

## Lead-Free Flux Technology and Influence on Cleaning

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### ABSTRACT

Lead-free flux technology for electronic industry is mainly driven by high soldering temperature, high alloy surface tension, miniaturization, air soldering due to low cost consideration, and environmental concern. Accordingly, the flux features desired included high thermal stability, high resistance against burn-off, high oxidation resistance, high oxygen barrier capability, low surface tension, high fluxing capacity, slow wetting, low moisture pickup, high hot viscosity, and halogen-free. For each of the feature listed above, corresponding desired chemical structures can be deduced, and the impact of those structure on flux residue cleanability can be speculated. Overall, lead-free flux technology results in a greater difficulty in cleaning. Cleaner with a better matching solvency for the residue as well as a higher cleaning temperature or agitation are needed. Alkaline and polar cleaner are often needed to deal with the larger quantity of fluxing products. Reactive cleaner is also desired to address the side reaction products such as crosslinked residue.

**KEY WORDS:** lead-free, flux, flux residue, solder, soldering, cleaner, cleaning, SMT

### Introduction

The electronic industry has been driven by miniaturization and low cost for many decades. Since mid 1990's, environmental consideration also joined the main theme. The resultant European RoHS and REACH essentially pushed the whole world toward lead-free soldering as well as halogen free. For industries which cannot tolerate flux residue on the finished products, the combined constraints caused by the main drivers posed major challenges toward cleaning of post-soldering flux residue, as will be discussed below.

### CHALLENGES

#### Temperature

Although some other alloys such as eutectic BiSn, eutectic SnZn or their modification are also in use, the main stream lead-free solder alloys adopted by electronic industry include Sn-Ag-Cu (SAC), Sn-Ag (SA), Sn-Cu (SC), and modification of those alloys, as shown in Fig. 1 [1].

The most commonly used alloys include Sn95.5Ag4.0Cu0.5 (SAC405), Sn96.5Ag3.0Cu0.5 (SAC305), Sn98.5Ag1.0Cu0.5 (SAC105), Sn96.5Ag3.5, Sn99.3Cu0.7, with a melting temperature ranging from 217 to 227°C. This is about 40°C above the melting temperature of Sn63Pb37 (183°C) or Sn62Pb36Ag2 (179°C). Consequently, the soldering process employed for those alloys is also elevated to a higher temperature. For reflow process, the peak temperature ranges from 230 to 260°C. For wave soldering, the peak temperature ranges from 255 to 270°C. Thus, the soldering temperature typically is 20-40°C higher than that of SnPb.

The use of a higher soldering temperature inevitably results in (1) a greater amount of flux thermal decomposition and flux side-reaction, (2) a greater amount of flux burn-off, particularly at temperature above the melting temperature of solder, and (3) a higher extent of oxidation of both fluxes and metals. The resultant phenomena described above further induce poorer wetting and more voiding.

