ROBUST SMT NO-CLEAN SOLDER PASTE FOR SIP AND 01005 ASSEMBLY

Ning-Cheng Lee
Indium Corporation
nclee@indium.com

ABSTRACT

For SiP or SMT assembly process, solder paste has been the choice of primary soldering material. In the meantime, miniaturization has been the trend of electronic industry. While the size of components, pads, stencil thickness, aperture, pitch, and solder powder has been shrinking continuously so far, it is about time to ask whether the solder paste technology is able to support this trend forever. In this study, solder powder oxygen content was observed to increase linearly with increasing powder surface area up to Type 5. Beyond Type 5, it is getting difficult to maintain oxide thickness. Beyond Type 8, the oxide thickness always higher than Type 5 or coarser. The flux burn-off rate increased linearly with decreasing flux size plotted in log scale. However, for solder paste, the paste residue showed a sharp drop initially with decreasing flux quantity, then levelled off at 3 mg flux (~30 mg paste), and maintained at around 30% residue through the remaining range down to 0.3 mg flux (~3 mg paste). The constant residue level at small sample size was attributed to the surface adsorption phenomenon, or "Flux Shell" phenomenon, where a layer of flux was strongly adsorbed on the solder powder surface. For solder paste, the flux workload increased rapidly with decreasing powder size. The flux capacity needed in removing oxide was derived as volume fraction of COOH functional group in flux residue, with 10% maximum being set as a guideline for no-clean applications. Type 8 paste may be the limit of SiP or SMT printable no-clean solder paste due to corrosivity consideration. Oxygen barrier and alloy dopants may expand the miniaturization potential. When reviewing the brittleness of solder joint formed, Type 6 may be the limit of fine pitch applications. Beyond that, the joints may be too brittle to be reliable, unless underfill is applied.

Key words: solder paste, miniaturization, SMT, miniaturization, Limitation

I. INTRODUCTION

For SiP or SMT assembly process, solder paste has been the choice of primary soldering material. In the meantime, miniaturization has been the trend of electronic industry. While the size of components, pads, stencil thickness and aperture, pitch, and solder powder has been shrinking continuously so far, it is about time to ask whether the solder paste technology is able to support this trend forever. And, if not, when the solder paste technology may come to the end? In this study, the effect of solder powder size, flux chemistry, stencil aperture, stencil surface technology, printing technology, reflow process, reflow atmosphere, and intermetallic thickness were investigated. The data will be presented and discussed. The results indicate that 0.1 mm pitch and type 6 or 7 powder may be the limit of solder paste technology for supporting SiP or SMT assembly process. Beyond that, an alternative bonding technology should be needed to continue to support further miniaturization trend.

II. POWDER SIZE

With miniaturization trend, both pitch and stencil aperture sizes reduce rapidly. It has been reported that the solder powder size shall not be greater than 1/7 of the aperture width, if the print defect rate is to be kept below 0.1%, as shown in Figure 1 [1].

Recent advancement in the nano-coating on stencil allowed a chance for better stencil release, thus promised successful print with a coarser powder. The effect on transfer efficiency has been reported ranging from a 14% decrease to a 30% increase [2,3]. Due to the wide variation in industry experience, the 1/7 rule is still a valid guideline overall.

On the other hand, Table 1 shows the relation between powder type, particle size distribution (PSD), median dimension, and powder surface area per gram.
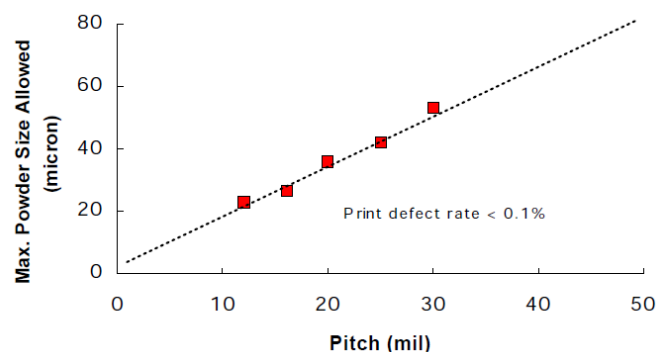

Figure 1. Relation between pitch dimension and maximum powder size allowed [1].

Table 1. Powder size and surface area of various powder type.

