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Studies on Flux Action of Soldering (Report III)[†]

—Organic Metal Salts—

Ikuo OKAMOTO*, Akira OMORI** and Hiroshi KIHARA***

Abstract

In previous paper on flux action of aniline hydrochloride for soldering, it was shown that the reaction of CuCl_2 and Cu-complex with molten Sn-Pb alloy solder and the dissolution of Cu into the solder played an important role in spreading of solder on copper plate.

In this paper, flux action of various metal salts for soldering has been studied from the view point of the reaction of the flux with molten Sn-Pb eutectic alloy solder and spreading of solder.

The flux action of metal salt may be considered as follow;

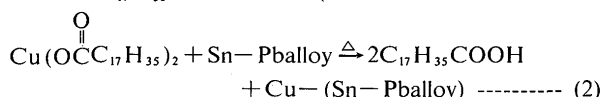
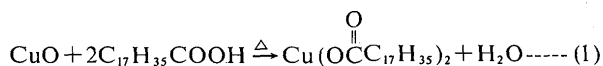
Metal salt (metal benzoate and various metal stearates) reacts with molten Sn-Pb eutectic alloy solder to give metal and Sn salts.

The metal dissolves immediately into the molten solder. The wetting of Sn-Pb solder on copper plate is improved by the reaction and the dissolution of the metal into molten solder. So, Sn-Pb alloy solder spreads well over copper plate.

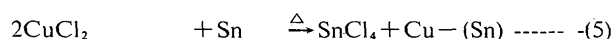
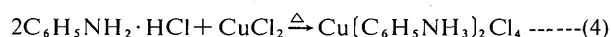
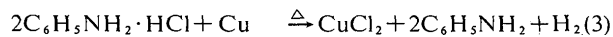
And, the reaction of metal salts with molten Sn-Pb eutectic alloy solder may depend on the oxidation and reduction potentials of metal and free energy (ΔF) for a formation of metal stearate.

1. Introduction

We have reported on the stearic acid flux action^{1,2)} of soldering as follows; Molten stearic acid reacts with copper oxide to give copper stearate (eq-1), which reacts with molten Sn-Pb eutectic alloy solder, and the Cu-rich layer at outer surface of solder is formed (eq-2). The spreading of solder on copper specimen is improved by the reaction and the dissolution of Cu into the solder.



The flux action of aniline hydrochloride^{3,4)} may be considered as follows; Molten aniline hydrochloride reacts with copper to give CuCl_2 and copper complex (eq-3 and eq-4), which react with molten Sn-Pb alloy solder to give metal copper (eq-5). The wetting of solder on copper plate is improved.



In this report, we report the flux action of organic metal salts (copper benzoate and copper abietate),

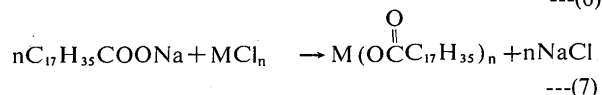
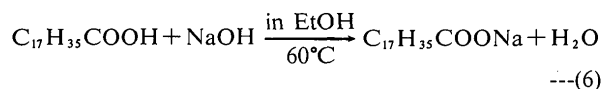
and the relation between the reaction of various metal stearates (Ag-stearate, Ni-stearate and etc.) with Sn-Pb eutectic alloy solder and the flux action for spreading of solder.

2. Experimental Procedure

The same apparatus and test specimens for spreading test of previous studies^{3,4)} were used. The spreading test and the reaction of the flux with solder were tried at 240°C under the similar conditions as described in earlier paper.

The reaction products were identified by infrared spectrum and chemical analysis. And the cross section of the spreading specimens was analyzed by EMX analyzer.

The various metal salts used in these experiment were synthesized by the methods⁵⁾ as shown in eq (6) and eq (7).



In the case of the formation of Ag-stearate, AgNO_3 was used in place of chloride.

