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Studies on Flux Action of Soldering (Report VII)†
—Flux Action of various Silver and Copper Salts on Ni and Fe plates—

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Abstract

In previous paper, the flux action of various inorganic metal salts (chloride, sulfate and nitrate) for soldering was reported in the relation between the reaction of flux with molten Sn solder and spreadability of Sn solder on Cu plate.

In this report, authors have studied on the relation between the reaction of base plate (Ni, Fe) or Sn solder with flux and spreading phenomenon of Sn solder on Fe plate or Ni plate, when $C_6H_5NH_2HCl$-silver salt or copper salt system flux is used.

The results obtained were as follows;

(1) Corrosion reactivity of base plate increases as we go from Ni, to Cu, and to Fe when $C_6H_5NH_2 \cdot HCl$ is used as flux.

(2) The effect of corrosion product on spreadability increased as we go to $FeCl_3$, to $FeCl_2$, to $NiCl_2$, and to $CuCl_2$.

(3) $FeSn_2$ coated on Sn solder obstructs spreading of Sn solder on Fe plate, when $FeCl_2$ or $FeCl_3$ flux was used.

(4) The amount of $FeSn_2$ produced on Sn solder by the reaction of molten Sn with Fe salt controlled flow and spread on Fe plate, depending on the amount of Ag or Cu in Sn solder, when various Ag or Cu salts were used as flux.

(5) When Ni plate was used, Ni dissolved little in Sn solder and spreadability is dependent on the reactivity of Sn solder with flux.

1. Introduction

The flux action of $C_{17}H_{35}COOH$[1], $C_6H_5NH_2 \cdot HCl$[2] or various metal chlorides[3] on Cu plate has been studied, and it was noticed that the reaction of metal salt with molten Sn-Pb solder or the dissolution of metal into Sn-Pb solder from metal salt is an important factor controlling spread.

And recently, it has been reported on the relation between the spreadability of solder and the reaction of molten Sn with various metals in inorganic metal salt (eq. (1)) or the dissolution of various metals into molten Sn, using inorganic metal salt (sulfate and nitrate salt)-$C_6H_5NH_2HCl$ system fluxes.[4]

$$MSO_4 + Sn \longrightarrow SnSO_4 + M-(Sn) \quad (1)$$

In this report, the flux action of above fluxes on Ni and Fe plates was studied on the basis of reactivity of the flux with the substrates, or with Sn solder.

2. Experimental Procedures and Experimental Apparatus

The same apparatus and procedure for spreading test of previous paper[5] were used. Commercially available reagent grade $C_6H_5NH_2 \cdot HCl$, various silver and copper salts were used for corrosion or spreading test after drying. The property of various silver and copper salts used in this test is shown in **Table 1.** Ni plate (99.9 %) and Fe (mild steel) (40×40×0.4 m/m) polished with #06 emery paper were used as base metal, and Sn (99.999 %) is used as solder. The dissolution into Sn solder of Ag and Cu produced by the reaction of molten Sn with various Ag salts and Cu salts was elucidated by analyzing by EPMA the cross section of specimens after spreading test.

Table 1. Properties of Cu and Ag salts.

Compound	M. P. (°C)	Decomp. Temp. (°C)
Ag_3PO_4	849	—
Ag_2SO_4	652	—
Ag_2CO_3	—	218
$AgNO_3$	212	444
$Cu(NO_3)_2 \cdot 3H_2O$	—	26.4 ($-3H_2O$)
$CuSO_4$	—	>600