Type	PSD (μ)	Median D (μ)	Surface area (cm²/g)
2	45-75	60	11
3	20-45	32.5	21
4	20-38	29	23
5	15-25	20	34
6	5-15	10	68
7	2-11	6.5	104
8	2-8	5	135
9	1-5	3	225

For designs where aperture size being one half of the pitch dimension, the relation between pitch dimension, type of powder allowed, and the powder surface area is shown in Figure 2.
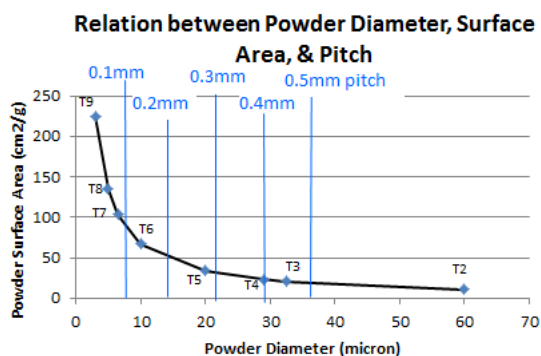

Figure 2. Relation between powder diameter, type of powder, powder surface area, and pitch dimension.

POWDER OXIDE THICKNESS
In Figure 2, the surface area of solder powder was calculated as a function of solder powder size, and the surface area increases rapidly at powder size finer than Type 5. Since the solder oxide is expected to increase with increasing surface area, the work load of flux definitely becomes higher with finer powder. Figure 3 showed the oxygen content as a function of powder surface area for SAC305 solder alloy, where only the lowest oxygen content data for Type 6 and Type 7 were plotted. For Type 2 to Type 5, the oxygen content was very consistent from lot to lot. It is interesting to note that a linear relationship was observed, reflecting oxygen content increased linearly with increasing surface area, or the thickness of the oxide layer on solder powder was constant.
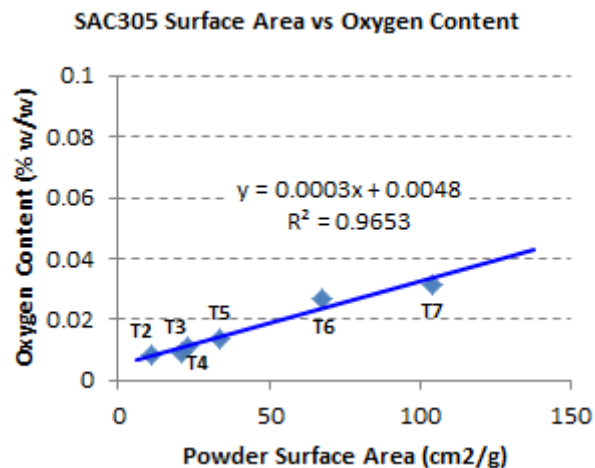

Figure 3. Oxygen content of SAC305 solder powder as a function of surface area, where only the lowest oxygen content data were plotted.
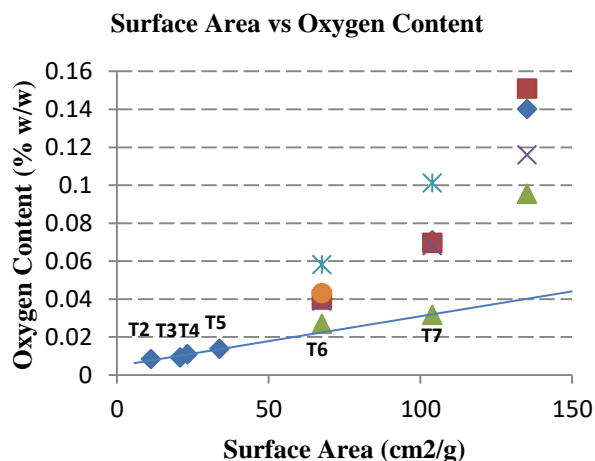

Figure 4. Oxygen content of SAC305 solder powder as a function of surface area, with all data points being plotted.

However, when all of the data points were plotted, the linear relation maintained for powder down to Type 5 only. For powder finer than Type 5, the majority of the data points were above the linear line, as shown in Figure 4. The higher oxygen content observed for most lots of Type 6, 7, and 8 indicated the challenge of maintaining a fixed oxide layer thickness for very fine powder. This challenge appeared to be greater for finer powder, and zero lot of Type 8 powder could be made with the same oxide layer thickness as Type 5 or coarser powder. In other words, the flux work load was linearly proportional to powder surface area until Type 5. Beyond that, the flux work load got higher than what reflected by surface area, supposedly due to formation of a thicker oxide layer for powder finer than Type 5.

NON-PROPORTIONAL MINIATURIZATION
The rapid rise in powder surface area and oxide layer thickness with reducing powder diameter bring up the concern about fluxing capacity being sufficient or not. This concern is further aggravated by considering the non-

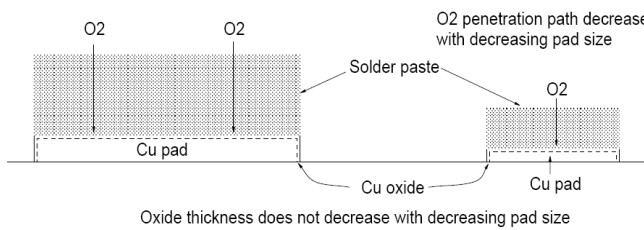proportional miniaturization. Figure 5 shows schematic diagram of solder paste printed on pads.