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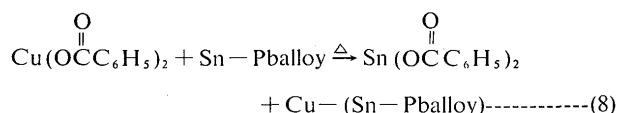
*** Director and Professor

3. Results and Discussions

3.1 Flux action of copper benzoate

3.1.1 Reaction of copper benzoate with molten Sn-Pb eutectic alloy

In order to confirm the flux action of benzoic acid, the reaction of copper benzoate, produced by the reaction of CuO with benzoic acid, with molten Sn-Pb eutectic alloy solder was studied. Copper benzoate (5g), Sn-Pb eutectic alloy (5g) and tetralin (30ml) were mixed in a 100ml round bottomed flask equipped with reflux condenser. The flask was heated at 270°C for 1.5hr under nitrogen atmosphere. After completion of the reaction, the products were filtered to remove the solid. The solid was dissolved by chloroform, and insoluble white solid (1.4g) was identified as Sn(OCC₆H₅)₂ by mass spectral analysis (Sn=120, M⁺362, 241) and ir spectral analysis. (1608cm⁻¹, >C=O). Benzoic acid (1.9g) was extracted with aq. 5% sodium bicarbonate solution and identified by infrared spectra. It was recognized that Cu deposited on the surface of Sn-Pb alloy recovered after the reaction. By the reaction of benzoic acid with Sn-Pb alloy, no Sn-benzoate were given and benzoic acid only were recovered. From this result, it was confirmed that Cu-benzoate reacted with Sn-Pb alloy solder to give Sn-benzoate and Cu as shown in eq-8.



3.1.2 Spreadability of Sn-Pb eutectic alloy solder with Cu-benzoate, or Sn-benzoate

Copper benzoate with Sn-Pb eutectic alloy to give Sn-benzoate as shown in section 3.1.1. In this section, the spread was tested at 240°C using Sn-Pb eutectic alloy solder and metal benzoate (Sn, Cu)/stearic acid system flux with different compositions, in order to elucidate the effect of the reaction and the products on spreading of solder. The results are shown in Fig. 1 in the case of both Cu-benzoate and Sn-benzoate. As the figure shows, the addition of Cu-benzoate to stearic acid has a considerable effect on the improvement of spreading in similar manner as Cu-stearate. And Sn-benzoate affected a little spreadability. The cross section of specimens after spreading of solder on copper plate with 40 mol% benzoate flux was analyzed by EMX analyzer. We note that metal Cu from the flux dissolves into solder.

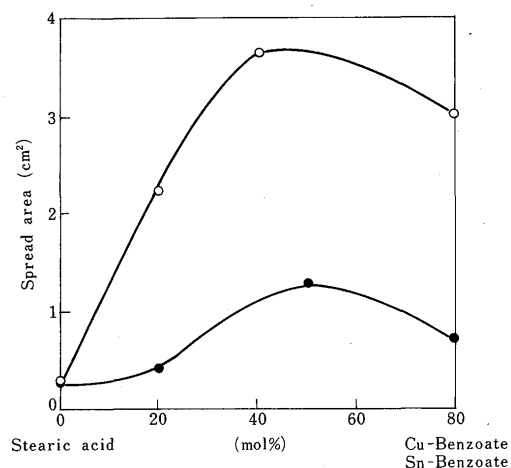
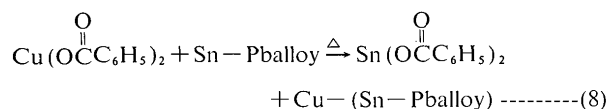


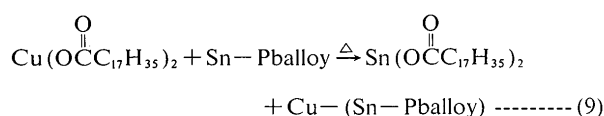
Fig. 1. Spreading of Sn-Pb eutectic alloy solder on copper plate with Cu-benzoate and Sn-benzoate.
○: Cu-Benzoate, ●: Sn-Benzoate

3.1.3 Flux action of Cu-benzoate for soldering

From the results in 3.1.2 section, it became clear that Cu-benzoate showed the similar flux action as Cu-stearate did. However, in this flux, Sn-benzoate was isolated through the reaction with solder, so the flux action of benzoic acid is considered as follows: Benzoic acid reacted with CuO to give Cu-benzoate (eq-9)



, which reacted with molten Sn-Pb eutectic alloy solder to give Sn-benzoate and metal Cu (eq-8). Successively, the metal dissolves into molten solder. And the wetting of Sn-Pb solder on copper is improved by the reaction and the dissolution. In the case of Cu-stearate, Sn-stearate may be considered to produce through the reaction of Cu-stearate with molten Sn-Pb eutectic alloy solder (eq-9).



