Flux Development for Lead-Free Solders Containing Zinc

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New lead-free solders containing zinc are promising candidates to replace near-eutectic tin-lead solders because the solders melt at lower temperatures than Sn-Ag-base solders. They also possess good mechanical and fatigue properties and are less expensive. However, the contact angle on copper for Sn-Zn solders is high when fluxes used for Sn-Pb solders are utilized. A novel approach for flux development to improve wetting of copper surfaces by tin-zinc eutectic solder was developed: tin containing organic compounds, which decomposes at soldering temperatures and produces metallic tin on surfaces to be soldered was added to several specially formulated fluxes. This process improves wetting of copper surfaces by molten tin-zinc eutectic solder. Fluxes were developed that give a contact angle as low as 20°.

Key words: Tin-zinc eutectic, solder, flux, wetting angle

INTRODUCTION

New tin-base lead-free solders that contain zinc are promising candidates to replace near-eutectic tin-lead solders, because they posses good mechanical and fatigue properties[1] and are less expensive than alternative tin-based solders containing silver, indium, or bismuth. In addition, the melting point of the tin-zinc eutectic (198°C) is much closer to the melting point of commonly used tin-lead eutectic (183°C) than the melting point of Sn-Ag eutectic (221°C), one of the leading candidate for lead-free solder. However, Zn-bearing solders oxidize easily during soldering and for this and perhaps other reasons the contact angle on copper for Sn-Zn solders is rather high when utilized with fluxes developed for Sn-Pb solders. Tin chloride containing fluxes give satisfactory wetting, but they are corrosive and, therefore, unacceptable by the electronics industry. Thus, new active but non-corrosive and preferably no-clean fluxes are needed. This paper investigates a novel approach for flux development to improve wetting of copper surface by tin-zinc eutectic solder.

The function of the flux is to clean the substrate, protect molten solder and substrate from oxidation, and promote solder spreading. Usually fluxes contain activators that clean the substrate, vehicles that protect the surfaces of the substrate and molten solder from re-oxidation during soldering, and improve heat-transfer. Also, fluxes may contain some additives such as surfactants that improve the flux's performance.

It is well known that pre-tinning of surfaces promotes wetting of the substrate by solder. At the present time tin or tin-lead solders are used for pre-tinning. This procedure adds to the production cost. Also Sn-Pb coatings are unacceptable for a lead-free soldering system. Our research showed that $SnCl_2$ promotes good spreading of solders on copper not only because it is a very good activator but also because it reacts with copper to give tin or tin-copper intermetallics on the copper surface.[2] As this paper demonstrates, tin containing organic compounds that decompose at soldering temperatures and produce metallic tin on surfaces to be soldered can be added to the flux. This addition improves wetting of the copper surface by molten tin-zinc eutectic solder.

EXPERIMENTAL PROCEDURE

The fluxes were prepared by mixing together vehicles, activators, and additives. The polymers (from Aldridge Chemical Company) listed in Table I were used as vehicles. Thermal stability of the polymer at the soldering temperature and non-reactivity toward other components of the flux were the main criteria used for polymer selection. Poly(vinyl acetate) easily

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Table I. Polymers Used in the Research

	Polymer	Wt.% of Polymer in:	
Polymer	Abbreviation Used in Text	Methyl Alcohol	Isopropyl Alcohol
Poly(vinyl acetate) (m.w.$_{ave}$=83,000)	PVA	10%	1.3%
Poly(methyl methacrylate-co-methacrylic acid) (m.w.$_{ave}$=34,000)	PMM-MA	*	2.4%
Poly(methyl methacrylate) (m.w.$_{ave}$=999,000)	PMM	*	2.0%

