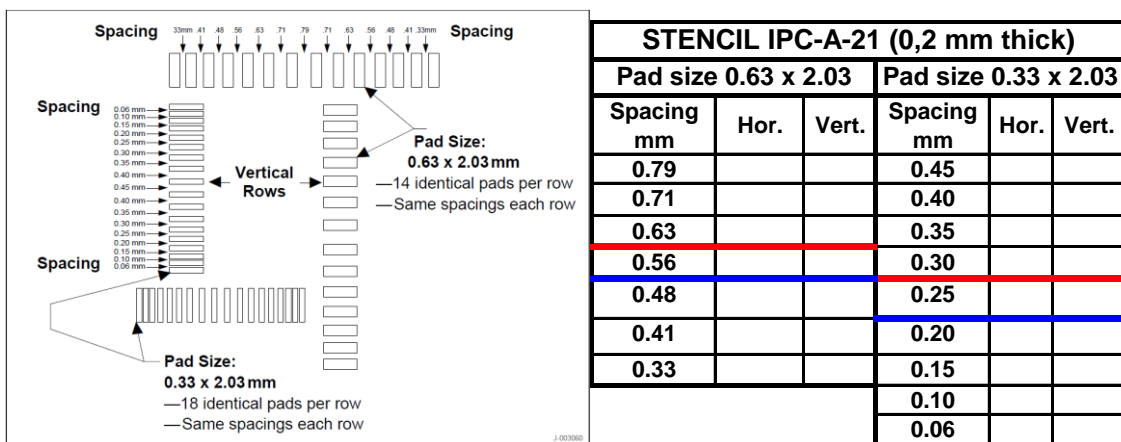


Figure 3. IPC A-21 stencil (extracted from IPC TM-650 2.4.35)

No bridge was seen on 0.63x2.03 pad size whatever the paste. Bridges with spacing of 0.06 to 0.10mm was observed for 0.33x2.03 pad size. None paste are prone to cold slump. Pastes A and C results are shown in Figure 4.

