Studies on Flux Action of Soldering (Report II)†
—Amine Hydrochloride—

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Abstract

In this report, aniline hydrochloride flux action of soldering was studied on the relation between the reaction of flux with base metal (Cu) or with Sn-Pb alloy solder and spreading phenomenon.

The flux action of aniline hydrochloride may be considered as follows:

Molten aniline hydrochloride reacts with copper of base metal to give $CuCl_2$ and copper complex, which react with molten Sn-Pb alloy solder to give metal copper. Copper dissolves immediately into molten solder and the thin Cu-rich layer at the outer surface of molten solder is formed. The wetting of Sn-Pb alloy solder on copper plate is improved by the reaction and the dissolution of Cu into molten solder. So, Sn-Pb alloy solder spreads well over copper plate.

1. Introduction

Rosin is generally used as flux for soft soldering, however, the rosin flux is less active than fluxes like $ZnCl_2$-NH_4Cl, $C_6H_5NH_2\cdot HCl$ etc. Therefore, the activate rosin flux, added $C_6H_5NH_2\cdot HCl$ to rosin, is used in order to improve spreading for solder on base metal. The improvement for spread with $C_6H_5NH_2\cdot HCl$ flux has been reportedly attributed to be the elimination[1] of oxides on copper plate. However, the basic factors controlling flow and spread with respect to the flux are not well understood.

In our recent publication[2], we have reported on the stearic acid flux action of soldering, as follows: Molten stearic acid reacts with copper oxide to give copper stearate which reacts with molten Sn-Pb eutectic alloy solder, and the Cu-rich layer at outer surface of solder is formed. The spreading of solder on copper specimen is improved by the reaction and the dissolution of Cu into the solder.

The main purpose of this study is to elucidate the reaction of molten flux ($C_6H_5NH_2\cdot HCl$ etc.) with copper plate, and the relation between the one of the copper compounds with molten Sn-Pb alloy solder and the spreading of the solder, in comparison with the results in the case of stearic acid flux.

2. Experimental Procedure

The same apparatus for spreading test of previous study[2] was used. Copper specimens were polished with 06# emery paper and electropolished to obtain a uniformly bright surface. Grease and dust were removed by washing with acetone just before the testing. Both Sn-Pb alloy solder (100 mg) and flux (100 mg) placed in the center of the copper plate, and the specimen was maintained for 45 sec at required temperature (250°C).

The treatment after spreading test was done by using the same method as described in the earlier paper. The reaction of the flux with copper plate was tried in test tube under similar conditions as described in the spreading test. The reaction products were identified by chemical analysis. And the cross section of the spreading specimens was analyzed by EMX analysis.

3. Results and Discussions

3.1 EMX analysis of cross section of specimens after spread test

In the case of stearic acid flux, the reaction of Cu-stearate with molten Sn-Pb eutectic alloy solder and the dissolution of Cu-metal into solder played an important role in spreading.

In order to reveal the flux action and the dissolution of Cu-metal into solder in the case of aniline hydrochloride ($C_6H_5NH_2\cdot HCl$), the cross section of the specimen after Sn solder spread on copper plate using aniline hydrochloride flux was analyzed with EMX analyzer. **Figure 1** shows the concentration distribution curve obtained by the EMX analysis of the specimen. The left half of the concentration curve in the figure shows surface layer of Sn solder, and the right one shows bonded layer between solder and base metal (Cu). From this result, it was recognized

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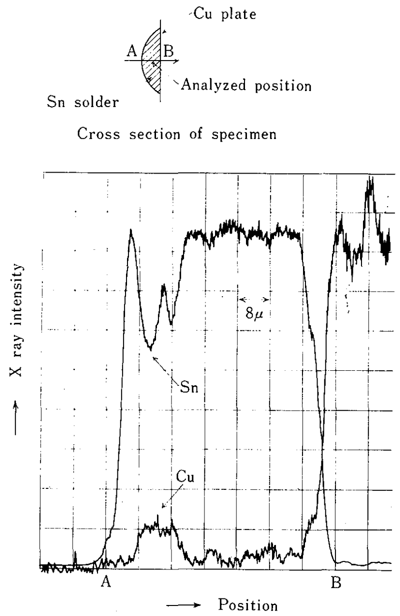

Fig. 1. Analysis of cross section of Sn spread on copper plate with $C_6H_5NH_2 \cdot HCl$.

that Cu-metal dissolved into Sn solder as shown in **Fig. 9** in previous paper[2].