*—Very low solubility

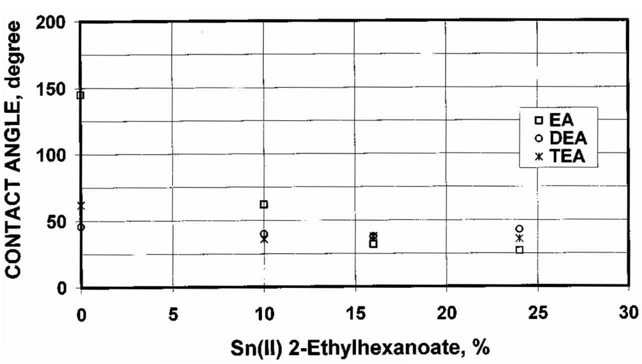

Fig. 1. Effect of tin(II) 2-ethylhexanoate concentration on wetting of copper by tin-zinc eutectic when poly(vinyl acetate) solution in isopropyl alcohol is used. Polymer solution to amine ratio is 1:1. Polymer solution + amine + SnII equals 100%.

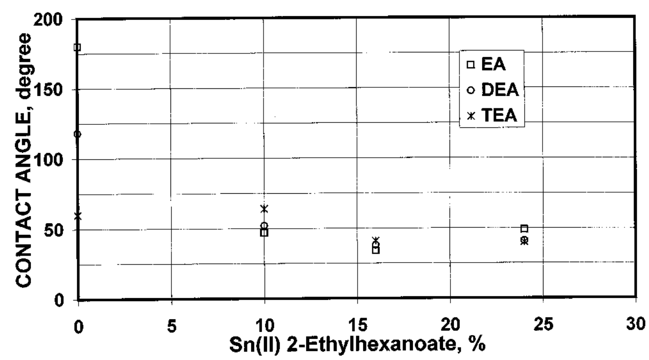

Fig. 2. Effect of tin(II) 2-ethylhexanoate concentration on wetting of copper by tin-zinc eutectic when poly(vinyl acetate) solution in methanol is used. Polymer solution to amine ratio is 1:1. Polymer solution + amine + SnII equals 100%.

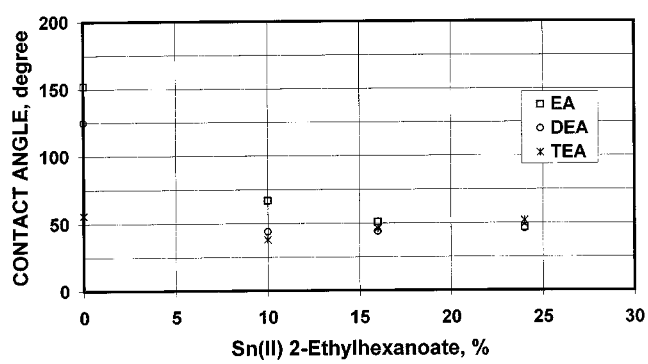

Fig. 3. Effect of tin(II) 2-ethylhexanoate concentration on wetting of copper by tin-zinc eutectic when poly(methyl methacrylate) solution in isopropyl alcohol is used. Polymer solution to amine ratio is 1:1. Polymer solution + amine + SnII equals 100%.

dissolves in either methyl alcohol or isopropyl alcohol; the other two polymers, poly(methyl methacrylate-co-methacrylic acid) and poly(methyl methacrylate), used in this study dissolve only in isopropyl alcohol.

Amines are commonly used as activators in fluxes. Three amines were used in the present research: ethanol amine, di-ethanol amine, and tri-ethanol amine (abbreviated in text as EA, DEA, and TEA, respectively).

Tin(II) 2-ethylhexanoate (from Aldridge Chemical Company) was selected as the additive that decomposes to coat the copper surface with tin to promote wetting of copper by tin-zinc eutectic. This organometallic was selected because when it decomposes, it does not release any harmful compounds.