3.2 Flux action of Cu-abietate for soldering

As the flux action for stearic acid and benzoic acid was confirmed, the flux action of abietic acid or other organic acid were studied in this section, in order to elucidate whether the flux action of stearic acid applied in the case of other organic acid or not.

3.2.1 Spreadability of Sn-Pb eutectic alloy solder with Cu-abietate

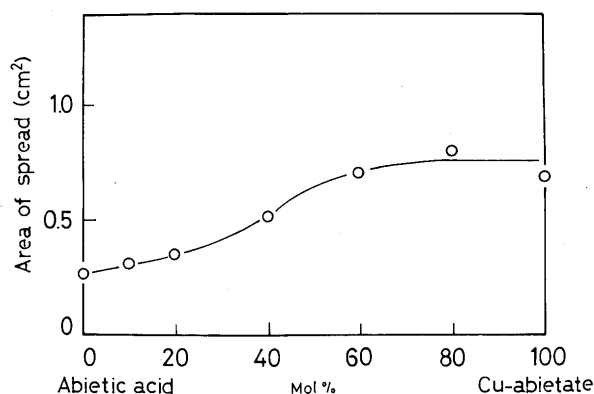


Fig. 2. Spreading of Sn-Pb eutectic alloy solder on copper plate with Cu-abietate.

The results of spreading test at 280°C using Cu-abietate/abietic acid system flux are shown in **Fig. 2**. From the figure, the addition of Cu-abietate to abietic acid has a small effect on improvement of spreading. And, from the results of EMX analysis, it was recognized that Cu from the Cu-abietate flux dissolved. Moreover, spreading was improved by the addition of Cu-oleate or Cu-rozinate. From the above results, Cu-salts of various organic acids showed the similar flux action as Cu-salt of stearic acid did.

3.3 Flux action of various metal stearates for soldering

It was recognized in earlier section that Cu-salts reacted with Sn-Pb eutectic alloy solder and played an important role in spreading.

In this section, the flux action of the various metal stearates (Na, Co, Ni, Ag and etc.) for soldering was studied in comparison with that of Cu-stearate.

3.3.1 Spreadability of Sn-Pb eutectic alloy solder with various metal stearates/stearic acid system flux

Various metal stearates which used for flux and reaction were synthesized by such method as shown in eq-6 and eq-7 and the properties of stearates are shown in **Table 1**. The results of spreading test with using various metal stearates/stearic acid system flux are shown in **Fig. 3** and **Fig. 4**. From the figure, spread area increased greatly by the addition of metal stearates such as Ag, Cu, Pb and Ni salts to stearic acid, however, in the case of Na-, Mg-, Zn-, Fe- and Co- stearates, the effect on spreading was scarcely recognized. In order to clear the differences of flux action by various metal stearates the cross section of spreading specimens was analyzed by EMX analyzer in next section.

Table 1. Properties of various metal stearates.

Metal stearate	Melting point (°C)	Normal potential of metal (V vs. NHE)	ΔF^0 (at 25°C) (kcal/mol)
Na-Stearate	223	-2.714	-90.0
Mg-Stearate	148	-2.363	-136.13
Zn-Stearate	129	-0.763	-76.5
Fe ²⁺ -Stearate	96	-0.440	-58.4
Fe ³⁺ -Stearate	103	—	-177.1
Co-Stearate	114	-0.278	-51.0
Ni-Stearate	300	-0.250	-51.7
Sn-Stearate	—	-0.136	-61.5
Pb-Stearate	116	-0.127	-45.3
Cu-Stearate	215	0.337	-30.4
Ag-Stearate	280	0.799	-2.6