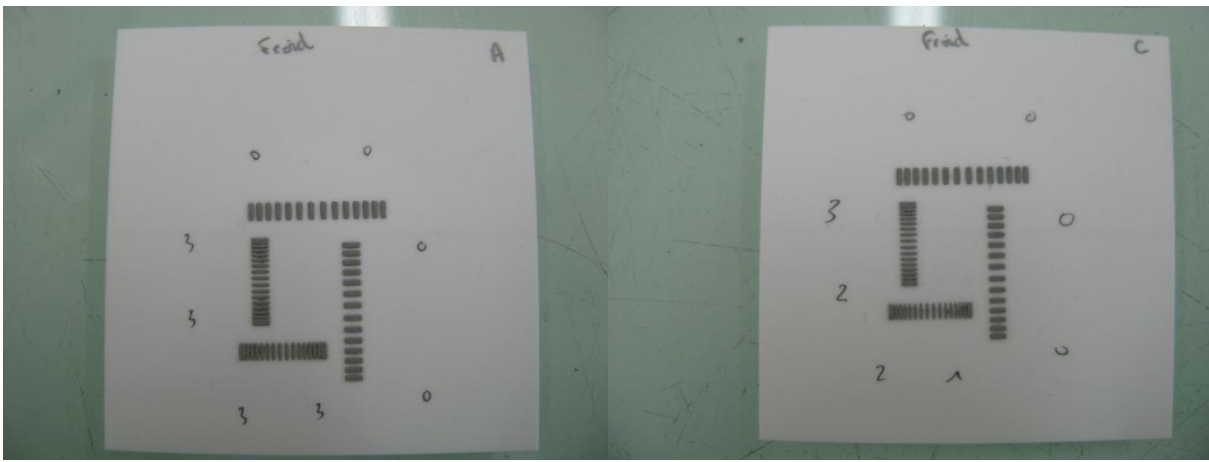


Figure 4. Cold slump a) Paste A, b) Paste C

For hot slump the substrates were observed after 10 to 15 minutes at 150°C preheating and cooling to ambient temperature. The paste shall show no evidence of bridging when spacing is 0.63mm or greater (0.63x2.03 pad size) and 0.30mm or greater (0.33x2.03 pad size) to conform to J-STD-005 paragraph 3.6.1. The general trend is to obtain better results with no-clean solder pastes than with water-soluble (WS) solder pastes: the no-clean are all below the limits. Among the WS, Paste A is more prone to slump than the other pastes and exceeds the limits. Because a quick preheat at 150°C does not really reflect the reality of a thermal profile, a slower preheat was evaluated: first, the substrate is placed on a hotplate at 100°C during one minute, then immediately on another hotplate at 140°C for one minute and finally on a hotplate at 160°C for one minute. The slump behavior was improved for all the pastes and only paste A was still above the limit. Pictures of pastes A and C are gathered in Table 3 and all the results are summarized in Figure 5 and 6.

Table 3. Paste A and C slump test

Image	Image	Image	Image
Paste A 150°C	Paste A 3x1 min	Paste C 150°C	Paste C 3x1 min