The fluxes were evaluated in spread tests by measuring the contact angles between Sn-Zn eutectic solder and copper. The copper plates were cleaned prior to spread testing by immersion for 10 sec in 50% nitric acid and then for 10 sec in 10% sulfuric acid aqueous solutions. They were then rinsed in deionized water and methanol and dried. Solder disks (3 mm in diameter and 1 mm thick) were degreased with acetone, placed on the fluxed copper surface (two drops of flux applied from an eyedropper were used), and covered with another drop of flux. The copper plates with solder discs on them were placed on a hot plate pre-heated to 260°C. After the solder had melted, the copper plate was kept on the hot plate for another two minutes, removed, cooled in air, and cross-sectioned for examination. The contact angles were measured and recorded.

Each point in the figures that follow is an average of 2 or 3 measurements. Reproducibility was within 10–15%.

RESULTS AND DISCUSSION

When a mildly-activated rosin flux (Kester #197) was used at 260°C reflow temperature, the wetting angle of pure Sn on a copper surface was 37°; however, the wetting angle for Sn-Zn eutectic on copper was

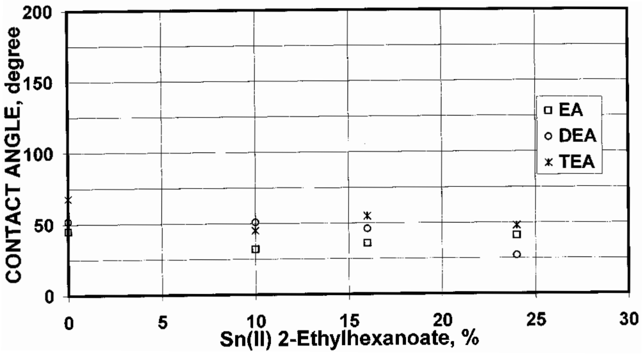

Fig. 4. Effect of tin(II) 2-ethylhexanoate concentration on wetting of copper by tin-zinc eutectic when poly(methyl methacrylate co-methacrylic acid) solution in isopropyl alcohol is used. Polymer solution to amine ratio is 1:1. Polymer solution + amine + SnII equals 100%.

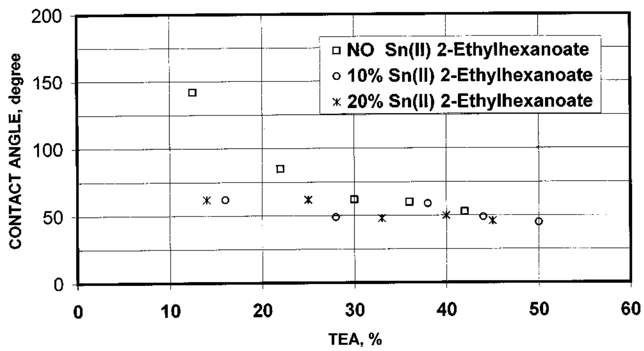

Fig. 5. Effect of tri-ethanol amine concentration on wetting of copper by tin-zinc eutectic when poly(vinyl acetate) solution in methanol is used. Polymer solution + amine + SnII equals 100%.

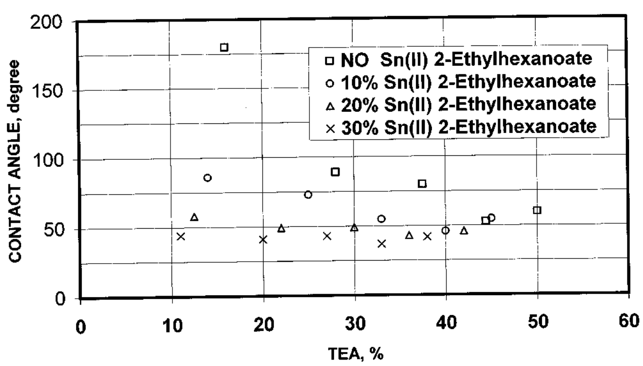

Fig. 6. Effect of tri-ethanol amine concentration on wetting of copper by tin-zinc eutectic when poly(methyl methacrylate) solution in isopropyl alcohol is used. Polymer solution + amine + SnII equals 100%.