3. Results and Discussions

3.1 Reaction of Cu, Ni and Fe plates with $C_6H_5NH_2 \cdot HCl$

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The flux action of soldering on various base metals may be elucidated only by knowing the reaction of the substrates with flux. So, $C_6H_5NH_2 \cdot HCl$ (2g) and test specimen (10×10×0.4 m/m) reacted in test tube at 250°C as shown in previous paper[6]. And weight loss of Cu, Ni and Fe per unit area (1 cm^2) was measured with time. The results of above test are shown in **Fig. 1.** As shown in Fig. 1, the corrosion amount of various metals showed linear relationship to the corrosion time, then the increase in the corrosion rate as we go from Ni, to Cu, and to Fe was shown. The corrosion amount of various metals per 1 min. is 14 mg/cm^2, 4mg/cm^2 and 0.5 mg/cm^2 respectively for Fe, Cu and Ni plates. It is considered that $CuCl_2$, $NiCl_2$, $FeCl_2$ and $FeCl_3$ are produced by the reaction of these metals with $C_6H_5NH_2 \cdot HCl$ as shown in the following equations. A large amount of corrosion product is produced especialy in the case of Fe base plate.

$$2C_6H_5NH_2 \cdot HCl + Ni \longrightarrow NiCl_2 + 2C_6H_5NH_2 + H_2 \text{ ----(2)}$$

$$2C_6H_5NH_2 \cdot HCl + Cu \longrightarrow CuCl_2 + 2C_6H_5NH_2 + H_2 \text{ ----(3)}$$

$$2C_6H_5NH_2 \cdot HCl + Fe \longrightarrow FeCl_2 + 2C_6H_5NH_2 + H_2 \text{ ----(4)}$$

$$6C_6H_5NH_2 \cdot HCl + 2Fe \longrightarrow 2FeCl_3 + 6C_6H_5NH_2 + 3H_2 \text{ ----(5)}$$

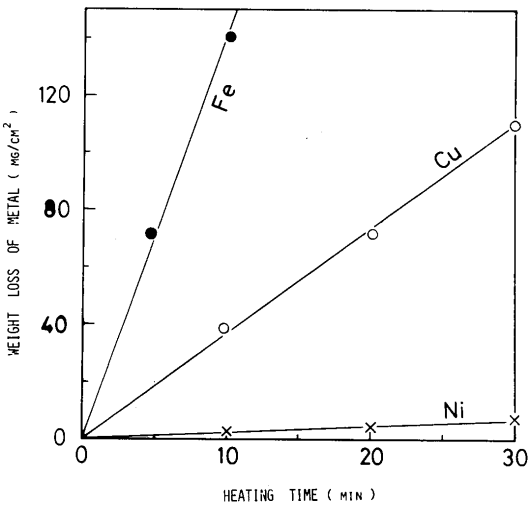

Fig. 1. Corrosion of Cu, Ni and Fe by $C_6H_5NH_2 \cdot HCl$.

3.2 The effect of various corrosion products on spreadability

The reaction between $C_6H_5NH_2 \cdot HCl$ and various substrates was clarified in above section. So, the spreading test on Cu, Ni and Fe plates at 250°C during 45 sec was tried in order to study the effect of the corrosion products ($NiCl_2$, $CuCl_2$, $FeCl_2$ and $FeCl_3$) by above reactions on spreading.

The results obtained are shown in **Fig. 2.** From Fig. 2, the effect of corrosion products on spread increases as we go from $FeCl_3$, to $FeCl_2$, to $NiCl_2$ and