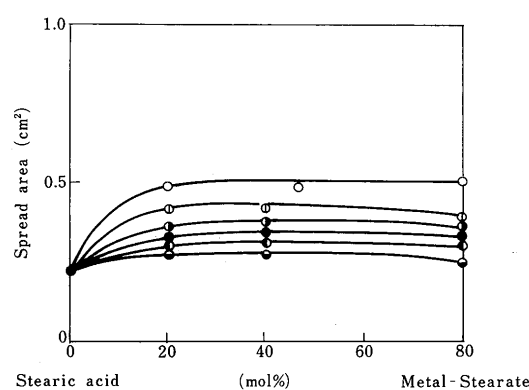


Fig. 3. Spreading of Sn-Pb eutectic alloy solder on copper plate with various metal stearates (Na, Mg, Zn, Fe, Co).
○: Co-Stearate, ⊕: Na-Stearate, ⊙: Zn-Stearate, ●: Mg-Stearate, ⊙: Fe³⁺-Stearate, ⊙: Fe²⁺-Stearate.

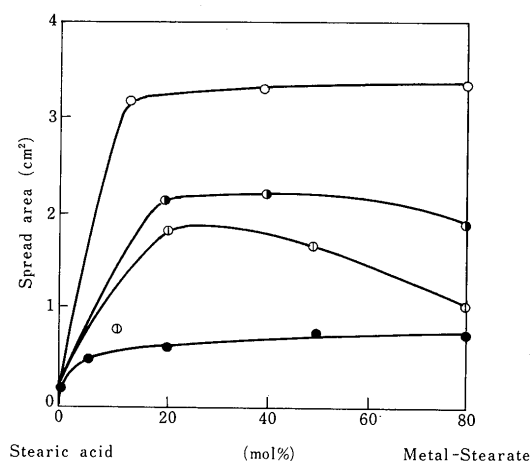


Fig. 4. Spreading of Sn-Pb eutectic alloy solder on copper plate with various metal stearates (Ni, Pb, Cu, Ag).
○: Cu-Stearate, ●: Ni-Stearate, ⊕: Ag-Stearate, ●: Pb-Stearate.

3.3.2 EMX analysis of spreading specimens.

In the case of Cu-stearate flux, the reaction of Cu-stearate with molten eutectic alloy solder and the dissolution of metal copper into solder played an important role in spreading. In order to reveal the dissolution of metals into Sn-Pb alloy solder from the

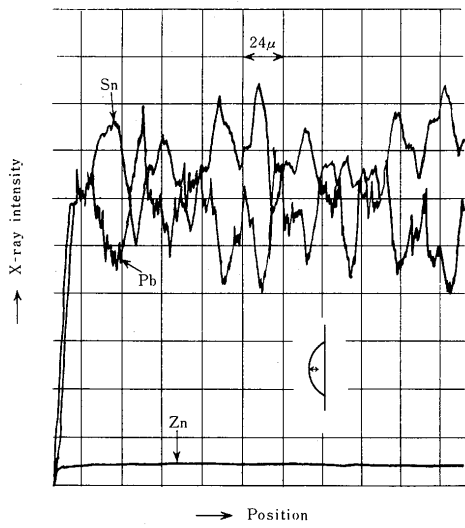


Fig. 5. X-ray microanalysis of cross section of Sn-Pb eutectic alloy solder spread on copper plate with Zn-stearate.

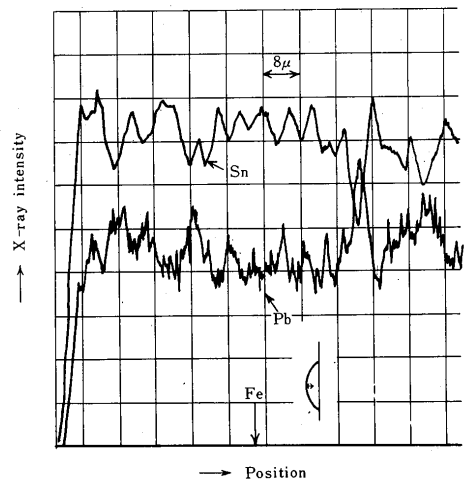


Fig. 6. X-ray microanalysis of cross section of Sn-Pb eutectic alloy solder spread on copper plate with Fe-stearate.