Slump 150°C and 3x1 min 100-140-160 for 0,63x2,03 pad size

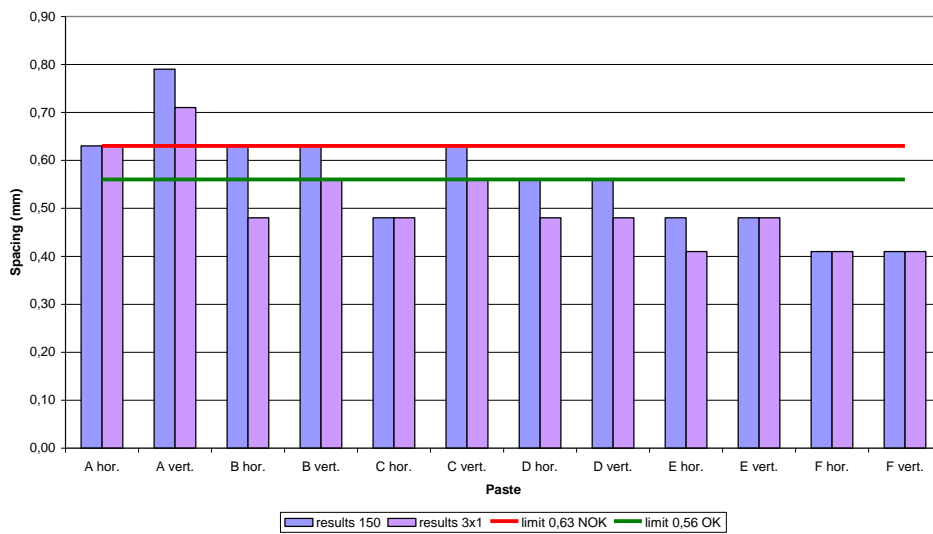


Figure 5.a) Slump for 0.63x2.03 Pad Size

Slump 150°C and 3x1 min 100-140-160 for 0,33x2,03 pad size

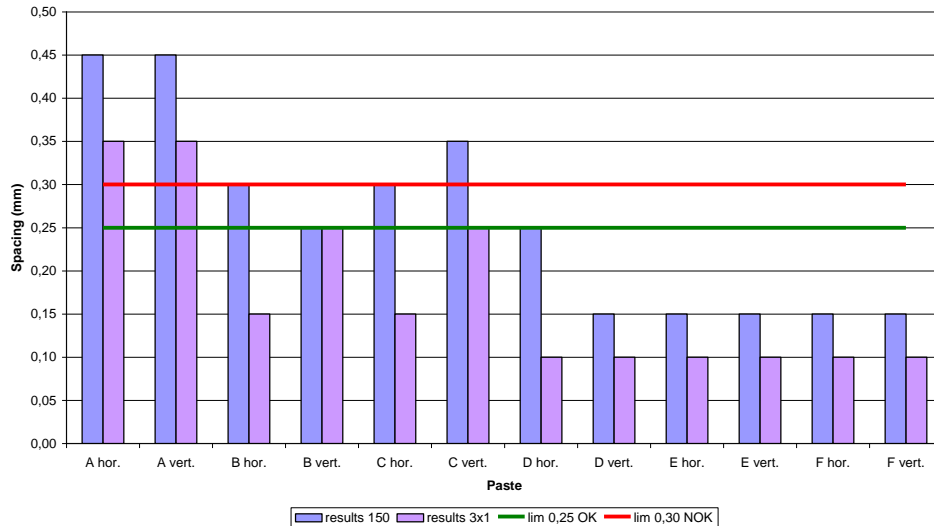






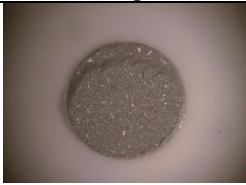

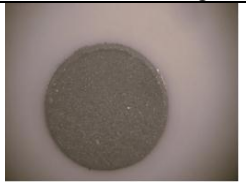

Figure 5.b) Slump for 0.33x2.03 Pad Size

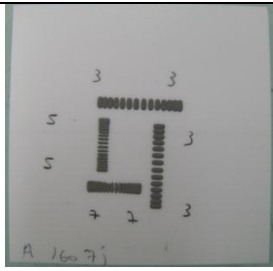
The last revision of IPC-TM-650 method 2.4.35 procedure mentions a change in the preheat temperature: the samples shall be tested at a temperature of 35 ° C below the melting point which means 180°C for SAC 305 solder pastes. The test was performed at 180°C: A, B, C and D were above the defined criteria.

Stability at elevated temperature

The stability of the paste being part of its reliability, the influence of storage at elevated temperature was examined: the pastes were stored at 40°C and checked after four days and seven days. A decantation phenomenon occurred for paste A after four days: after mixing many lumps were found in the paste. Paste C surface looked dry and dull after seven days but resumed its shiny appearance after mixing. The other pastes did not exhibit any change. A simple printability test was done: the pastes were printed on an alumina substrate using a 0.250mm thick stencil with round openings of 5mm diameter. Only paste A was difficult to print correctly, resulting in a non-planar surface. The tackiness was also measured on each paste after seven days. Paste A showed a higher tackiness but the decrease was fast: it lost completely its tackiness after eight hours. There was no significant change for the other pastes neither in value nor in duration. Slump trials showed an “improvement” for paste A at 150°C but no change for pastes B, C, D, E and F. The modification of paste A properties is due to an internal reaction due to the exposure to temperature: this paste is sensitive to temperature. Pictures and results are given in the Table 4 for paste A, B, C and E.

Table 4. pastes A, B, C, E after 7 days at 40°C

	Paste A	Paste B	Paste C	Paste E
Appearance after 7 days 40°	 Decantation lumps	 OK	 Dull OK after stirring	 OK
Printability After 7 days 40°C	 Bad	 Good	 Good	 Good
Tack T0 before storage	1.2	1.4	1.5	1.4
Tackiness T0 After 7 days 40°C	1.8	1.5	1.5	1.5
Tack 8h before storage	1.2	1.4	1.6	1.4
	Paste A	Paste B	Paste C	Paste E

Tack 8h after 7 days 40°C	0.5	1.4	1.5	1.4
Slump after 7 days 40°C	 0.48 Hor. and Vert. 0.30 Hor. 0.40 Vert	x	x	x

Viscosity over time

A more drastic viscosity test was done on each solder paste: the test consists in the follow-up of viscosity over time using a Malcom spiral pump viscometer at 25°C and 10RPM. The test simulates solder paste ageing when it is submitted to a permanent mixing and reproduces the shearing it undergoes during printing. The measure of viscosity evolution versus time during the stirring allows predicting the premature solder paste ageing by correlation.

A stable paste keeps a constant viscosity over time (figure 6.a). On the contrary, an unstable paste leads to a sudden increase of viscosity after a few hours only (figure 6.b). The overall appearance of the curve gives additional indications of the paste behavior.