Therefore, it may be considered that the Cu-metal in Sn solder is produced by the reaction of molten Sn with copper compound, which in return was produced by the reaction of molten aniline hydrochloride with base metal (Cu).

3.2 Reaction of various molten amine hydrochlorides with Cu-plate and spreadability

The reaction of molten $C_6H_5NH_2 \cdot HCl$ with Cu-plate was studied in this section, in order to comfirm that copper compounds were produced by the reaction.

$C_6H_5NH_2 \cdot HCl$ (1 g) and electropolished Cu-plate (0.34 g) reacted in test tube for 1 hr at 250°C.

Gaseous product and aniline were evolved from the reaction. Aniline was identified by comparing its infrared spectrum with that of authentic sample.

After the reaction, solid product was dissolved into water, and the non-water-soluble blue product was separated and identified as $Cu[C_6H_5NH_3]_2Cl_4$ by the elementary analysis. Moreover, Cu^{++} ion was detected in the aqueous solution. From this result, it was comfirmed that $C_6H_5NH_2 \cdot HCl$ reacted with Cu-plate to give $CuCl_2$ and $Cu[C_6H_5NH_3]_2Cl_4$ as shown in eq (1) and eq (2).

$$2C_6H_5NH_2 \cdot HCl + Cu \xrightarrow{\Delta} CuCl_2 + 2C_6H_5NH_2\uparrow + H_2\uparrow \quad (1)$$

$$2C_6H_5NH_2 \cdot HCl + CuCl_2 \xrightarrow{\Delta} Cu[C_6H_5NH_3]_2Cl_4 \quad (2)$$

Moreover, the effect of the reaction on time was studied using various amine hydrochlorides ($C_6H_5NH_2 \cdot HCl$, $C_2H_5NH_2 \cdot HCl$ etc.).

- Electropolished Cu-plate (1 g) and amine hydrochloride flux (0.023 mol) reacted in test tube at 250°C. **Figure 2** shows the change of the reaction with time.

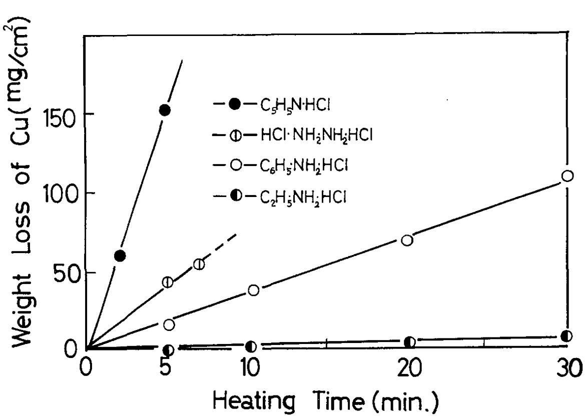

Fig. 2. Corrosion of copper plate in various amine hydrochloride fluxes at 250°C.

The corrosion rate (k) is expressed as variation in the weight per unit surface and unit time, and the increase in the corrosion rate on going to $C_2H_5NH_2 \cdot HCl$, to $C_6H_5NH_2 \cdot HCl$, to $HCl \cdot NH_2NH_2 \cdot HCl$, and to $C_5H_5N \cdot HCl$ is shown in **Fig. 2.**

In order to know the relation between the corrosion rates for various amine hydrochlorides and spreadability, spread for Sn solder on copper plate was tested for 20 sec using these fluxes. The relation between the corrosion rate (k) in **Fig. 2** and the spread area with respect to various fluxes was shown in **Fig. 3.** From this result, the increase in the corrosion rate (k) caused the increase in the spread area. So, it may be considered that $CuCl_2$ or Cu-complex produced by the reaction of aniline hydrochloride flux with Cu-plate plays an important role in spreading of Sn solder using the flux.

3.3 Effect of reaction between $CuCl_2$ and molten solder on the spreadability

3.3.1 Reaction of $CuCl_2$ with molten Sn

The reaction of Cu-stearate with molten Sn-Pb

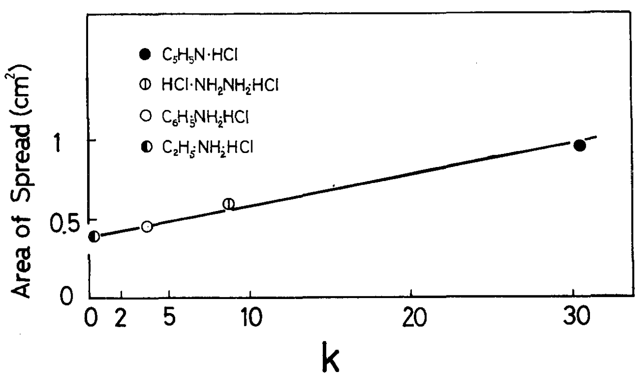

Fig. 3. Relation between spread area and corrosion rate (k) in Fig. 2.

eutectic alloy solder was an important factor, controlling spread of the solder as described in previous paper[2].