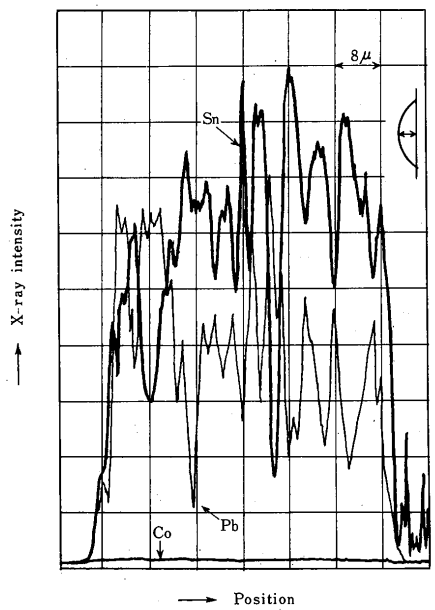


Fig. 7. X-ray microanalysis of cross section of Sn-Pb eutectic alloy solder spread on copper plate with Co-stearate.

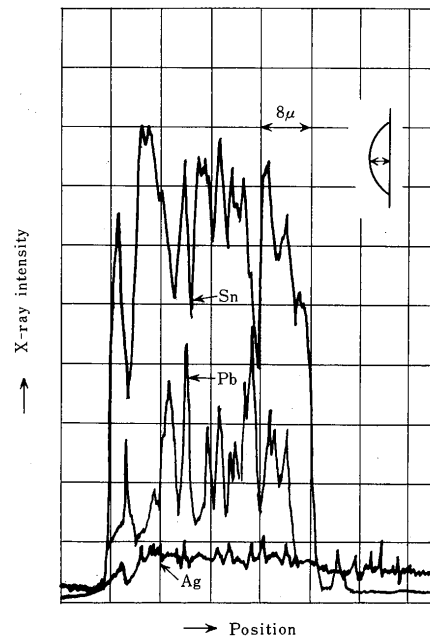


Fig. 8. X-ray microanalysis of cross section of Sn-Pb eutectic alloy solder spread on copper plate with Ag-stearate.

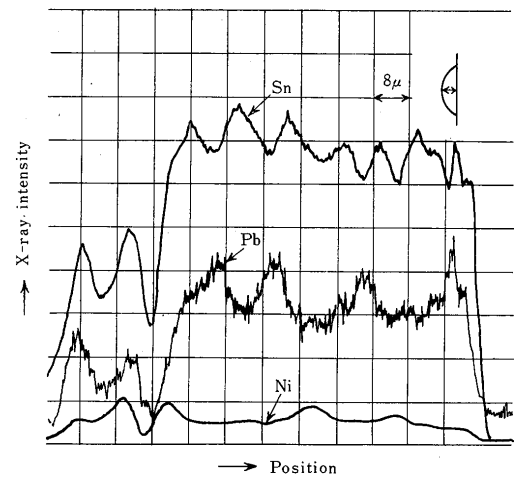


Fig. 9. X-ray microanalysis of cross section of Sn-Pb eutectic alloy solder spread on copper plate with Ni-stearate.

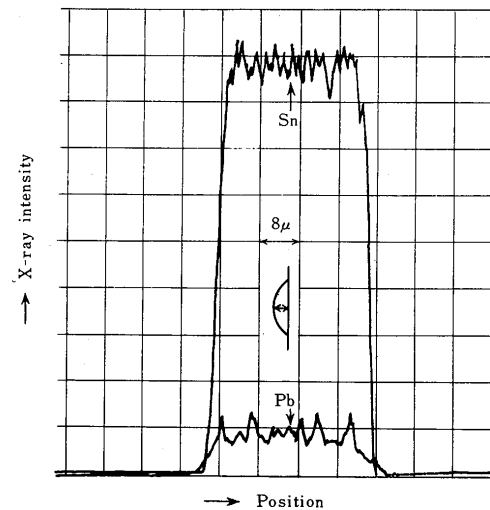


Fig. 10. X-ray microanalysis of cross section of Sn spread on copper plate with Pb-stearate.

various metal stearates, the cross section of spreading specimens was analyzed with EMX analyzer. And, in the case of Pb-stearate, pure Sn solder was used to discriminate Pb in solder from Pb of Pb-stearate. The results are shown in Fig. 5~Fig. 10 for Zn-stearate, Fe-stearate, Co-stearate, Ag-stearate, Ni-stearate and Pb-stearate, respectively.