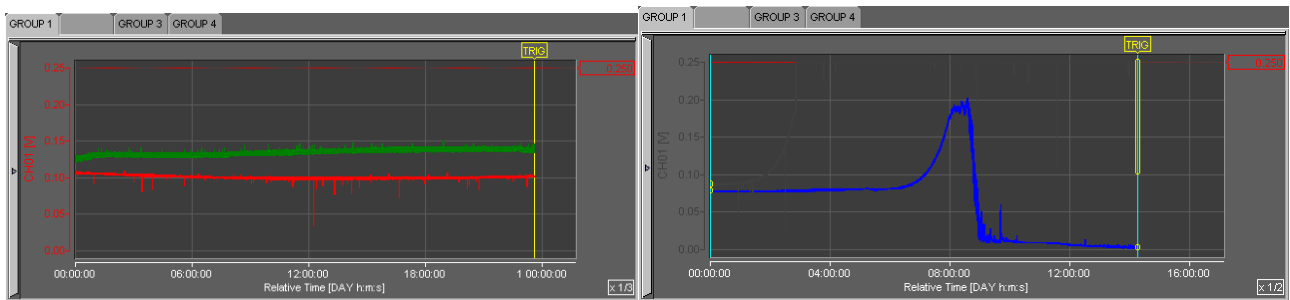


Figure 6. a) Stable viscosity, b) Sudden increase of viscosity after 7 hours

The viscosity curves as a function of time were summarized in the same file (Figure 7). No sudden increase was seen. However, pastes A viscosity increased during the three first hours before decreasing. Pastes A and C curves are irregular while B, D, E and F curves are smoother. According to these results, it is likely that A and C have a lower printability performance.

Viscosity over time

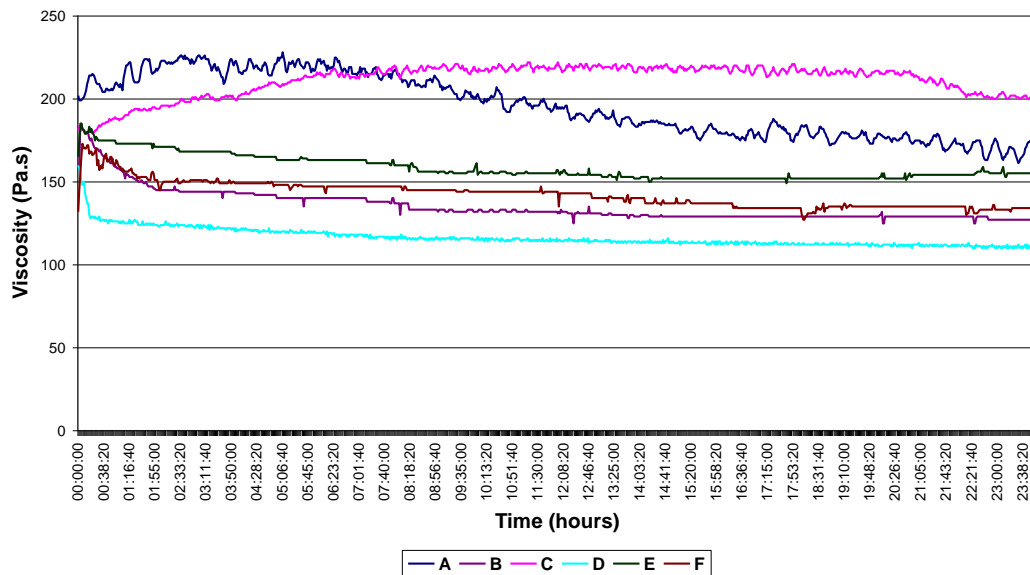


Figure 7. Viscosity curves over time

Printing performance

Printing tests were performed at 25°C in a Dek Horizon 05 printer using the Efsot Verification board [1] with a 120 microns laser cut stainless steel stencil and 250mm length squeegees. The test board includes a printing pattern test area (horizontal and vertical), 0.4mm pitch QFN, 0402 and 0201 printing areas (Figure 8). The minimum pressure according to printing speed was determined (Table 5, Figure 9). Paste C requires much more pressure than the other pastes and is not able to stand high printing speeds (Figure 10).