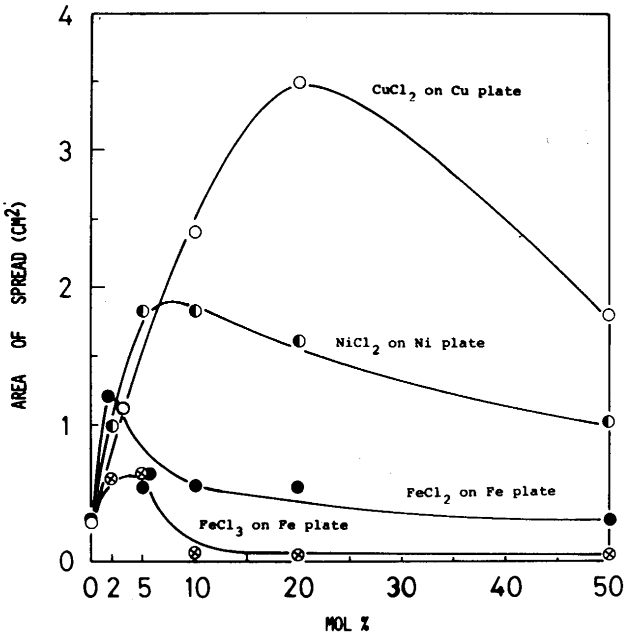

Fig. 2. Spreading of Sn solder on various plates (Cu, Ni and Fe) with $C_6H_5NH_2 \cdot HCl$/metal chloride flux at 250°C.

to $CuCl_2$. The large effect of $CuCl_2$ on Cu plate or $NiCl_2$ on Ni plate on spread is explained by the flux action as described in previous papers[9]. However, the effect of $FeCl_2$ and $FeCl_3$ on spread decreases largely in proportion to increase of added amounts of $FeCl_2$ and $FeCl_3$, and is little recognized.

By analyzing by EPMA in **Fig. 3,** the flux action of iron chlorides is considered to be due to $FeSn_2$ produced on Sn solder by the reaction between molten

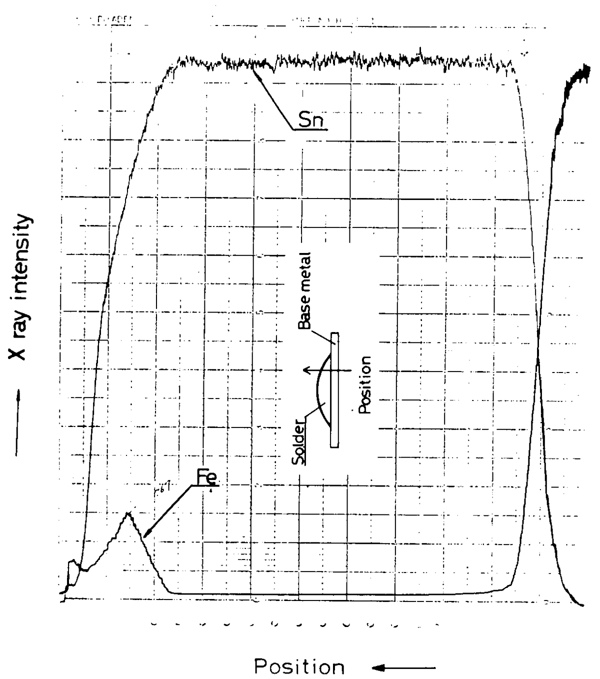

Fig. 3. X-ray micro-analysis of Fe and Sn of cross section of Sn solder spread on Fe plate with $FeCl_3$.

Sn and $FeCl_2$ or $FeCl_3$ (eq. (6)~(7)), because $FeSn_2$ is solidified on the surface of Sn solder at test temperature (250°C), therefore, the flow of Sn on Fe plate is obstructed.

$$FeCl_2 + Sn \longrightarrow SnCl_2 + Fe \quad \text{------------------------------(6)}$$

$$Fe + 2Sn \longrightarrow FeSn_2 \quad \text{------------------------------------(7)}$$

Degree of wetting of Sn molten on Fe plate, by using $C_6H_5NH_2 \cdot HCl + 2$ mol% $FeCl_2$, $C_6H_5NH_2 \cdot HCl + 5$ mol%$FeCl_2$ and $C_6H_5NH_2 \cdot HCl + 10$ mol%$FeCl_2$ flux is shown in **Photo. 1.** From Photo. 1, addition of $FeCl_2$ to $C_6H_5NH_2 \cdot HCl$ is known to decrease wetting on Fe plate, morover to increase the amount of $FeSn_2$ on Sn solder surface*. (White part in photo shows the existence of $FeSn_2$).