From the results of EMX analysis, we know that metal from the flux dissolves in solder, respectively in the case of Ni-, Cu-, Pb- and Ag-stearates, with which spread area increased greatly in comparison with one using stearic acid. However, the dissolution of metal from flux into solder was not recognized, when Na-, Mg-, Zn-, Fe- and Co-stearates were used as flux, respectively. It may be considered that the dissolution of metal into solder controls spread on copper plate. And the dissolution may be dependent on the reaction of various metal stearates with molten Sn-Pb eutectic alloy. So, the reaction between the flux and solder was studied in next sec-

Table 2. Weight of stearic acid given by reaction with Sn-Pb eutectic solder.

Metal stearate	Stearic acid ^{a)} (mg)	Stearic acid ^{b)} (mg)
Na-Stearate	0	0
Mg-Stearate	0	0
Zn-Stearate	0	0
Fe ²⁺ -Stearate	360	0
Fe ³⁺ -Stearate	380	0
Co-Stearate	107	0
Ni-Stearate	64	370
Sn-Stearate	—	—
Pb-Stearate	0	124
Cu-Stearate	185	815
Ag-Stearate	692	29

a) Weight of stearic acid produced by self-decomposition.

b) Weight of stearic acid produced by reaction with Sn-Pb eutectic solder.

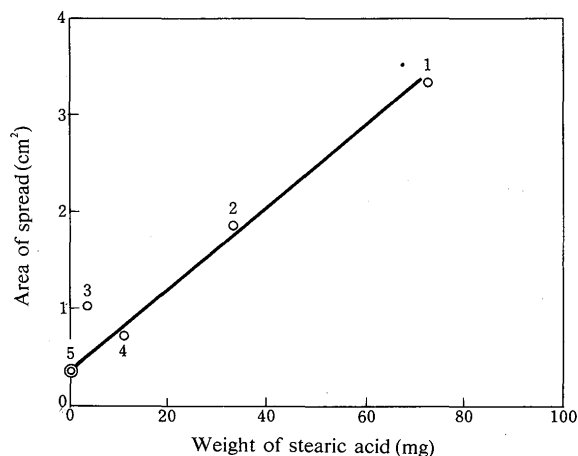


Fig. 11. Relationship between the amount of metal stearates and spread area.

1: Cu-Stearate, 2: Ni-Stearate, 3: Ag-Stearate,
4: Pb-Stearate, 5: (Na, Mg, Zn, Fe²⁺, Fe³⁺, Co)-Stearate.

tion to know the relation between the reaction and spreadability.

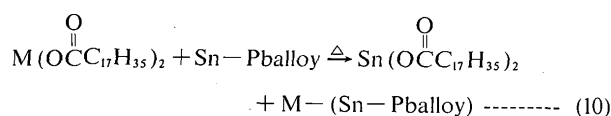
3.3.3 Reaction of various metal stearates with Sn-Pb eutectic alloy solder

Various metal stearates (1g) reacted with Sn-Pb eutectic alloy solder (1g) in test tube for 10 min. at 240°C under similar conditions as spreading test. After the reaction in all the case of various stearates, the amount of stearic acid produced was measured. However, as the self decomposition of various metal stearates by heating is considered in above reaction, the amount of stearic acid produced only by self decomposition reaction was measured under the same conditions. And the amount of stearic acid produced only by the contact reaction of metal stearates with molten Sn-Pb eutectic alloy was given by the balance of amount of stearic acid between the two reactions. The results are shown in Table 2. Stearic acid was identified by ir spectral analysis. As shown in Table 2, various metal stearates of Ni, Cu, Pb and Ag, with which spreadability were improved greatly and from which metal dissolved into solder, reacted with molten Sn-Pb eutectic alloy solder to give metal and stearic acid. However, in the case of metal stearates of Na, Mg, Zn, Fe and Co, it was not recognized that stearic acid produced by the contact reaction of metal stearate with Sn-Pb alloy. From these results, the flux action of various metal stearates may be dependent on the reaction and the dissolution of metal. So, in order to know the relation between the spreadability of solder with metal stearate and the reactivity of the flux with solder, spread area and the amount of stearic acid produced by the reaction were plotted in Fig. 11, when 80 mol% metal stearate flux was used. As the figure shows, the increase in the amount of stearic acid by the reaction with solder brings the increase in spread area of solder, with respect to Ni-stearate, Cu-stearate and Pb-stearate flux. Na-, Zn-, Mg-, Fe- and Co-stearates which did not react with molten Sn-Pb alloy has little flux action in spreading. And in the case of Ag-stearate, spread area showed more larger value than estimated from the amount of stearic acid produced by the stearate with solder, so the deviation can be explained as follows; The amount of silver from mono-valent Ag-stearate is equivalent to two time as much as metal (Ni, Cu, Pb) from divalent metallic stearate (Ni, Cu and Pb), when the same amount of stearic acid was produced by the reaction.