Figure 5. Schematic diagram of solder paste printed on pads for coarse and fine pitch.

With miniaturization, the paste volume printed is expected to reduce with decreasing pitch dimension, or decreasing pad size. However, in general, the oxide thickness of metal does not decrease with decreasing pad size or powder size. In the case of fine powder, the oxide layer thickness may even increase, as shown in Figure 4. In other words, when the flux volume decreases in proportion to the pad size, the work load of flux increases for finer pitch applications.

Furthermore, at a smaller paste deposit, the oxygen penetration occurred more readily, and the metal surface of both pad and solder powder can be oxidized more easily. This results in a further increase in the work load of flux.

FLUX BURN-OFF
The concern on fluxing capacity induced by oxide thickness and oxygen penetration is further aggravated by flux burn-off phenomenon.
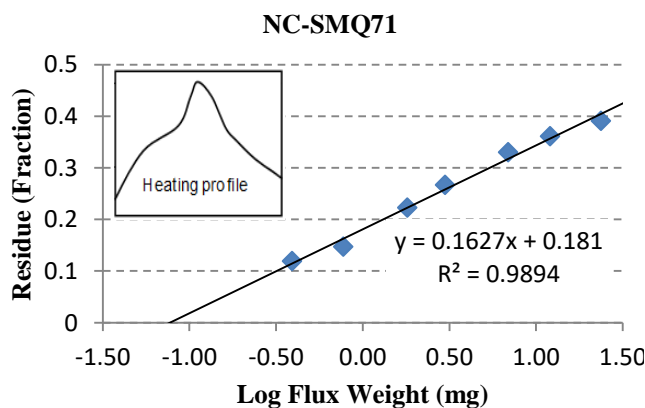

Figure 6. Flux residue amount as a function of flux deposit size in log scale for low residue flux NC-SMQ71.
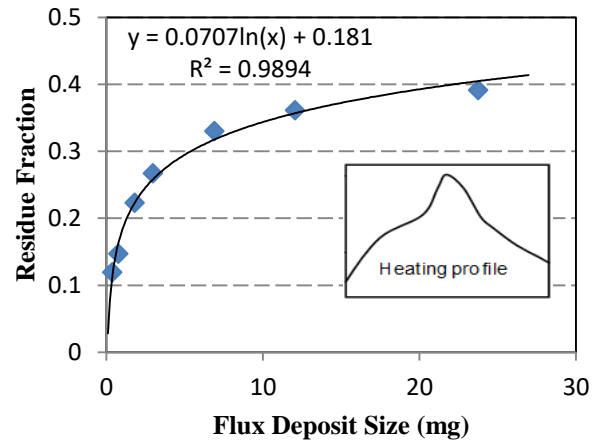

Figure 7. Flux residue amount as a function of flux deposit size in linear scale for low residue flux NC-SMQ71.

Figure 6 and 7 shows the residue level of the low residue flux NC-SMQ71 decreased with decreasing flux NC-SMQ71 quantity when reflowed with a typical heating profile, as determined with a thermal gravimetric analyzer (TGA). In other words, the flux amount remaining on the board at reflow to remove the oxide reduced rapidly with reducing flux deposit size. This increasing burn-off rate was caused by a greater surface area per unit flux volume for a smaller deposit.

Similar behavior was also observed for medium residue type flux 8.9HF when plotted in log scale and linear scale, as shown in Figure 8 and 9, respectively.
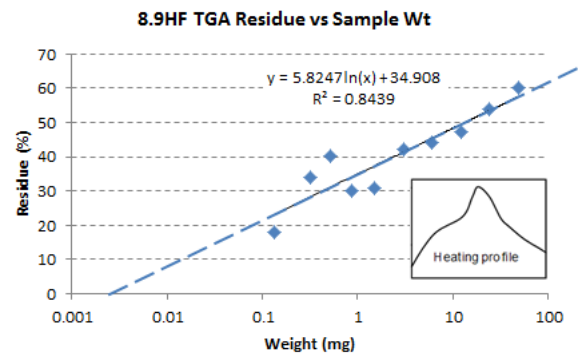

Figure 8. Flux residue amount as a function of flux deposit size in log scale for low residue flux NC-SMQ71.