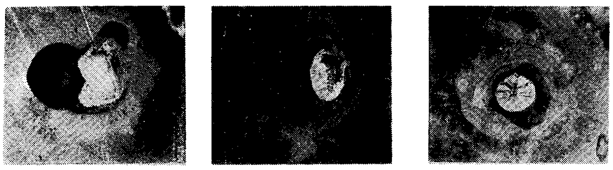
2Mol.%FeCl2 5Mol.%FeCl2 10Mol.%FeCl2

Photo. 1. Outward appearance of Sn solder spread on Fe plate with $C_6H_5NH_2 \cdot HCl/FeCl_2$ system flux.

The formation of $FeSn_2$ by the reaction of Fe substrate was recognized at 430°C, 350°C and 460°C, respectively in the case of pure iron (0.005 %C), low carbon steel (0.4 %C) and high carbon steel (0.95 %C) by Ishii et al.[7], and at 350°C, when $SnCl_2$ is used as flux, by Ueda et al.[8]

From the above results, it was shown that the amount of $FeSn_2$ produced on Sn solder by the reaction of Sn with $FeCl_2$ or $FeCl_3$ controlled spread on Fe plate, when $C_6H_5NH_2 \cdot HCl$ flux was used.

3.3 Effect of $C_6H_5NH_2 \cdot HCl$/silver salt system flux on spread on Fe plate

As described in earlier paper[3], the large effect of silver sulfate and nitrate on wetting on Cu plate was shown. So, we consider that silver salt may be effective to the improvement of wetting on Fe plate, because silver salt reacts easier with Sn solder than Fe salts by reaction between Fe plate and $C_6H_5NH_2 \cdot HCl$, then the formation of $FeSn_2$ on solder may be disturbed.

Accordingly, the flux action of various silver salts on Fe plate was studied in this section. The results of spreading tests ate shown in **Fig. 4.** As shown in Fig. 4, we note that the flux action of silver salts on Fe plate shows large effect and increases on going to $AgNO_3$, to Ag_2SO_4, to Ag_3PO_4 and to Ag_2CO_3. The dissolution of Fe or Ag in Sn solder was investigated by EPM analysis of cross section of spreading test specimens, in order to elucidate the difference of flux action of each Ag salt.

The relation between spread area, the amount of Fe on Sn solder and the amount of Ag in solder is summarized in **Table 2,** when 5 mol% silver salts and copper salts are used. And line analysis of cross section are shown in **Fig. 5** and **Fig. 6,** respectively in the case of Ag_2SO_4 and $AgNO_3$ flux.

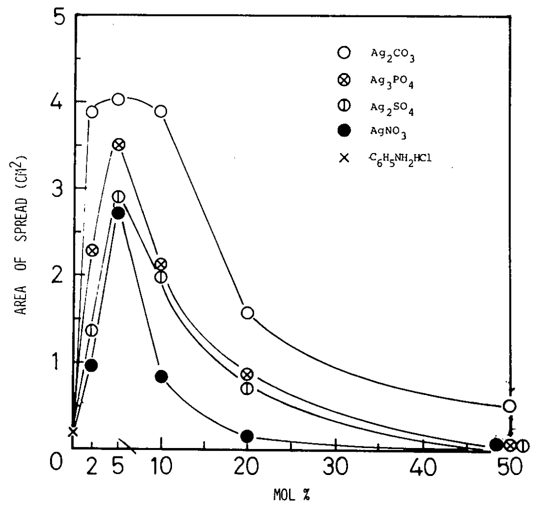

Fig. 4. Spreading of Sn solder on Fe plate with $C_6H_5NH_2 \cdot HCl$/silver salts flux at 250°C.

Table 2. The relation between spreading, the amount of Fe on Sn surface and the amount of Ag or Cu in Sn solder.

Flux	Spread area (max. cm^2)	Fe%* at Sn surface after spreading	Ag%* or (Cu%*) in Sn after spreading
Ag_2CO_3	4.0	0	15
Ag_3PO_4	3.5	4	12
Ag_2SO_4	2.9	10	5
$AgNO_3$	2.7	11	4
$CuSO_4$	3.0	2.7	(6)
$Cu(NO_3)_2 \cdot 3H_2O$	0.8	13	(0.6)
$FeCl_3$	0.6	16	——

* Relative intensity by EPMA, ( ) indicates the value in Sn spread on Ni plate.