The dissolution of Cu-metal into Sn solder was found as shown in **Fig. 1** in the case of aniline hydrochloride. The reaction of $CuCl_2$ with molten Sn-Pb alloy was taken in consideration on the basis of thermal kinetics. ΔF° values for the reaction at 250°C was calculated and the values were shown in eq. (3) ~(5). Since the $-\Delta F^\circ$ values for the formation of $SnCl_2$, $SnCl_4$ and $PbCl_2$ were plus, such reactions may proceed. Then the reaction of $CuCl_2$ with Sn was experimented.

$CuCl_2$ (13.6 g) reacted with molted Sn (17.08 g) at 250°C for 15 min. to give $SnCl_4$ (11.33 g, b. p. 114°C).

After the reaction, Cu-metal was found on the surface of Sn solidified. This result shows that the formation of $SnCl_4$ through the reaction is easy thermaly to proced. In the case of Sn-Pb solder, $SnCl_4$ and $PbCl_2$ yielded by the reaction of $CuCl_2$ with molten solder.

$$CuCl_2 + Sn \rightarrow SnCl_2 + Cu \quad -\Delta F^\circ = 33.9 \text{ Kcal/mol} \quad (3)$$

$$2CuCl_2 + Sn \rightarrow SnCl_4 + 2Cu \quad -\Delta F^\circ = 43.0 \text{ Kcal/mol} \quad (4)$$

$$CuCl_2 + Pb \rightarrow PbCl_2 + Cu \quad -\Delta F^\circ = 36.5 \text{ Kcal/mol} \quad (5)$$

3.3.2 Spreadability of Sn-Pb alloy solder with $CuCl_2/C_6H_5NH_2 \cdot HCl$ system flux

In order to elucidate the effect of the reaction of $CuCl_2$ with Sn-Pb alloy solder on spreading of the solder, the spread was tested using Sn-Pb alloy solder, and $C_6H_5NH_2 \cdot HCl/CuCl_2$ system flux with different compositions. The results are shown in **Fig. 4.** As the figure shows, the addition of $CuCl_2$ to $C_6H_5NH_2 \cdot HCl$ has a great effect on the improvement of spreading of all the solders of Sn, Sn-5 % Pb and Sn-10 % Pb.

The concentration of $CuCl_2$ in the flux, with which spread area showed maximum value, increased with the decrease of amount of Pb in the solder. However spread area decreased in the case of Sn-Pb eutectic alloy solder, when a small portion of $CuCl_2$ was added to $C_6H_5NH_2 \cdot HCl$. Moreover the solder did not wet the copper plate when 60 mol % $CuCl_2$ flux was used, and white solid ($PbCl_2$) formed on the surface of the solder during spreading test.

3.3.3 Spreadability of Sn-Pb alloy solder with $CuCl_2/C_2H_5NH_2 \cdot HCl$ flux system

As **Fig. 2** shows, molten $C_2H_5NH_2 \cdot HCl$ reacted less with Cu-plate at 250°C and gave the smaller amount of $CuCl_2$ than $C_6H_5NH_2 \cdot HCl$, So, the effect