8.9HF

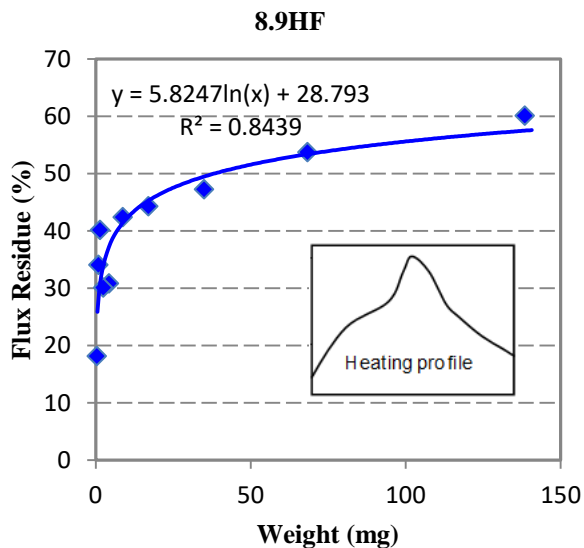$$y = 5.8247\ln(x) + 28.793$$
$$R^2 = 0.8439$$

Figure 9. Flux residue amount as a function of flux deposit size for medium residue flux 8.9HF.

HOW ABOUT PASTE BURN-OFF?
For the flux deposit size involved in Figure 6 and 7, its volume and print dimension can be calculated with the flux density being approximated as 1 g/cm^3. For printable solder paste to be deposited using the same amount of flux, the paste volume will be about 2 times of flux volume. The maximum powder size allowed can be calculated using a simple square block shape for paste deposition, with dimension ratio 1 (thickness) x 3 (width) x 3 (length), as shown in Figure 8. By applying the 1/7 rule reported [1], the corresponding maximum powder size allowed can be calculated with equation shown below, and the result is shown in Figure 9.
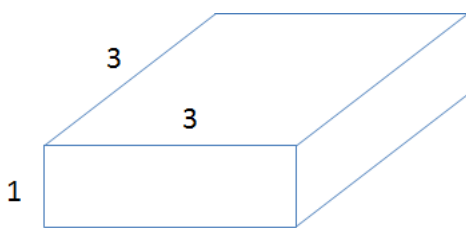
Area ratio = 3x3/(1x3x4) = 0.75

Figure 10. Schematic of solder paste printed from aperture with area ratio 0.75.

The paste volume V_P can be calculated from flux weight W_F

$$V_P \text{ (cm}^3) = W_F \text{ (mg)} \times 0.001\text{g/mg} \times 1\text{cm}^3\text{/g} \times 2 \text{ (paste volume/flux volume)}$$

Assuming flux burn-off rate for the same volume of flux is identical, whether as flux or as paste. For paste printed as 1x3x3 square block, the block width D_P can be calculated as below

$$D_P \text{ (}\mu\text{)} = [V_P \text{ (cm}^3) /9\text{(cm}^2)]^{1/3} \times 3 \times (10000 \ \mu\text{/cm})$$

$$= [(W_F \text{ (mg)} \times 0.001\text{g/mg} \times 1\text{cm}^3\text{/g} \times 2 \text{ (paste volume/flux volume))} / 9\text{(cm}^2)]^{1/3} \times 3 \times (10000 \ \mu\text{/cm})$$

Thus, the maximum powder size allowed = D_P (μ) x 1/7

Figure 11 shows the calculated flux residue fraction versus maximum powder size allowed for solder paste using low residue flux NC-SMQ71 with 90% SAC305.
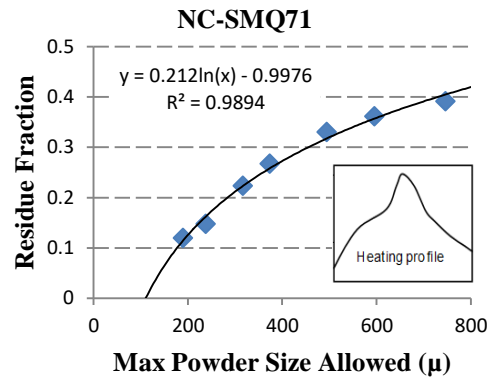
NC-SMQ71

$$y = 0.212\ln(x) - 0.9976$$
$$R^2 = 0.9894$$

Figure 11. Calculated flux residue fraction versus maximum powder size allowed for solder paste using flux NC-SMQ71.

This calculation showed that all flux will be burnt-off for solder paste deposit size around 700μ, or a maximum powder size allowed being ca. 100μ based on the 1/7 rule. This is incorrect, since many small discrete were successfully assembled with paste deposit sizes down to 200μ or smaller.

Similar poor correlation was also observed for paste using medium residue flux 8.9HF, as shown in Figure 12.