* Similar phenomenon was seen, in the case of $CrCl_3$ flux on Ni plate.

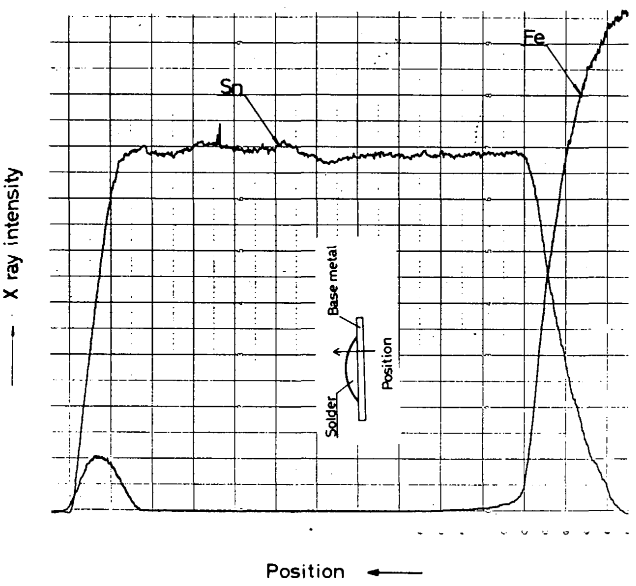

Fig. 5. X-ray micro-analysis of Sn and Fe of cross section of Sn solder spread on Fe plate with Ag_2SO_4.

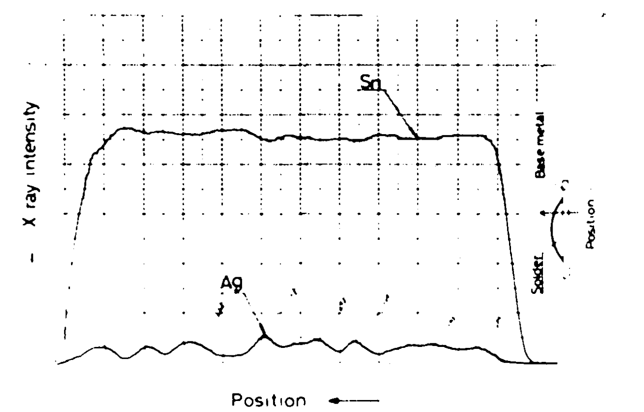

Fig. 6. X-ray micro-analysis of Sn and Ag of cross section of Sn solder spread on Fe plate with Ag_2SO_4.

From Table 2, we know that the greater Fe exists on Sn surface, the smaller the spread area becomes, and the more the amount of Ag in solder decreases. As described in above section, the increase of spread area by decrease of amount of Fe on solder surface is due to the effect of $FeSn_2$ produced by the reaction of Sn with Fe salts, which were given by the reaction between $C_6H_5NH_2 \cdot HCl$ and Fe plate. And the effect of Ag amount in solder on spread area is considered that Ag salt reacts more with Sn than Fe salts, so the formation of $FeSn_2$ on Sn surface is disturbed, and a large amount of Ag in Sn solder brings about the increase of wetting.

For example in the case of Ag_2CO_3, a large amount of Ag is produced in Sn solder as shown in Table 2, because molten Sn reacts only with Ag_2CO_3 and $FeSn_2$ does not form, so spreading is promoted. However, in the cases of other silver salts ($AgNO_3$ etc.) the decrease of spread area in comparison with the case of Ag_2CO_3 is considered to depend on the formation of $FeSn_2$ on Sn surface.