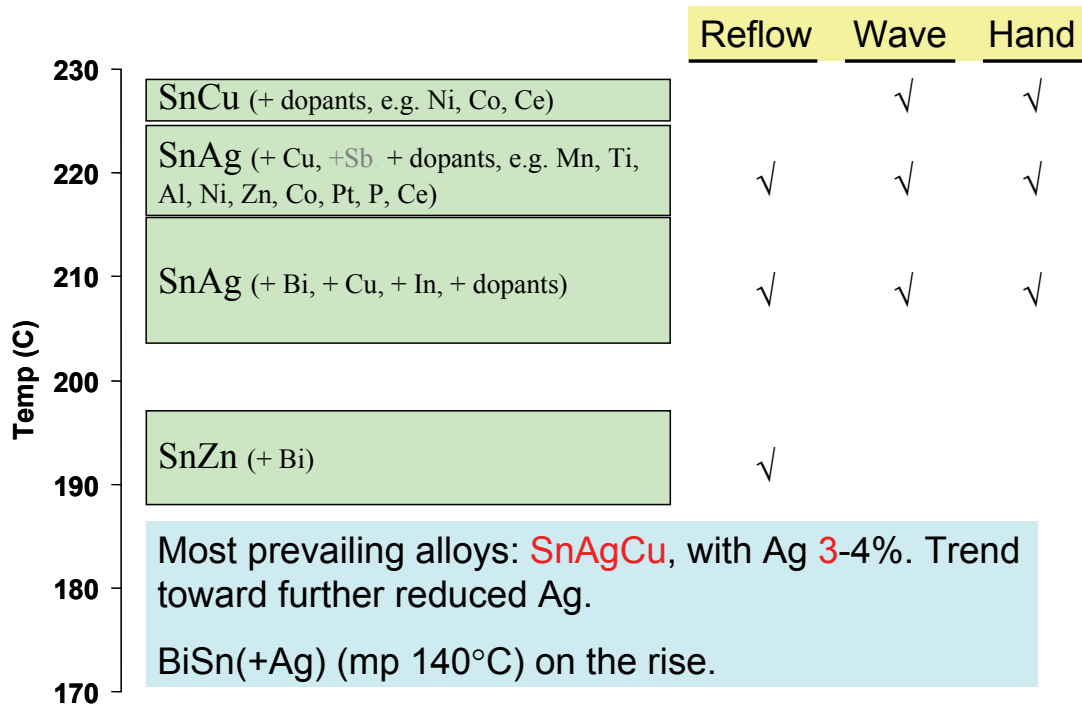


Fig. 1 Status of main stream lead-free solder alloys and their applications [1]

To avoid problems caused by the higher soldering temperature, fluxes with the following features are desired: (1) a higher thermal stability, (2) a higher resistance against burn-off, (3) a higher oxidation resistance, and (4) a higher oxygen barrier capability.

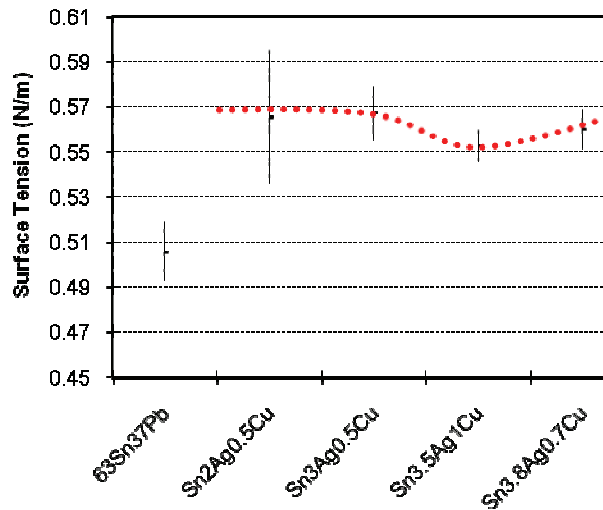


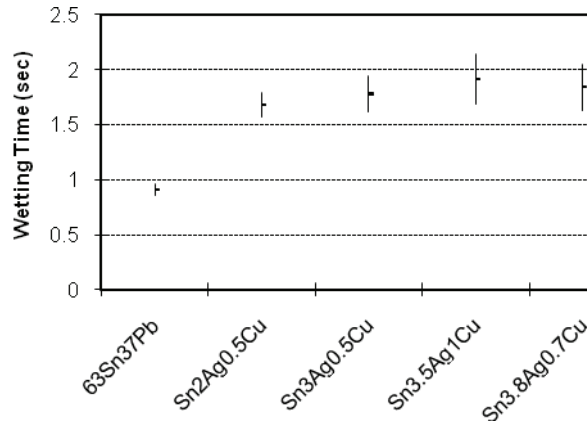
Fig. 2 Surface tension of Sn63Pb37 and SnAgCu alloys determined at 245°C and 260°C, respectively [2].