8.9HF

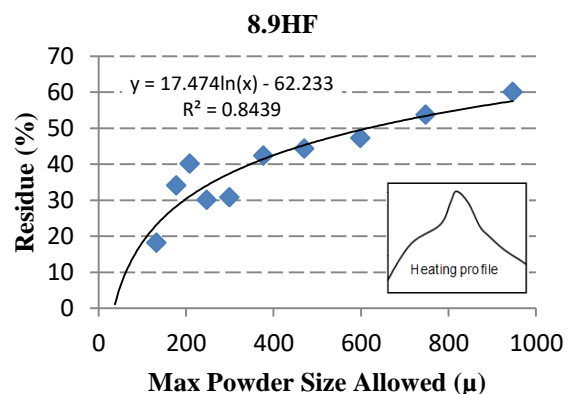$$y = 17.474\ln(x) - 62.233$$
$$R^2 = 0.8439$$

Figure 12. Flux amount remaining on the board at reflow decreased with reducing flux deposit size for medium residue flux 8.9HF.

PASTE VS FLUX BURN-OFF
Apparently the paste burn-off did not follow the same behavior as that of flux.

The flux burn-off behavior was investigated by comparing flux and paste containing approximately the same amount of flux 8.9HF, as shown in Table 2 and Figure 13.

Table 2. 8.9HF samples used in flux burn-off study. The weight of paste was ca. 10X of flux.

Flux (mg)	Flux residue (%)	Paste (mg)	Paste residue (%)
0.33	21.56	2.87	31.7
1.00	26.72	10.59	27.8
3.23	35.95	30.51	32.2
10.49	49.12	102.64	55.0

Note: (1) 8.9HF with 90% SAC305, Type 4 powder, (2)

The paste residue (%) refers to that of flux in paste.

The flux burn-off behavior of solder paste and flux alone followed two distinctively different trends, as shown in Figure 13. The flux residue decreased linearly with decreasing flux quantity in log scale, similar to that in Figure 6 and 8. The paste residue showed a sharp drop initially with decreasing flux quantity, then levelled off at 3 mg flux (~30 mg paste), and maintained at around 30% residue through the remaining range down to 0.3 mg flux (~3 mg paste).
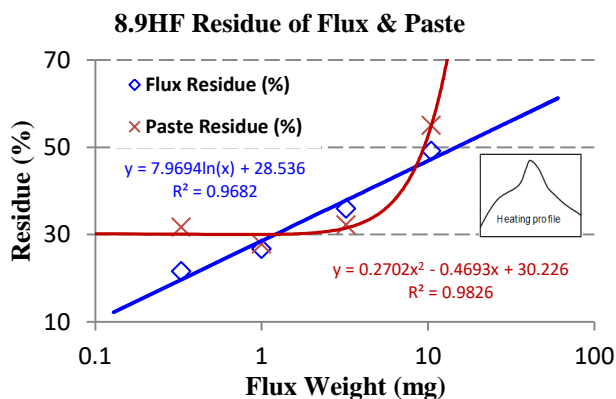

Figure 13. 8.9HF flux residue of flux or solder paste when determined at flux weight ranging from 0.3 to 10 mg (paste weight 3 to 100 mg, with 10% flux content).

For solder paste, the constant residue level at small sample size was attributed to the surface adsorption phenomenon, or "Flux Shell" phenomenon, where a layer of flux was strongly adsorbed on the solder powder surface.

Therefore, upon reflow, at paste sample size above 30 mg, the flux burn-off increased with decreasing sample size, driven by the increasing paste surface area per unit volume. This increasing burn-off trend continued until it reached the Flux Shell, and further increase in paste surface area per unit volume did not help in removing this Flux Shell, as illustrated in Figure 14.
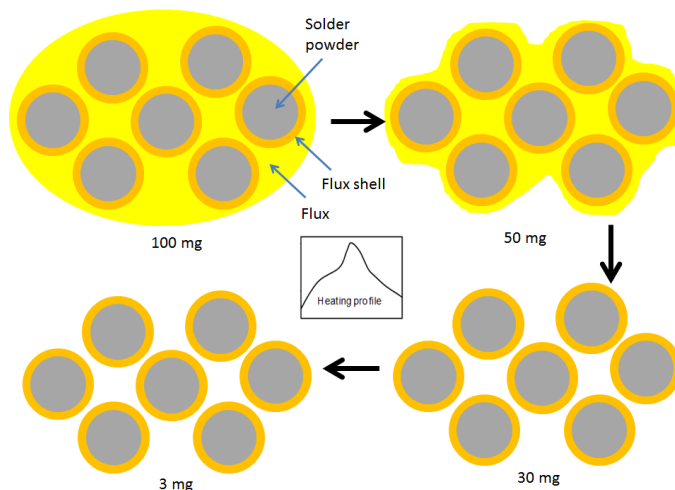

Figure 14. Flux burn-off process of solder paste from large to small paste volume.

On the other hand, for flux alone situation, the burn-off rate increased continuously with increasing surface area per unit volume of flux, as shown in Figure 6 and 8.