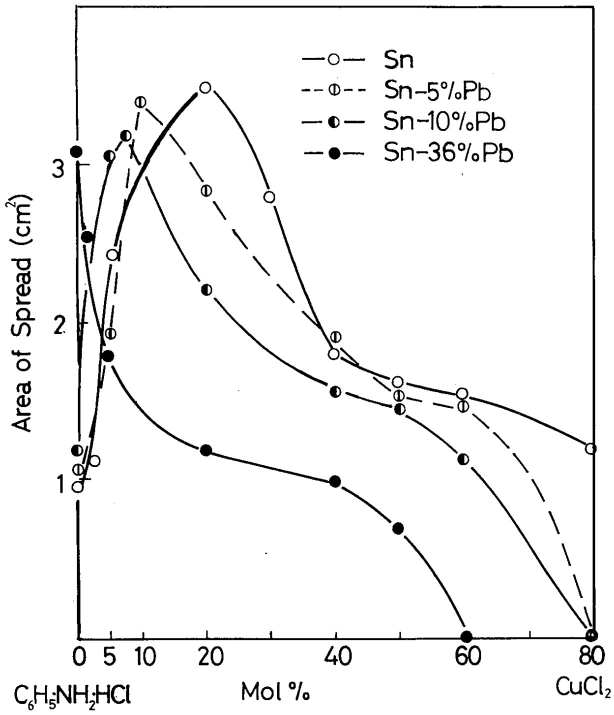

Fig. 4. Spreading of various solders on copper plate with $C_6H_5NH_2 \cdot HCl/CuCl_2$ flux.

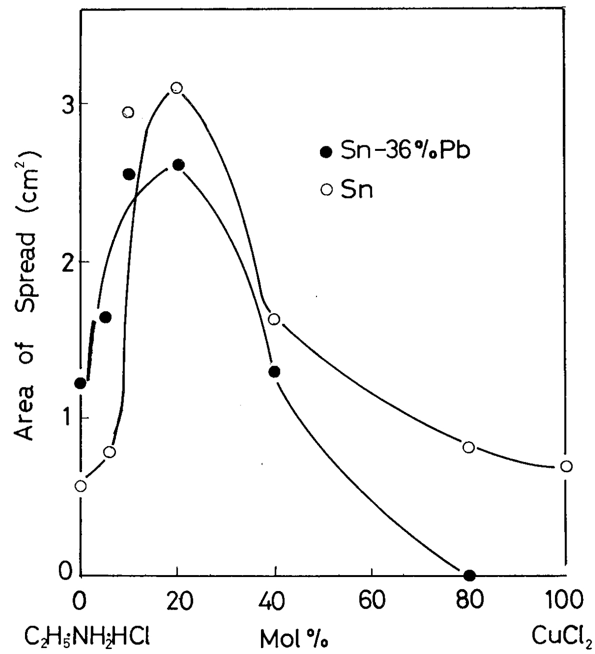

Fig. 5. Spreading of solder on copper plate with $C_2H_5NH_2 \cdot HCl/CuCl_2$ flux.

of the addition of $CuCl_2$ on spreading may be estimated more precisely using $C_2H_5NH_2 \cdot HCl$ rather than $C_6H_5NH_2 HCl$. The results of spreading test using $C_2H_5NH_2 \cdot HCl/CuCl_2$ flux system are shown in **Fig. 5.**

The addition of $CuCl_2$ to $C_2H_5NH_2 \cdot HCl$ had a great effect on improvement in spreading of both Sn and Sn-Pb eutectic alloy solder in contrast with results in section 3.3.2.

3.3.4 Effect of $CuCl_2$ on spreadability of Sn-Pb alloy solder

Spreadability on Sn solder was improved by the addition of $CuCl_2$. The effect of $CuCl_2$ on spreading may depend on both the reaction of $CuCl_2$ with molten Sn and the dissolution of Cu into Sn.

However, spreading was inhibited when the flux of more than 30 mol % $CuCl_2$ was used.

The inhibition for spreading may be explained as follows: The higher the concentration of $CuCl_2$ in the flux becomes, the easier the reaction of $CuCl_2$ with Sn is to give more amount of Cu. The Cu-metal, which does not dissolve into Sn solder and coats the surface of the solder, inhibiting the spreading. On the other hand, the spread for Sn-Pb eutectic alloy solder increases when in the addition of $CuCl_2$ to $C_2H_5NH_2 \cdot HCl$ and decreases when a small portion of $CuCl_2$ was added to $C_6H_5NH_2 \cdot HCl$. The reason may depend on the difference in corrosion rate of two fluxes with Cu-plate, and in the difference of the amount of $CuCl_2$ produced by the reaction of the fluxes with Cu-plate. Then, the difference in spreadability of two solders, in the case of $CuCl_2$-amine hydrochloride system flux, may depend on the reaction of metal copper with the two solders (It is reported[3] that Sn reacts with Cu at the rate about three orders of magnitude greater than Pb, and a Pb-rich solder causes less reaction). So, spreadability of solder on Cu-plate depends on the concentration of Pb in solder and the amount of Cu-metal produced by the reaction of $CuCl_2$ with solder. In order to know the dissolution of Cu-metal into solder, when $CuCl_2$ was added to $C_6H_5NH_2 \cdot HCl$, the cross section of the sprecimens after spreading of Sn and Sn-5 % Pb solder on copper plate with $CuCl_2/C_6H_5NH_2 \cdot HCl$ flux system was analyzed with EMX analyzer.