From the above results, it may be considered that the reaction of various metal stearates with Sn-Pb eutectic alloy solder plays an important role in spreading.

3.3.4 Flux action for soldering of various metal stearates

From the results in above sections, various metal stearates showed the similar flux action for soldering of solder as Cu-stearate did. As shown in the case of Cu-stearate, the reaction of metal stearate with solder and the dissolution of metal from the stearate have great effect on the improvement of spreading, and spreadability with metal stearate increased linearly with the reaction. The reaction as shown in eq-10 may play an important role in spreading, irrespective of a variety of metal in metal stearate.



Whether the reaction of molten solder with metal stearate with respect to metals Na, Ag and etc. proceed or not, can be considered as follows; When the reaction in eq-10 takes place, it may be necessary that electron exchange reaction between Sn on solder and metal of metal stearate comes about at the surface of solder as shown in Fig. 12.

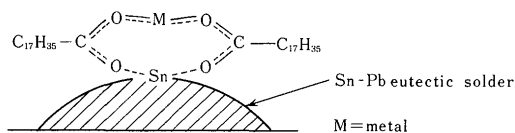


Fig. 12. Reaction of metal salt with Sn at the surface of molten Sn-Pb alloy solder.

So, the reaction of metallic stearate with Sn in solder (eq. -10) was taken in consideration on the basis of oxidation and reduction potentials of metal as shown in Table 1. And the reaction by the electron exchange between Sn metal and the metal may proceed in the case of Pb-stearate, Cu-stearate and Ag-stearate, as Pb, Cu and Ag respectively are more noble than Sn. However, Ni-stearate reacted with Sn and showed the flux action for soldering, notwithstanding that Ni is more base than Sn.

The reaction of Ni-stearate with Sn may be considered as follows; the electrochemical series (the potentials) in solvent used in this experiment is different with that in aqueous solution, and Ni may be more noble than Sn in this experimental solvent.

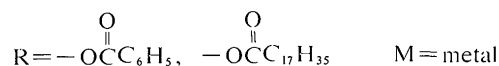
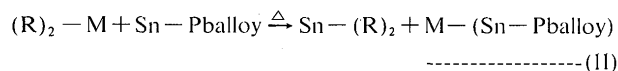
Then, the reaction of metal stearate with Sn was taken in consideration on the basis of thermal kinetics. ΔF values at 25°C for the formation of various metal oxides are shown in Table 1, as ΔF values for the formation of metal stearate at 240°C are not given. ΔF values for the reaction (eq-10) from the values in

the table were calculated and as the $-\Delta F$ values for the reaction in the all case of Cu, Ni, Pb, Co and Ag stearate were plus respectively, such reaction may proceed. However, the $-\Delta F$ values in the case of Na, Mg, Zn and Fe stearate were minus and the reaction may not proceed. Practically, in the case of every metal except Co in this experiment, the reaction can be explained from these experimental results. In the case of Co-stearate, $-\Delta F$ values is 10.5 Kcal/mol and the reaction may proceed. But, the reaction of Co-stearate with Sn did not proceed in this experiment, because of the effect of such factor as alloying energy or solvent effect.

The reaction of metal stearate with Sn in molten solder may be dependent on oxidation and reduction potentials and the free energy (ΔF) for the formation of metal stearate.

4. Conclusion

From the above results, the flux action of Cu-benzoate, Cu-abietate and various metal stearates for soldering may be considered as follows; Metal salts react with molten Sn-Pb alloy solder to give Sn salts and metal, which dissolves into solder, as shown in eq-11.



And solder spread over the Cu plate by the reaction and the dissolution. The reaction in eq (11) may be important factor for spreading of solder and depend on the oxidation and reduction potentials of metal and the free energy.

Acknowledgment

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