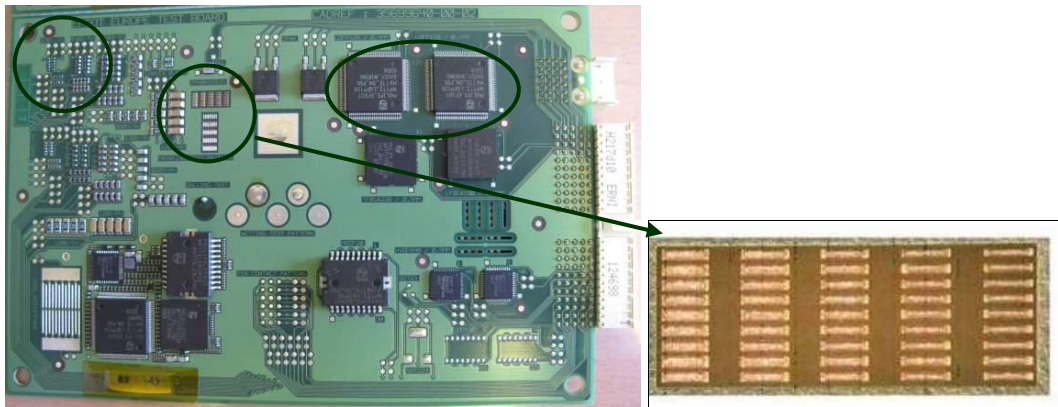


Figure 8. a) Efsot Verification Board b) Detail of printing pattern

Table 5. Printing pressure according to speed

	A	B	C	D	E	F
Speed	Pressure	Pressure	Pressure	Pressure	Pressure	Pressure
30	3	2	5	2	2	3
50	5	3	6	3	3	4
80	6	4,5	9	3,5	4	6
100	8	6	11	4,5	5	7
120	9	7	13	6	6	8
150	10	8	16	6,5	7	9

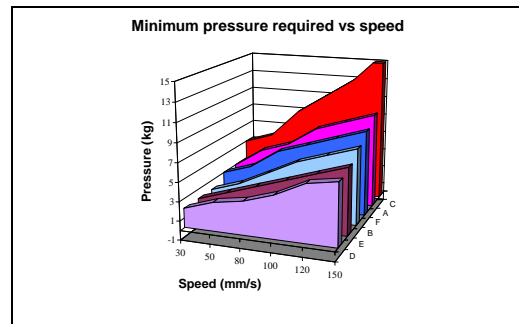


Figure 9. Graph of pressure according to speed

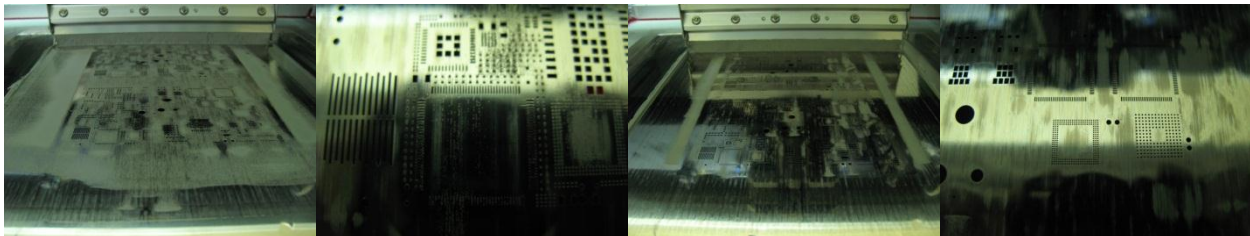
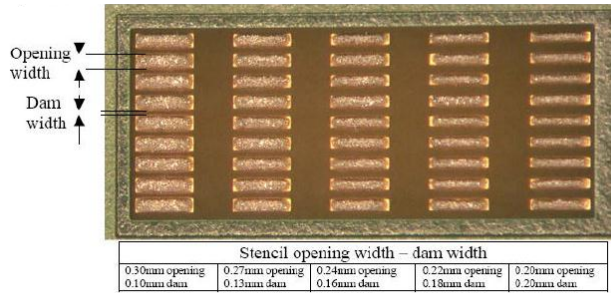


Figure 10. a) and b) Insufficient pressure, c) and d) Minimum pressure

The printing quality was assessed mainly on the printing test patterns using criteria according to Philips Notation [1]: the results are rejected if the smearing result is below or equal to 2 on 0,27mm opening width and 0,13 space width or if the printing result is below or equal to 2 on 0,22/0,18: under stencil cleaning is then required. The details to assess printing quality are explained in Figure 11 and Figure 12.