### Wetting

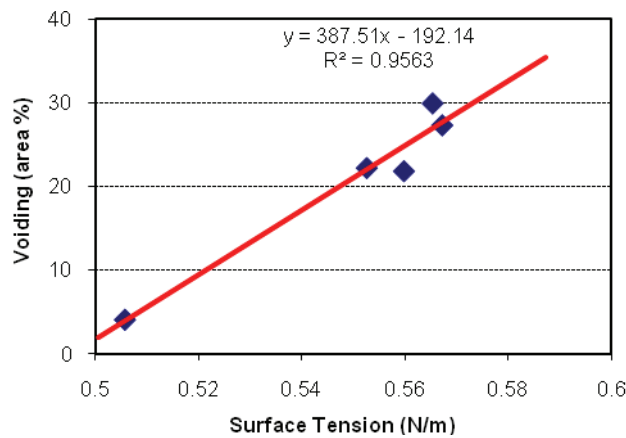
The surface tension of lead-free alloys (0.55-0.57N/m for SAC) is about 20% higher than Sn63Pb37 (0.51N/m), as shown in Fig. 2 [2]. This higher surface tension results in poorer wetting, as reflected by the longer wetting time shown in Fig. 3 [2].

The impact of high surface tension, or poor wetting is tremendous, and may include symptoms such as (1) low solder joint strength, (2) high voiding, (3) poor solder joint reliability. The relation between high surface tension and high voiding rate is demonstrated in Fig. 4 [2].

This deficiency in alloy wetting needs to be compensated with a flux with a better wetting. Thus, fluxes with the following features are needed: (1) a lower surface tension facilitating a better solder spread [3], and (2) a higher flux capacity and/or a higher flux strength.



**Fig. 3** Wetting time of Sn63Pb37 and SnAgCu solder alloys determined at 245°C and 260°C, respectively [2].



**Fig. 4** Relation between surface tension and voiding rate at microvia for Sn63Pb37 and SnAgCu alloys [2].

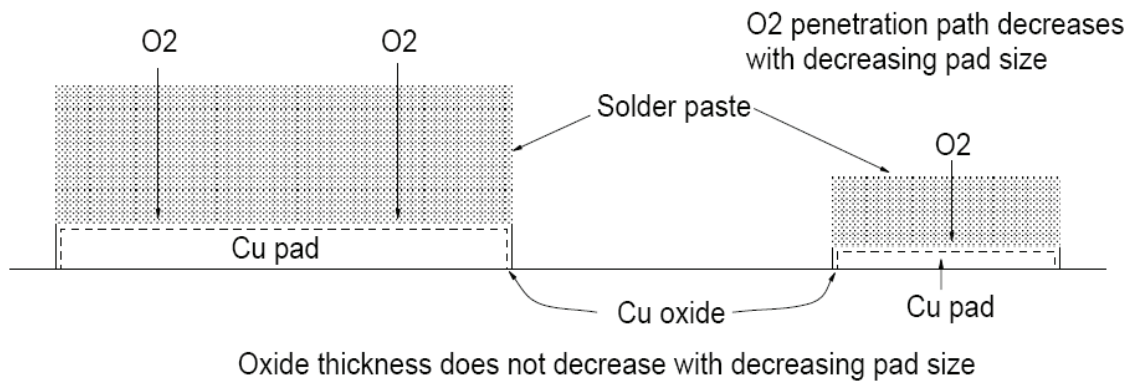
## Miniaturization

### 3.1 Oxide Thickness

The trend toward miniaturization has driven solder joints to shrink continuously. In general, the volume of soldering materials, including fluxes and solder, reduces in proportion with decreasing pitch. This proportional reduction trend is mainly driven by the (1) simplicity of design, (2) necessity of processing.

The first factor is easily understandable. The second factor is actually a result of physics. For instance, in SMT solder paste printing, the amount of solder paste deposited is limited by the "area ratio" rule. If the area ratio of aperture opening to that of aperture side wall is smaller than 0.65, then the paste volume transfer efficiency decreases significantly. In other words, the adhesion of paste toward pads cannot be pushed to be much smaller than the adhesion toward aperture side wall in order to have the paste properly released from stencil.