From the above results, the wetting of Sn on Fe plate by using Ag salt-$C_6H_5NH_2 \cdot$ HCl system flux, is considered to be dependent on the amount of Ag dissolved into Sn solder and the amount of Fe on Sn surface, that is, on reactivity among molten Sn and Ag salt or Fe salt produced by the reaction of $C_6H_5NH_2 \cdot$ HCl with Fe plate.

3.4 Effect of $C_6H_5NH_2 \cdot HCl$/copper salt system flux on spread on Fe plate

The flux action of copper salts ($CuSO_4$, $Cu(NO_3)_2$) to spread on Fe plate was studied by the same method as in section 3.3., to know the relation between spread and amount of Cu dissolved in solder or amount of Fe on Sn surface.

The spreading test results are shown in **Fig. 7.** From the figure, the remarkably differente effect on spread between sulfate and nitrate was noticed. The flux action of $CuSO_4$ shows greater effect than that of $Cu(NO_3)_2$.

In order to know the cause for difference of the action, EPM analysis was tried. The results are shown in Table 2 and line analysis by EPMA is shown in **Fig. 8** for nitrate.

From Table 2 and Fig. 8, we know that the formation of $FeSn_2$ on Sn surface is little recognized and copper of flux dissolves markedly in all the part of Sn solder, when $CuSO_4$ is used as flux. Nevertheless, in the case of $Cu(NO_3)_2$, $FeSn_2$ forms evidently on Sn surface and the dissolution of Cu from flux into Sn solder is barely observed as shown in Fig. 8. These

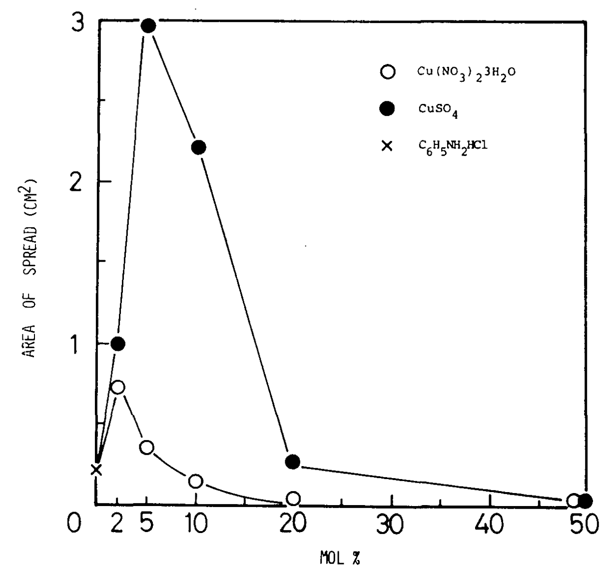

Fig. 7. Spreading of Sn solder on Fe plate with $C_6H_5NH_2HCl$/Cu salts flux at 250°C.

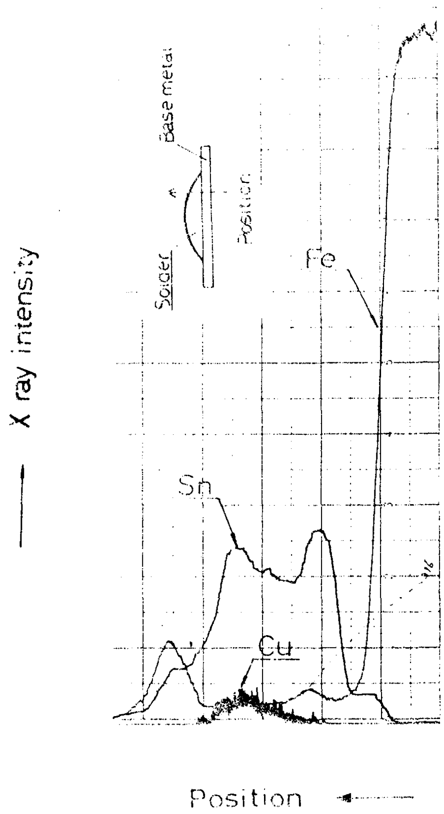

Fig. 8. X-ray micro-analysis of Fe, Sn and Cu of cross section of Sn solder spread on Fe plate with $Cu(NO_3)_2$.

facts for copper salts showed similar results as in the case of various silver salts.