<= <= <= Dam width decreases: more shorts <= <= <=



=> => => Opening width decreases: less transfer => => =>

Figure 11. Printing pattern opening width and dam description

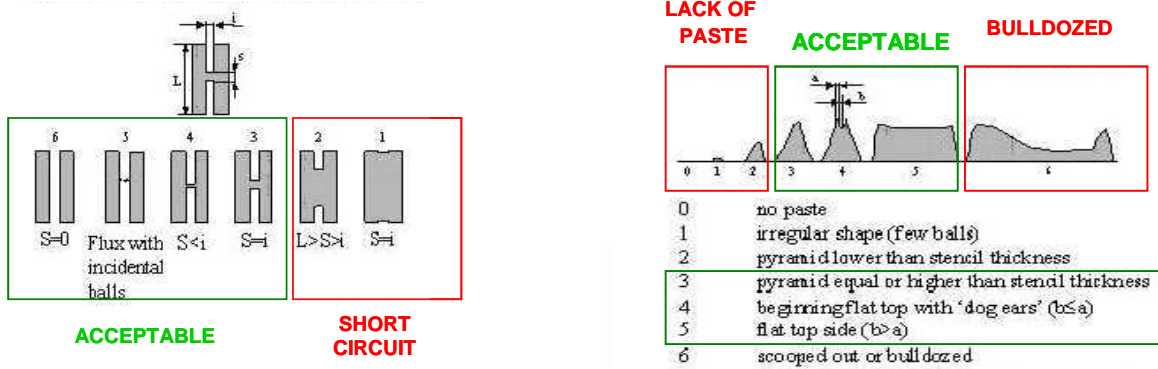


Figure 12.

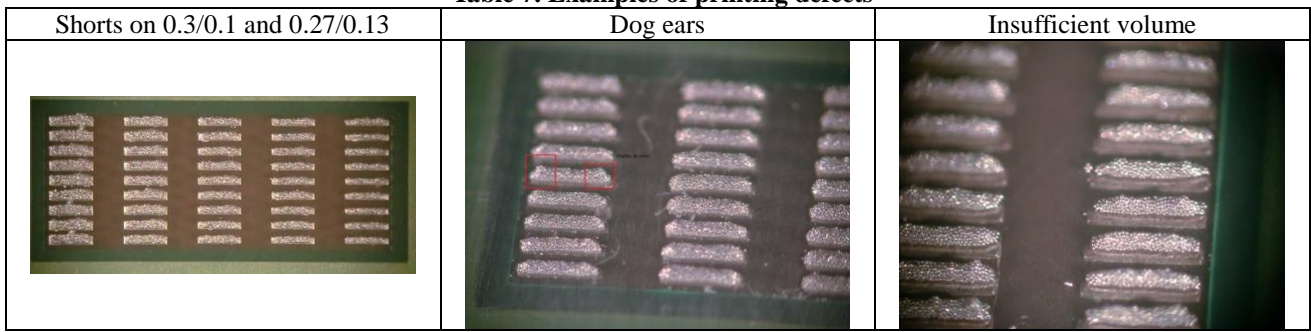
12.a) Evaluation criterion for smearing / shorts

12.b) Evaluation criterion for printing definition

The printing definition and the smearing ability were evaluated for each solder paste at a medium speed of 50mm/s. The pressure applied is the minimum pressure determined before plus one bar additional. The first board is printed and the quality is visually inspected, then, without any cleaning, a second board is printed, etc, until the criteria are reached. The table 6 shows the example of pastes C and F. For shorts, paste C reached the criterion after thirteen (13) prints and paste F reached this criterion after fifteen (15) prints. Printing definition was better for paste F too: sixteen (16) prints against fourteen (14) prints. The detailed table for A, B, D and E is not reported. B, D and E were almost similar to F whereas A was below. The final ranking was, from the best to the worst: F, E, B, D, A and C. Examples of printing defects are illustrated in Table 7.