However, when the solder materials are shrunk in proportional to the pitch, the thickness of metal oxide does not shrink in proportion, as illustrated in Fig. 5.



**Fig. 5 Schematic drawing showing relation between oxide thickness, oxygen penetration path length, and pad dimension.**

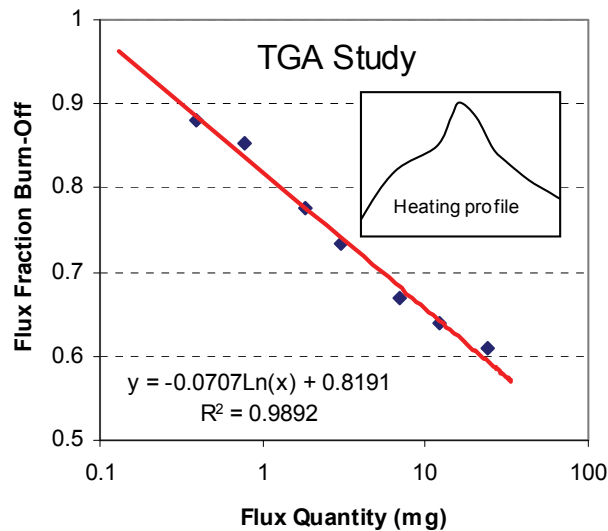
The metal here refers to PCB pads, component leads, and solder powder. Consequently, the amount of oxide to be removed by unit volume of flux increases with decreasing pad dimension. To compensate for this increasing work load, the fluxing capacity per unit amount of flux needs to be increased.

### 3.2 Oxygen Penetration Path

Another challenge associated with decreasing pad dimension is the decreasing oxygen penetration path through flux or solder paste, as also shown in Fig. 5. This inevitably results in a more rapid oxidation of both flux materials and metals covered by the flux if soldered under air. Hence, a flux with greater oxidation resistance as well as a greater oxygen barrier capability is desired for finer pitch applications.

### 3.3 Flux Burn-Off

To make things even more difficult, the flux burn-off increases with decreasing flux quantity deposited, as shown in Fig. 6 [4].



**Fig. 6 Relation between flux fraction burn-off and flux quantity [4].**

Apparently, the flux burnt-off during heating will not be able to participate oxide removal. To offset this unfavorable trend, the flux desired for finer pitch needs to be (1) more resistant to flux burn-off, or (2) higher in flux capacity per unit amount of flux.

### 3.4 Wetting Speed

At SMT assembly, defects due to unbalanced wetting force, such as tombstoning or swimming, increases with decreasing component size. Under this situation, fluxes with a slower wetting speed would allow more time for the wetting force to be balanced. Fig. 7 shows tombstoning rate decreases with increasing wetting time [5]. Hence, fluxes with a slower wetting speed are desired with further miniaturization.

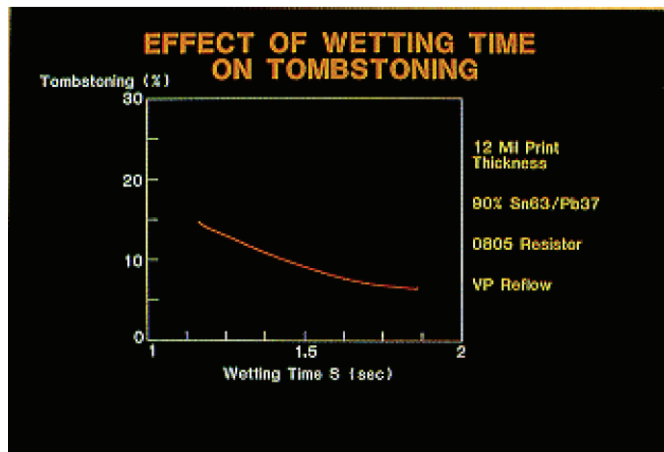


Fig. 7 Relation between tombstoning rate and flux wetting time [5].