The results were shown in **Fig. 6** for Sn solder

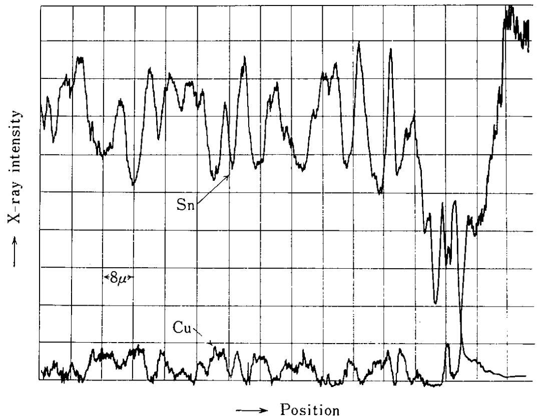

Fig. 6. Analysis of cross section of Sn spread on copper plate with $C_6H_5NH_2 \cdot HCl/CuCl_2$ flux.

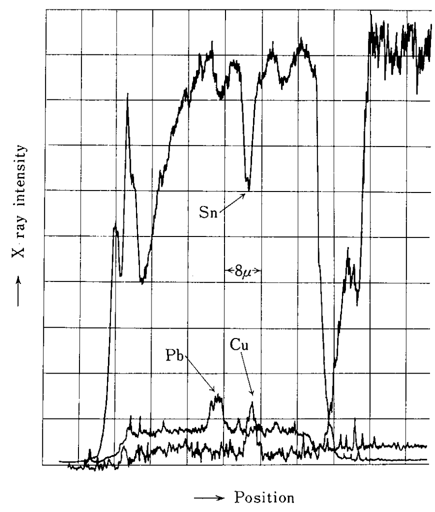

Fig. 7. Analysis of cross section of Sn-5 % Pb spread on copper plate with $C_6H_5NH_2 \cdot HCl/CuCl_2$ flux.

and in **Fig. 7** for Sn-5 % Pb solder.

We note that Cu-metal dissolves more greatly in Sn solder than in Sn-5 % Pb solder.

3.4 Effect of Cu-amine complex on spreadability

3.4.1 Spreadability of Sn-Pb alloy solder with Cu-complex/$C_6H_5NH_2 \cdot HCl$ flux system

Aniline hydrochloride ($C_6H_5NH_2 \cdot HCl$) reacted with $CuCl_2$ to give Cu-complex [$Cu(C_6H_5NH_3)_2Cl_4$]. Then spread was tested using Cu-complex/$C_6H_5NH_2 \cdot HCl$ flux system in order to elucidate the effect of the Cu-complex on spreadability.

As **Fig. 8** shows, the values of spread area increased markedly with the addition of Cu-complex to

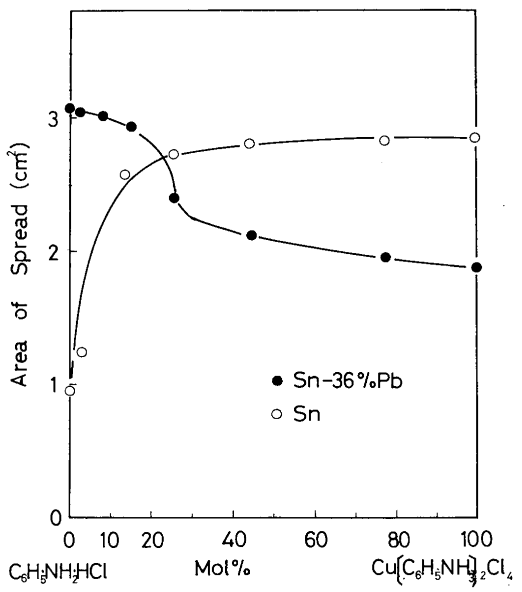

Fig. 8. Spreading of solder on copper plate with $C_6H_5NH_2 \cdot HCl$ /Cu-complex flux.