Table 6. Pastes C and F printing quality

Board Number	Pad width/Pad distance perpendicular to print 120µm stencil																				
	0,3/0,1 - C		0,3/0,1 - F		0,27/0,13 - C		0,27/0,13 - F		0,24/0,16 - C		0,24/0,16 - F		0,22/0,18 - C		0,22/0,18 - F		0,2/0,2 - C		0,2/0,2 - F		
	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	Print definition	Shorts	
1	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	
2	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	
3	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	5	6	
4	5	5	5	5	5	6	5	6	4	6	4	6	5	6	5	6	5	6	5	6	
5	5	5	5	5	5	6	5	6	4	6	4	6	5	6	5	6	4	6	4	6	
6	5	4	5	4	5	6	5	6	4	6	4	6	4	6	4	6	3	6	4	6	
7	5	4	5	4	5	6	5	6	4	6	4	6	4	6	4	6	3	6	4	6	
8	5	4	5	4	5	5	5	5	4	6	4	6	4	6	4	6	3	6	4	6	
9	5	3	5	4	5	5	5	5	4	6	4	6	3	6	4	6	3	6	4	6	
10	5	3	5	4	5	5	5	5	4	6	4	6	3	6	4	6	3	6	3	6	
11	4	3	4	3	5	4	5	4	4	6	4	6	3	6	3	6	3	6	3	6	
12	4	3	4	3	4	4	4	4	4	6	4	6	3	6	3	6	3	6	3	6	
13	4	2	4	3	4	3	4	4	4	6	4	6	3	6	3	6	2	6	3	6	
14	4	2	4	3	4	2	4	4	4	5	4	6	3	6	3	6	2	6	3	6	
15	4	2	4	2	4	2	4	3	4	5	4	6	2	6	3	6	2	6	3	6	
16	4	2	4	2	4	2	4	2	4	5	4	6	2	6	3	6	2	6	2	6	
17	4	2	4	2	4	2	4	2	4	4	5	4	5	2	6	2	6	2	6	2	6

Table 7. Examples of printing defects

The idle time was determined: it is defined as the maximum time allowed for the paste to remain on the stencil for a good restart without the need of under-stencil cleaning. The same criteria were used: paste E showed the best idle time (3h30) followed by F and D, then A and B, then C (1h30). Results are summarized in Table 8.

Table 8. Idle time

Paste	A	B	C	D	E	F
Maximum abandon time (idle time)	2h	2h	1h30	3h	3h30	3h

Paste ageing under shearing was assessed: 600 printing cycles without paste consumption at 50mm/s were made. All the pastes still looked smooth after the test, so the Brookfield viscosity at 20°C was measured: a decrease was observed due to the shearing for all the pastes (Table 9).

Table 9. Viscosity after cycling test

Paste	A	B	C	D	E	F
Initial viscosity	940	920	1160	880	950	930
Viscosity after cycling	720	800	1050	690	810	830

Solderballing

Solderballing performances were checked on a hotplate using our internal procedure. The pastes are printed on alumina substrates through a 0.250mm thick stencil with two round opening of 5mm diameter, with a distance between centers of 25mm. The temperature of the hotplate was set at 250°C and several temperatures and times of preheat were tested. The goal was to classify the paste according to preheat. The solderballing classification ranks from class 1 to class 5, the balls being counted with 30x magnification (Table 10).

Table 10. Solderballing classification (NF-C-90550)

Class 1	Class 2	Class 3	Class 4	Class 5
5 solderballs maximum	6 - 10 solderballs	11 - 20 solderballs	21 - 50 with possibility of a slight lisere	> 50 solderballs with clusters and lisere

Solderballing was class 5 for paste B without preheat. Otherwise, the pastes gave good results whatever the preheat, except for the most demanding condition (180°C 2 during 2 minutes) where solderballing ranked from class 2 to class 5. After four hours at ambient conditions (21°C / 50%RH) pastes A and B have exploded upon contact with the hotplate and a significant degradation occurred for B and C after 2 minutes at 160°C, respectively class 4 and class 5 instead of class 1 for both initially. The summary is presented in Table 11 and some pictures in Figure 13.