### 3.5 Spattering

Miniaturization brings the solder joints closer to the gold fingers, hence is more vulnerable toward solder spattering.

Spattering can be caused by moisture pickup of the solder paste. It can also be caused by solder coalescence action. At reflow, the interior of solder powder melts. Once the solder powder surface oxide is eliminated by the fluxing reaction, the millions of tiny solder droplets will coalesce and form one integral solder piece. The faster the fluxing reaction rate, the stronger the coalescence driving force, and accordingly the more severe the spattering should be expected [3].

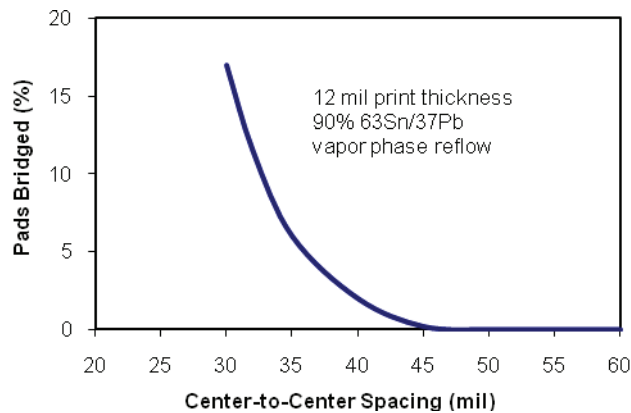


Fig. 8 Effect of center-to-center spacing on bridging [5].

To minimize solder spattering, fluxes with low moisture pickup and slow wetting speed would be desired.