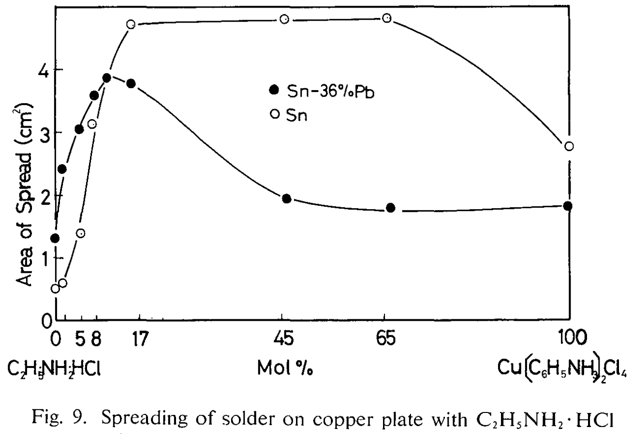

Fig. 9. Spreading of solder on copper plate with $C_2H_5NH_2 \cdot HCl$ /Cu-complex flux.

$C_6H_5NH_2 \cdot HCl$, and did not decrease with the increase of the concentration of Cu-complex in the case of Sn solder. Moreover, the values of spread area for Sn-Pb eutectic alloy solder decreased more gradually with the increase of concentration of Cu-complex than those for the same solder using $CuCl_2$.

3.4.2 Spreadability of Sn-Pb alloy solder with Cu-complex/$C_2H_5NH_2 \cdot HCl$ flux system

As **Fig. 9** shows, spreadability for both Sn solder and Sn-Pb eutectic alloy solder was improved markedly by the addition of Cu-complex to $C_2H_5NH_2 \cdot HCl$.

The Cu-complex affected spreadability of Sn solder and Sn-Pb solder in similar manner as Cu-stearate did. As Cu-complex reacted slowly with molten Sn solder in comparison to $CuCl_2$ to yield Cu-metal, Cu-metal produced by the reaction did not coat the surface of solder and did not inhibit the spreading of the solder. The EMX analysis of the spread specimen using Cu-complex is shown in **Fig. 10.** The dissolution of Cu produced by the reaction of molten Sn solder with Cu-complex is observed. It became clear that the reaction of Cu-complex with solder and the dissolution of Cu into solder play an important role in spreading of solder on Cu-plate in the case of Cu-complex.

4. Conclusion

The reaction of Cu-plate with various molten amine hydrochloride fluxes played an important role in spreadability of Sn-Pb solder. Moreover, the addition of a small portion of $CuCl_2$ or Cu-complex had a great effect for the improvement of spreadability of the solder. $CuCl_2$ and Cu-complex reacted with molten Sn-Pb solder to give Cu-metal, which in return dissolved into the molten solder.

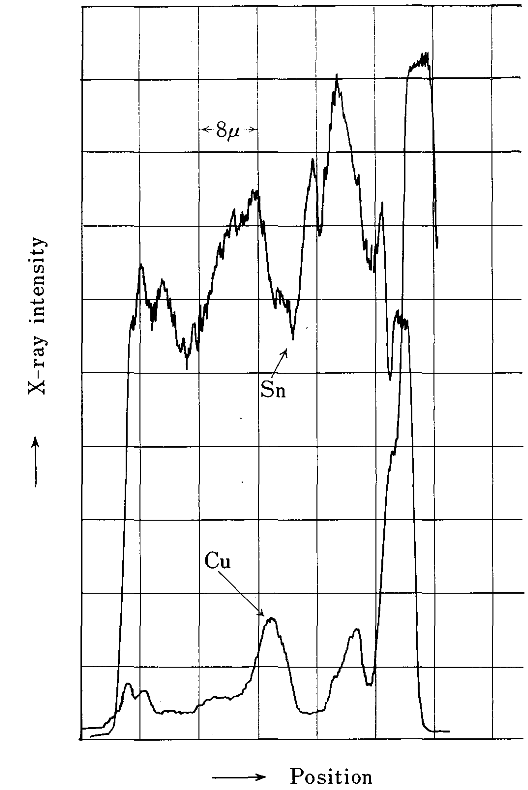

Fig. 10. Analysis of cross section of Sn spread on copper plate with $C_6H_5NH_2 \cdot HCl$/Cu-complex flux.

From these results, the flux action of aniline hydrochloride may be considered as follows:

Molten aniline hydrochloride reacts with Cu to produce $CuCl_2$ and Cu-complex, which then react with molten Sn-Pb alloy solder to give Cu-metal. The Cu dissolves immediately into molten solder and the thin Cu-rich layer at the outer surface of molten solder is formed. The wetting of Sn-Pb alloy solder on Cu-plate is improved by the reaction and the dissolution of Cu into molten solder. So, Sn-Pb alloy solder spreads well over Cu-plate.

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