III. FLUX WORKLOAD

With reducing deposit size, as reflected by the maximum powder size allowed, the projected minimum powder oxygen content and residue amount can be plotted on the same graph for 8.9HF, as shown in Figure 15.
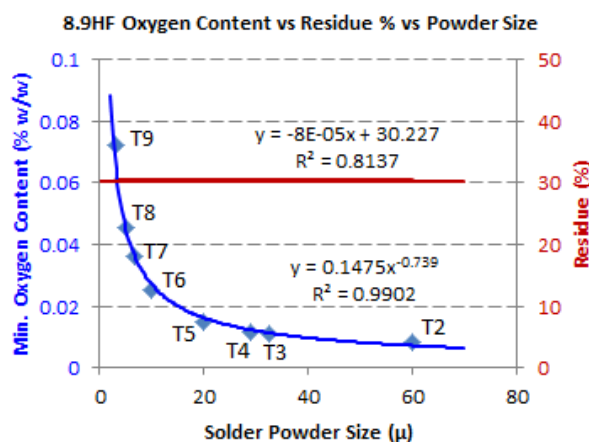

Figure 15. Powder oxygen content and flux residue as a function of deposit size, as reflected by the maximum powder size allowed, for paste using medium residue flux 8.9HF with 90% metal load.

For the part of flux burnt off, its contribution to fluxing is negligible, and mainly the flux remaining on the board contributes to the oxide removal. The flux remaining on the board can be measured by the residue amount.

The workload of flux on oxide removal can be calculated by dividing the oxygen content by the residue amount for various type of powder, as shown in Figure 16. Here the workload was normalized, with that of Type 2 being set as 1.
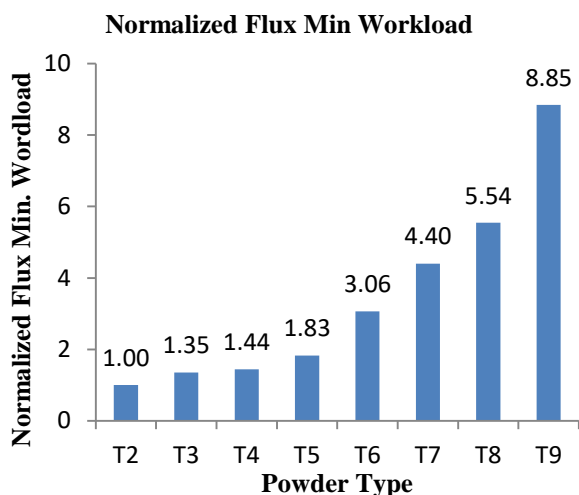
Normalized Flux Min Workload

Figure 16. Normalized workload of flux in solder paste for various type of powder, with that of type 2 being set as 1.

Using Figure 16, the relative flux workload of various powder size can be calculated easily. For instance, the relative workload of Type 7 against Type 4 is 4.40/1.44, or 3.06.

IV. FLUX CAPACITY NEEDED

The normalized relative flux workload serves as a starting point on understanding qualitatively the extent of challenge. To assess the feasibility and potential of solder paste at miniaturization, quantitative estimate becomes necessary.

The fluxing reaction can be represented by the following equation.

In this equation, two carboxylic acid COOH functional groups (formula weight 45) are needed to remove one oxygen atom from solder.

The oxygen content of various powder sizes was shown in Figure 15.

Min. COOH wt/g solder needed = (oxygen (% w/w)/16)*2*45
Min. COOH Volume fraction of flux needed = (COOH wt/(1 g/ml))/(1g solder/(7.4g/ml, for SAC305), approximate COOH density = 1 g/ml
In the calculation, the flux volume of solder paste is ~ solder volume for System in Package (SiP) or SMT print application, and within flux, the solid flux is approximated as 50%, with remaining 50% as solvents and others.

For paste using 8.9HF flux, only 30% of the flux remained on the board at reflow, as shown in Figure 15. If all of the oxygen is to be removed, the minimal COOH volume fraction in the flux residue needed can be calculated as shown in Table 3, with the results shown in Figure 17.

Table 3. Calculation of COOH volume fraction needed in flux residue to remove the minimal amount of oxygen.

$$SnO_2 + 4\ RCO_2H \rightarrow Sn(RCO_2)_4 + 2\ H_2O$$
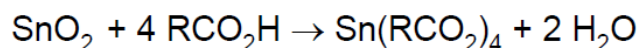
Type	PSD (μ)	Median D (μ)	Surface area (cm2/g)	Projected oxygen content %w/w	COOH wt needed/g solder	COOH Volume fraction needed in flux	COOH volume fraction needed in residue
2	45-75	60	11	0.008178	0.00046	0.003404	0.011348
3	20-45	32.5	21	0.011037	0.000621	0.004594	0.015314
4	20-38	29	23	0.01179	0.000663	0.004907	0.016358
5	15-25	20	34	0.014935	0.00084	0.006217	0.020723
6	5-15	10	68	0.02507	0.00141	0.010436	0.034785
7	2-11	6.5	104	0.035985	0.002024	0.014979	0.049929
8	2-8	5	135	0.045341	0.00255	0.018873	0.06291
9	1-5	3	225	0.072368	0.004071	0.030123	0.10041