We note that wetting of Sn on Fe plate is dependent on the formation of $FeSn_2$ on Sn surface and the dissolution of copper metal, as is shown in the case of Ag salt flux, when $C_6H_5NH_2\cdot HCl$-copper salt system fluxes are used.

3.5 Effect of various Ag salts and Cu salts on spread of Sn solder on Ni plate

In comparison with the reaction of $C_6H_5NH_2\cdot HCl$ with Fe substrate, the reaction with Ni substrate was little recognized in this spreading conditions. Accordingly, we need not consider the effect of $NiCl_2$ on spread, but only flux action of Ag salt or Cu salt on Ni plate. Spreading tests were tried by the same method as on Fe plate, in order to know the flux action of Ag salt or Cu salt on Ni plate.

The results are shown in **Fig. 9** and **Fig. 10,** respectively for Ag salt and Cu salt. As shown in Fig. 9, the spread increases on going to $AgNO_3$, to Ag_2SO_4, to Ag_3PO_4, and to Ag_2CO_3 and the degree of effect of Ag salts on spread shows the similar results as in the case of Fe plate. However, spread area on Ni plate showed larger value than on Fe plate, in all the case of Ag salts. EPM analysis of test specimens in each case of various Ag salts was tried in order to know the difference of Ag salt flux action between both plates. **Fig. 11** shows line analysis for Ag_2SO_4.

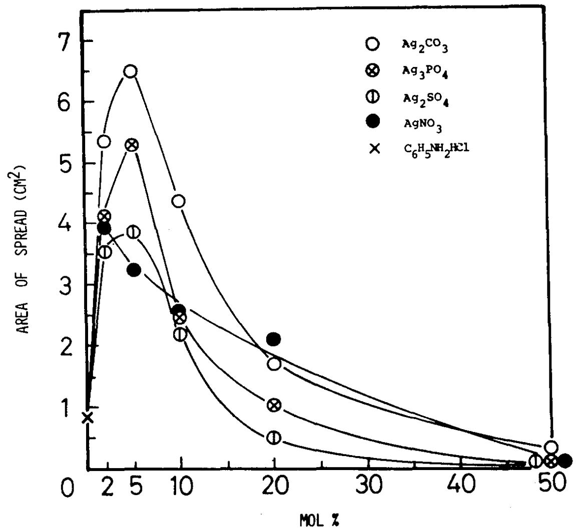

Fig. 9. Spreading of Sn solder on Ni plate with $C_6H_5NH_2\cdot$ HCl/silver salts flux at 250°C.

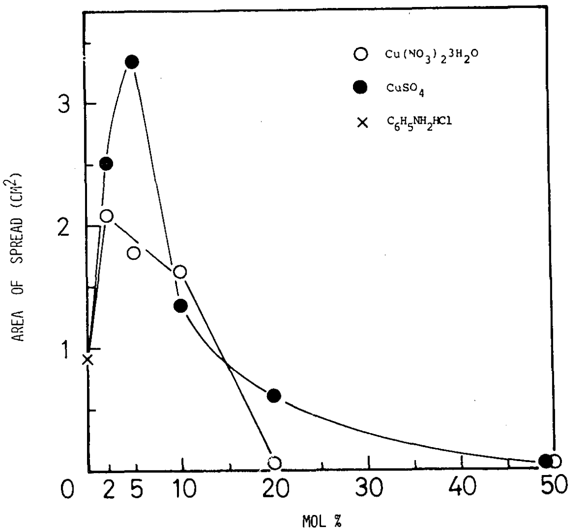

Fig. 10. Spreading of Sn solder on Ni plate with $C_6H_5NH_2\cdot$ HCl/Cu salts flux at 250°C.