Table 11. Solderballing Test

Paste	A	B	C	D	E	F
Solderballing on fresh paste						
No preheat	C1	C5	C1	C1	C1	C1
160°C 2 min	C2	C1	C1	C1	C1	C1
140°C 2 min	C1	C1	C1	C1	C1	C1
100°C 3 min	C1	C1	C1	C1	C1	C1
100-140-160 1min/1min/1min	C1	C1	C1	C1	C1	C1
180°C 2min	C4	C3	C5	C3	C2	C2
Solderballing after 4 hours at 21°C / 50%RH						
No preheat	explosion	explosion	C1	C1	C1	C1
160°C 2 min	C1	C4	C5	C1	C1	C1
140°C 2 min	C1	C1	C1	C1	C1	C1
100°C 3 min	C1	C1	C1	C2	C1	C1
100-140-160 1min/1min/1min	C1	C2	C3	C1	C1	C1
180°C 2min	C5	C4	C5	C4	C2	C2

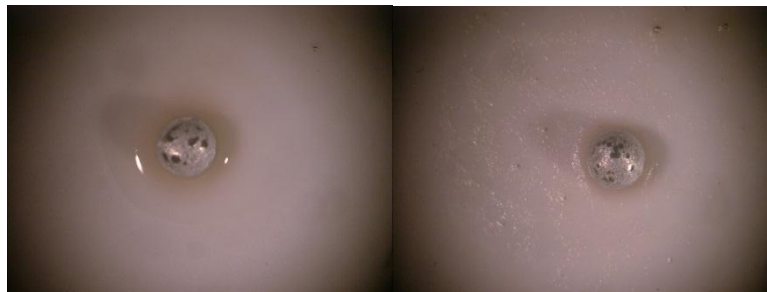


Figure 13. a) Class 1 b) Class 4



Figure 13. c) A, B, C without preheat after 4 h ambient temperature d) Explosion

Discussion

After checking the initial properties of the pastes, which were all in their specification in terms of metal content and viscosity, several tests were done to evaluate their printing performance. In terms of viscosity, spiral pump type viscometer results and spindle type viscometer results showed the same tendency, except for paste A and C. These two pastes also had a different behavior and a different curve shape, compared to B, D, E and F as far as viscosity according to time was concerned. Paste C was far the worst in terms of high printing speed ability. Regarding tackiness, adhesion of paste C started to decrease before the other pastes, the idle time was also the lowest. Hot slump was generally worse for the WS pastes than for the no-clean pastes. Paste A was extremely sensitive to storage at 40°C and lost its printing properties after four days only. The printing definition as well as the anti-bridging ability all along the prints was acceptable for all the pastes and, although C and A ranked last, the difference was not significant enough to draw any conclusion. The exposure to ambient conditions (21°C, 50%RH) between printing and reflow led to a degradation of solderballing performance for all the water-soluble solder pastes whereas the no-clean pastes were not affected at all.

Conclusion

The purpose of the paper was to highlight the reliability differences between water-soluble and no-clean solder pastes to guide users in their choice. To achieve this goal, six lead-free pastes were extensively studied, three being water-soluble and three being no-clean. The first part of the study focused on printing performance. The pastes were characterized using standardized tests and internally developed tests: dynamic viscosity, tackiness, slump and solderballing. The influence of accelerated storage at elevated temperature, the influence of time and conditions between printing and reflow and the influence of continuous shear according to time were shown.

The printing performances were also evaluated in a printer. Although the number of pastes studied was restricted, the water-soluble pastes generally yielded results below the no-clean pastes with sensitivity to temperature and humidity, a tendency to slump during preheat and a narrower printing window. Water-soluble solder pastes must be stored, handled and used with more caution before reflow.

In the second part of the paper, the reflow properties will be compared: wettability, reflow process window, anti-graping properties. Finally the residue cleanability with water, then with water and detergents will be examined. The cleanliness will be assessed using visual inspection, ionic contamination and surface insulation resistance tests.

References

[1] EFSOT Project