Note:
COOH wt/g solder needed = (oxygen (% w/w)/16)*2*45
COOH Volume fraction of flux = (COOH wt/(1 g/ml))/(1g solder/(7.4g/ml), approximate COOH density = 1 g/ml
The flux volume of solder paste is ~ solder volume for SMT print application
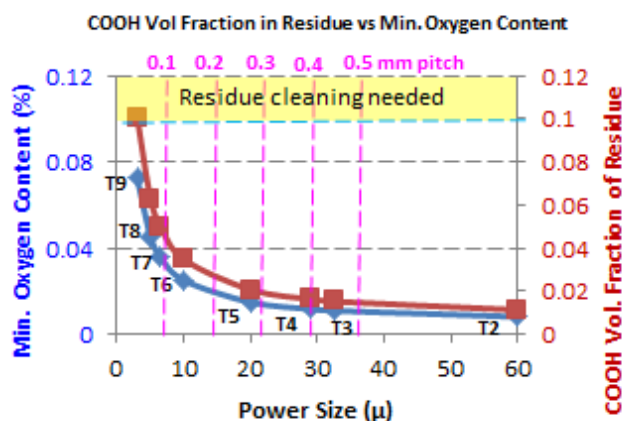Within flux, assuming COOH remaining % is in proportional to residue %

Figure 17. Minimal volume fraction of COOH needed in flux residue for removal of oxygen on solder powder. The pitch dimension was inserted assuming the aperture size is one half of the pitch dimension.

For no-clean applications, the volume fraction of hydrophilic COOH group in flux residue should be maintained at a minimum to avoid corrosion and leakage current. Although the threshold value is chemical structure dependent, a 10% volume fraction appears to be a reasonable value, assuming the rest flux structures are all hydrocarbons. By this criterion, Type 8 paste may be the limit of SMT printable solder paste when used at near 0.05mm pitch applications, as shown in Figure 17.

For Type 9 powder, the volume fraction of COOH needed in flux residue is just above 10%, strongly suggests major concern on flux-related reliability.

V. ADDITIONAL OXIDATION
1. Poor Powder Quality
All the relations discussed above were based on the existing oxide on the top quality powder with the lowest oxygen content. In reality, many of the fine powder produced exhibited a higher oxide content, as reflected in

Figure 4. For instance, the oxygen content of some Type 7 and Type 8 powder may reach 3 times to 4 times of extrapolated value. For those powder, the minimal volume fraction of COOH needed may reach 30-40% of flux residue, thus would fail for no-clean applications. For applications where the flux residue will be cleaned, solder pastes using powder finer than Type 7 may still be acceptable.

2. Oxides From Parts
Besides powder quality, the oxide on component leads or PCB pads would also demand a higher concentration of COOH group in the flux.

3. Oxidation At Reflow
Another major source of additional oxide came from oxidation of metal surface during reflow, particularly for air-reflow process [4]. This oxidation at reflow may cause more oxide formation far exceeding the pre-existing oxides.

Oxidation at reflow may be suppressed with the introduction of oxygen barrier technology in the flux, as shown in Figure 18 [5]. The concept of oxygen barrier technology is using chemicals with small free volume so that the oxygen cannot penetrate through. A solder paste uses flux with high oxygen barrier capability can be reflowed under air with negligible oxidation occurring. Therefore, fluxes with high oxygen barrier capability exhibited a nearly perfect soldering performance under air, as demonstrated by the fluxes with K=1 and 0.5, where K is oxygen penetration index. K=0 means zero oxygen penetration at soldering under air. A high K value indicates easy oxygen penetration, and will need the use of inert gas to achieve high soldering performance.

VI. INTERMETALLIC COMPOUNDS
For SMT assembled devices, sufficient ductility of solder joint is critical for reliability. When reflowed with SAC solders, the brittle intermetallic compound (IMC) layer CuSn formed at interface typically is around 2.5 μ on Cu after one reflow, and 5 μ all together for solder joints.
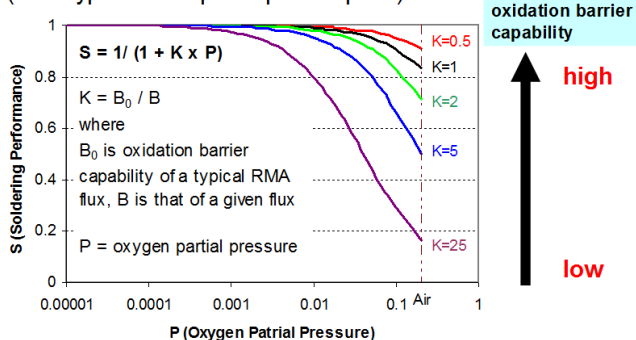