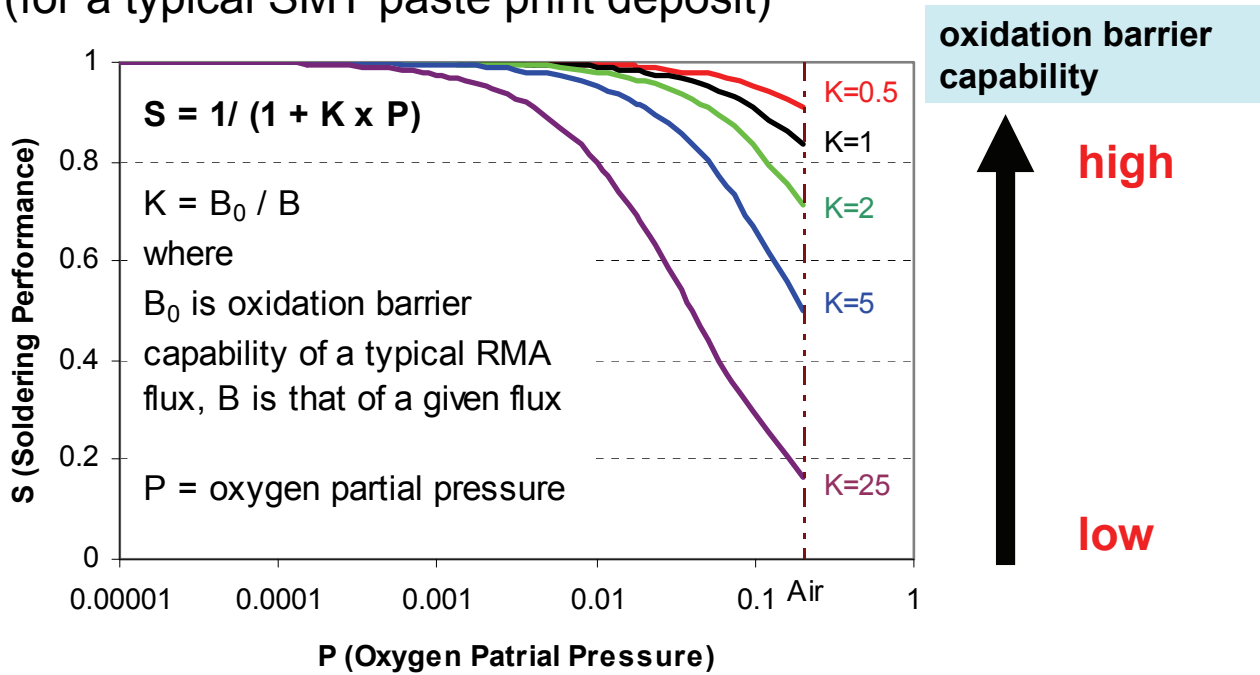
### 3.6 Slump

Bridging caused by slump of solder paste is another major concern at miniaturization. Fig. 8 shows the bridging rate increases with decreasing pitch dimension [5]. To prevent the slump from happening, fluxes with higher hot viscosity will be desired.

### Soldering Under Air

Low cost driver is pushing the industry hard to have soldering done under air. The immediate challenge is to achieve satisfactory soldering under air. Since oxidized surface is difficult to wet, the logical solution for this challenge is to employ fluxes with a good oxygen barrier capability so that oxidation can be minimized. The effect of oxygen barrier capability on soldering performance is illustrated in Fig. 9 [6]. It can be seen clearly that without the help of nitrogen atmosphere, a very high oxygen barrier capability of flux is needed in order to have high soldering performance.

Either use nitrogen, or use flux with higher oxidation barrier (for a typical SMT paste print deposit)



P. Jaeger and N.-C. Lee, "A Model Study of Low Residue No-Clean Solder Paste", in Proceeding of Nepcon West, Anaheim, CA, 1992.

Fig. 9 Soldering performance versus oxidation barrier capability versus oxygen partial pressure [6].

Table 1 Flux feature desired in order to meet the challenges

| Flux feature desired             | Challenge        |                             |                 |     |             |
|----------------------------------|------------------|-----------------------------|-----------------|-----|-------------|
|                                  | High temperature | High solder surface tension | Miniaturization | Air | Environment |
| High thermal stability           | x                |                             |                 |     |             |
| High resistance against burn-off | x                |                             | x               |     |             |
| High oxidation resistance        | x                |                             | x               | x   |             |
| High oxygen barrier capability   | x                |                             | x               | x   |             |
| Low surface tension              |                  | x                           |                 |     |             |
| High fluxing capacity/strength   |                  | x                           | x               |     |             |
| Slow wetting speed               |                  |                             | x               |     |             |
| Low moisture pickup              |                  |                             | x               |     |             |
| High hot viscosity               |                  |                             | x               |     |             |
| Halogen-free                     |                  |                             |                 |     | x           |

In conjunction with the miniaturization trend, as discussed in Section 3, the flux desired should exhibit the following properties: (1) a great oxidation resistance to prevent the flux from being oxidized, and (2) a great oxygen barrier capability to protect parts and solder from being oxidized.

Halogen-Free

Halogen-free is a trend of the industry, mainly out of human's perception instead of actual impact of halogen on environmental consideration or reliability. RoHS specifies that brominated flame retardants, including polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) as harmful to human health. On the other hand, REACH SIN (Substitute It Now) list contains 30 chemicals classified as EQUIVALENT LEVEL OF CONCERN, 17 chemicals as PBTs (persistent, bio-accumulative, and toxic substances), and 220 chemicals as Classified CMRs (carcinogenic,

mutagenic, or toxic). Out of a total 267 chemicals, only very limited number of halogen-containing chemicals such as 1,2-dichlorobenzene and hexabromocyclododecane are listed. In the REACH SVHC (Substance of Very High Concern) list, 3 out of 15 chemicals are halogenated chemicals.

Although most of the halogen-containing flux chemicals used in the industry are not on the list of RoHS or REACH, the industry still moves rapidly toward halogen-free fluxes. Besides the questionable perception that halogen-free is less-corrosive than halogen-containing fluxes, another driver is the difficulty in differentiating the banned halogenated chemicals from those not on the banned list.