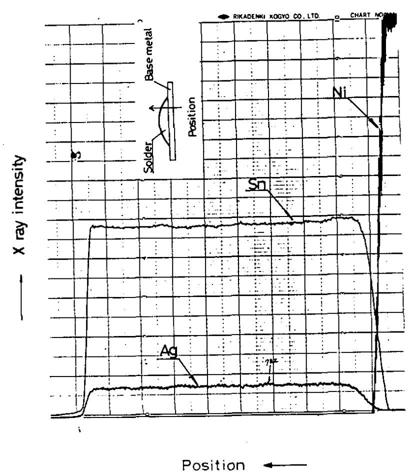

Fig. 11. X-ray micro-analysis of Ag, Sn and Ni of cross section of Sn solder spread on Ni plate with Ag_2SO_4.

From the EPM analysis, the dissolution of Ni into Sn solder was little recognized in all the case of Ag salt fluxes, but the remarkable difference in the the amount of Ag dissolved into Sn solder was recognized depending on the kind of Ag salts.

In the case of Cu salts, the results of EPM analysis is showed in **Fig. 12** for $Cu(NO_3)_2$. And the amount of Cu dissolved in Sn solder is shown in Table 2. From result of EPM analysis, we know that the more Cu dissolves in Sn solder, the greater the spread increases. However, the dissolution of Ni from flux produced by the reaction between Ni plate and $C_6H_5NH_2\cdot$ HCl, was little recognized too, in the case of Cu salts as described in the case of various Ag salts.

From above results, the effect of various Ag salts or Cu salts on wetting on Ni plate, was shown only by the difference in the amount of Ag or Cu dissolved into Sn solder, that is, the reactivity between molten Sn and fluxes.

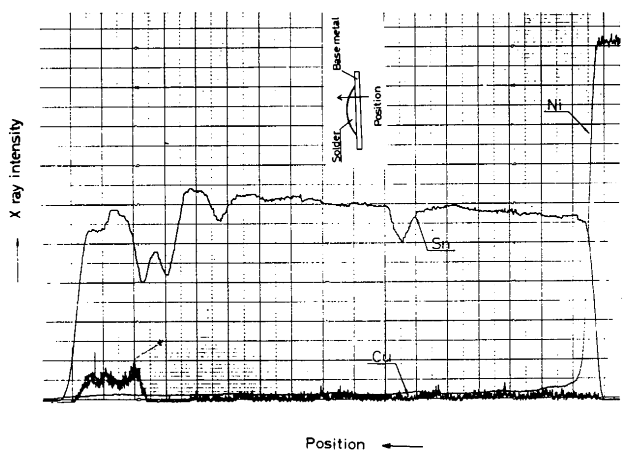

Fig. 12. X-ray micro-analysis of Sn, Cu and Ni of cross section of Sn solder spread on Ni plate with $Cu(NO_3)_2$.

4. Conclusion

Flux action of $C_6H_5NH_2\cdot$ HCl-Ag salt or $C_6H_5NH_2\cdot$ HCl-Cu salt on Fe or Ni plate was studied on the relation between the reaction of Sn solder or substrate with above fluxes and spreading phenomenon.

The results obtained were as follows:

1) It was shown that corrosion reaction between base metals and $C_6H_5NH_2\cdot$ HCl flux increased as we go from Ni, to Cu, and to Fe.

2) The effect of corrosion products on wetting increased as we go from Fe salt, to $NiCl_2$, and to $CuCl_2$.

3) $FeSn_2$ was formed on Sn solder surface by the reaction of molten Sn with $FeCl_2$ or $FeCl_3$, and obstructed the wetting of Sn solder, when $FeCl_2$ or $FeCl_3$ was used as flux.

4) The amount of $FeSn_2$ on Sn solder controlled flow and spread on Fe plate, depending on the amount of Ag or Cu in Sn solder, when various Ag salts or Cu salts was used as flux.

5) The effect of above fluxes on wetting on Ni plate was shown only by the amount of Ag or Cu dissolved in Sn solder.

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