89°, too large for any practical application. When fluxes containing the polymers listed in Table I as vehicles (one of the amines as an activator and tin(II) 2-ethylhexanoate as an additive) were used, much lower contact angles were obtained (Figures 1–6). This tin-containing organic compound was shown by x-ray diffraction to decompose with the formation of pure tin on the copper surface.

Figure 2 shows the effect of Sn(II)2-ethylhexanoate (referred to as SnII in text) concentration in a PVA/IPA flux with the three different amine activators on the contact angle of Sn-Zn eutectic solder on copper surfaces. The total of PVA solution in the solvent, amine and SnII compound equals 100%. The ratio of amine to PVA solution was kept at one. From this figure DEA is obviously the most effective amine of the three in this formulation, and by itself reduced the contact angle to about 48°. Addition of SnII reduced the contact angle further to about 35° at 16% of SnII. With the other two amines the effect of SnII on the contact angle is even more pronounced. The effect is more or less saturated at about 15% of the SnII. When EA was used as the activator, in the absence of the metallo-organic there was non-wetting, but when the metallo-organic was added the contact angle dropped rapidly and 24% gave the lowest contact angles, 25° (Fig. 1).

Figure 2 shows the same information for PVA with methanol as the solvent. With this solvent TEA gives the lowest contact angle in the absence of the metalo-organic. When EA and DEA are used Sn-Zn eutectic does not wet the copper surface. For all three amines the contact angle decreases with increasing SnII concentration in the flux. The effect of metallo-organic on the contact angle of Sn-Zn eutectic on copper again saturates at about 15% of metallo-organic in flux. The lowest contact angle obtained with this system was 40°.

The data for PMM in IPA is shown in Fig. 3. Again the ratio of PMM solution to amine was one to one and the PMM solution+amine+SnII equals 100%. In the absence of SnII the TEA is the most effective of the three in reducing the contact angle. The beneficial effect of SnII is also seen, but the lowest contact angle observed was over 40°.

In Fig. 4 PMM-MA is the polymer and IPA is the solvent. Wetting is observed for all three amines in the absence of SnII compound, but again the metallo-organic reduces the contact angle; the lowest value is about 25° with 24% of DEA as the activator. With EA there is little effect of adding SnII.

The effects of varying the concentrations of TEA and SnII in PVA-methanol solution and PMM-IPA solution are shown in Figs. 5 and 6, respectively. There is general improvement in the contact angles on increasing the TEA and SnII contents but the effects generally diminish as the concentrations increase. Without SnII a high concentration (up to 50%) of TEA is needed to significantly reduce the contact angle of Sn-Zn eutectic on copper surface.

Considering Figs. 1–6, it is obvious that the contact angle observed is a function of all of the components in the flux. It is desirable to keep the concentration of the activator in the flux as low as possible since the residue left after decomposition of the activator can be corrosive and, therefore, undesirable on the printed wiring boards. While high concentrations of amines reduce the contact angle to near 50°, a much lower concentration of activator is needed if tin-containing organometallic is also added to the flux and even lower contact angles are achieved.

Of all the combinations tested the lowest contact angles were in the 25° to 30° range with 24% SnII, 38% EA, and 38% PVA (Fig. 1) and 24%SnII, 38%DEA, and 38% PMM-MA (Fig. 4) both in IPA as the solvent. This preliminary investigation has shown that Sn-Zn eutectic solder wets copper with sufficiently low contact angles for interconnect use if appropriate flux is used. Such fluxes are achieved by adding to the flux a tin metallorganic compound that decomposes to plate tin on the substrate. Other metallorganics may possibly be more effective than Sn(II)2-ethylhexanoate, which was used in this research.

SUMMARY

Rosin fluxes do not provide adequate wetting of copper substrate by Zn-containing solders. Fluxes that contain tin-organic compounds give better wetting. This improvement is due to the decomposition of these compounds to give a tin coating on the substrate. The tin that forms on the surface of the copper leads to better spreading of solder. A flux was formulated that gave a contact angle of 25° with Sn-Zn eutectic solder on copper at 260°C.

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