The trend toward halogen-free flux is here to stay.

### REVIEW OF FLUXES DESIRED

Bu reviewing the challenges discussed above, the flux feature desired can be listed in Table 1.

The flux chemical structures implied which would support the flux features desired are shown in Table 2.

### SUMMARY

Overall, lead-free flux technology results in a greater difficulty in cleaning. Cleaner with a better matching solvency for the residue as well as a higher cleaning temperature or agitation are needed.

**Table 2 Chemical structure of flux implied supporting the flux feature desired**

| Flux feature desired             | Chemical structure implied   | Cleanability impact  |
|----------------------------------|--|--|
| High thermal stability           | Strong chemical bonds such as C-F, Si-O, cyclic or aromatic structures   | Non-polar cleaner needed. For crystalline residue, may need cleaner with high solvency and high cleaning temperature or agitation.   |
| High resistance against burn-off | High intermolecular force  |  |
|                                  | - high molecular weight  | Cleaner with high solvency needed. High cleaning temperature or agitation desired.   |
|                                  | - high polarity or hydrogen bonding concentration  | Require polar cleaner.   |
| High oxidation resistance        | Flux may contain more oxidation resistant chemical bonds such as aromatic structures, hydrocarbons, or silicone materials.       | Some non-polar cleaner needed.   |
| High oxygen barrier capability   | Low molecular free volume desired  |  |
|                                  | - high concentration of covalent bond, such as high MW, high cyclic or aromatic structure, high crosslink density                | Generally the residue will be high in viscosity and difficult to dissolve. Cleaner with high solvency needed. High dissolution temperature or agitation desired. If cross linked, reactive cleaner needed. |
|                                  | - high conc. of hydrogen bonding, such as high concentration of -OH, -NH, -SH, -O-, -N-, -S- functional groups                   | The high polarity of residue requires some polar solvents to dissolve them.  |
| Low surface tension              | Low polarity, light element, such as hydrocarbon or silicone   | Require non-polar cleaner.   |
| High fluxing capacity/strength   | More polar functional groups, mainly more organic acids or halides, needed to react with oxides. Side reactions are very likely. | Side reaction products may be difficult to clean. Require more alkaline and polar cleaner.   |
| Slow wetting speed               | Chemicals with protective group on flux desired to slow down wetting.  | Potential side reaction may cause greater difficulty in cleaning, reactive cleaner may be needed.  |
| Low moisture pickup              | Need non-polar functional group  | Need some non-polar cleaner  |
| High hot viscosity               | Need some high MW ingredients  | Cleaner with high solvency needed to dissolve the high MW residue. High  |

|              |  |  |
|--------------|--|--|
|              |  | cleaning temperature or agitation desired. If cross linked, reactive cleaner required. |
| Halogen-free | High content of organic acids plus organic bases needed to react with oxides | Side reaction products may be difficult to clean. Require alkaline and polar cleaner   |

Alkaline and polar cleaner are often needed to deal with the larger quantity of fluxing products. Reactive cleaner is also desired to address the side reaction products such as crosslinked residue.

### CONCLUSIONS

Lead-free flux technology for electronic industry is mainly driven by high soldering temperature, high alloy surface tension, miniaturization, air soldering due to low cost consideration, and environmental concern. Accordingly, the flux features desired included high thermal stability, high resistance against burn-off, high oxidation resistance, high oxygen barrier capability, low surface tension, high fluxing capacity, slow wetting, low moisture pickup, high hot viscosity, and halogen-free. For each of the feature listed above, corresponding desired chemical structures can be deduced, and the impact of those structure on flux residue cleanability can be speculated. Overall, lead-free flux technology results in a greater difficulty in cleaning. Cleaner with a better matching solvency for the residue as well as a higher cleaning temperature or agitation are needed. Alkaline and polar cleaner are often needed to deal with the larger quantity of fluxing products. Reactive cleaner is also desired to address the side reaction products such as crosslinked residue.

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