Figure 18. Soldering Performance vs Oxidation Barrier Capability vs Oxygen Partial Pressure [5]

Although no criteria is available about how much IMC is too much, the author use 50% maximum as a guideline. The solder joint configuration can be approximated with 1x3x3 square block paste print, and one half of the paste thickness printed as joint height for Bottom Terminated Components (BTC). Table 4 shows the calculation of IMC content within a SAC305 solder joint between Cu substrate.

Table 4. Calculation of content of IMC layer for SAC305 joint between Cu substrate

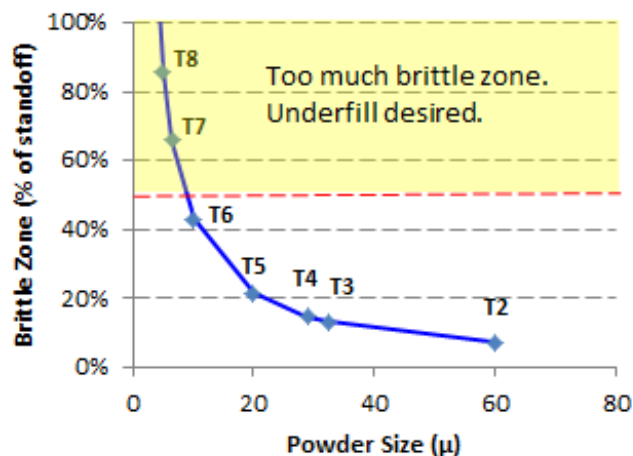| Type	PSD (μ)	Median D (μ)	BTC Joint Standoff (μ)	Total IMC Thickness (μ)	Solder Brittle Zone (%)
T2	45-75	60	70.00	5	7.1%
T3	20-45	32.5	37.92	5	13.2%
T4	20-38	29	33.83	5	14.8%
T5	15-25	20	23.33	5	21.4%
T6	5-15	10	11.67	5	42.9%
T7	2-11	6.5	7.58	5	65.9%
T8	2-8	5	5.83	5	85.7%
T9	1-5	3	3.50	5	142.9%

Area ratio = 3x3/(1x3x4) = 0.75
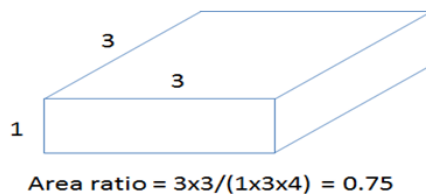
Figure 19. Brittle Zone % of the whole SAC305 joint between Cu substrates after one reflow.

Figure 19 showed the limit of paste miniaturization would be T6 powder. Beyond that, the IMC content of joint would exceed 50%, and the joint would be too brittle unless underfill is applied.

This limit may be pushed to finer powder, if additives in alloy are used to suppress the IMC growth rate, such as Zn, Mn, In, Co addition [6].

VII. CONCLUSION

For SiP or SMT assembly process, solder paste has been the choice of primary soldering material. In the meantime, miniaturization has been the trend of electronic industry. While the size of components, pads, stencil thickness, aperture, pitch, and solder powder has been shrinking continuously so far, it is about time to ask whether the solder paste technology is able to support this trend forever. In this study, solder powder oxygen content was observed to increase linearly with increasing powder surface area up to Type 5. Beyond Type 5, it is getting difficult to maintain oxide thickness. Beyond Type 8, the oxide thickness always higher than Type 5 or coarser. The flux burn-off rate increased linearly with decreasing flux size plotted in log scale. However, for solder paste, the paste residue showed a sharp drop initially with decreasing flux quantity, then levelled off at 3 mg flux (~30 mg paste), and maintained at around 30% residue through the remaining range down to 0.3 mg flux (~3 mg paste). The constant residue level at small sample size was attributed to the surface adsorption phenomenon, or "Flux Shell" phenomenon, where a layer of flux was strongly adsorbed on the solder powder surface. For solder paste, the flux workload increased rapidly with decreasing powder size. The flux capacity needed in removing oxide was derived as volume fraction of COOH functional group in flux residue, with 10% maximum being set as a guideline for no-clean applications. Type 8 paste may be the limit of SiP or SMT printable no-clean solder paste due to corrosivity consideration. Oxygen barrier and alloy dopants may expand the miniaturization potential. When reviewing the brittleness of solder joint formed, Type 6 may be the limit of fine pitch applications. Beyond that, the joints may be too brittle to be reliable, unless underfill is applied.

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