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Flux Reactions in Soldering

Effects of $ZnCl_2$-NH_4Cl fluxes on spreading of lead-tin solders and flux reactions with copper, brass and mild steel substrates are evaluated

BY N. K. BATRA, J. B. SEE AND T. B. KING

ABSTRACT. Thermodynamic considerations and experimental results reveal that NH_4Cl is the reactive constituent in $ZnCl_2$-NH_4Cl fluxes. The extent to which the flux reacts with the solder or substrate metal depends on the temperature and the NH_4Cl concentration. The flux may also act as an electrolyte for electrochemical deposition of solder constituents on the substrate ahead of the advancing liquid drop. The chemical and electrochemical reactions occurring between the phases alter the interfacial conditions and influence the spreading characteristics of the solder. With a $ZnCl_2$-NH_4Cl flux, pure lead spreads to a very large area, but with a $ZnCl_2$ flux, lead spreads very little. With a $ZnCl_2$ flux, the phenomenon of spreading of solder over copper and brass substrates, beneath the solidified flux, is observed.

N. K. BATRA is Postdoctoral Fellow, J. B. SEE is Assistant Professor, and T. B. KING is Professor, Department of Metallurgy and Materials Science, Massachusetts Institute of Technology.

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Introduction

Lead and tin form the major constituents of commercial solders; consequently the wetting properties and the spreading characteristics of lead-tin alloys have been studied by many investigators. It has been shown that, to be wetted by the solder, the metallic surface must be free of any tenacious oxide film or other nonmetallic substances such as sulfides, carbides or abrasive particles (Refs. 1,2). Another important observation is that the intermediate alloys of lead and tin possess better spreading properties than lead-rich or tin-rich alloys (Refs. 3-7). Tin is said to promote wetting because of its mutual solubility and tendency to form intermetallic compounds with substrate materials (Ref. 8), and lead to improve spreading because it lowers the surface tension of the liquid alloy (Ref 9).

The extent of wetting is normally promoted and accelerated by the application of liquid fluxes (Refs. 3,10). The flux removes any residual oxide left on the metallic surface after the usual precleaning operations, either dissolving or chemically reacting with the oxide; it then protects the surface from further oxidation. Fluxes may also improve the spreading properties if they have constituents which dissolve in and lower the surface tension of the liquid alloy (Refs. 10,11).

Certain reactive fluxes, such as those containing chlorides, participate in reactions which alter the surface conditions and influence spreading. Fine and Dowdell (Ref. 12) noted that extensive spreading of a lead-rich solder occurred on a steel plate due to the deposition of lead or tin on the plate from their salts. Ueda et al (Refs. 6,7) reported that the spreading of pure tin on an iron plate increased when $SnCl_2$ was added to the $ZnCl_2$ flux. However, the addition of $SnCl_2$ to $ZnCl_2$ decreased the area of spread of alloys containing 25 to 75% tin. On copper and brass plates, the spreading of lead-tin alloys was improved when $SnCl_2$ was added to the $ZnCl_2$ flux.

Earlier investigations by Latin (Ref. 10) and Bailey and Watkins (Ref. 3) described the tinning action of a $ZnCl_2$-NH_4Cl flux on copper. Tin in the solder dissolves in the flux and is deposited on the substrate to produce a gray or blue area ahead of the liquid drop. The deposition of tin was believed to be enhanced by an electrochemical reaction. Bailey and Wat-

kins (Ref. 3) reasoned that, with the reactive flux, the formation of a Cu-Sn layer ahead of the drop resulted in much more rapid and greater spreading of the alloys than when resin-based fluxes were used.

In contrast, Lewis (Ref. 13) explained the tinning action of the $ZnCl_2$-NH_4Cl flux by postulating that zinc chloride in the flux hydrolyzed to hydrochloric acid, which reacted with the molten solder to form stannous chloride which could in turn be reduced by copper. Lewis considered that ammonium chloride was added only to lower the melting point of the salt.

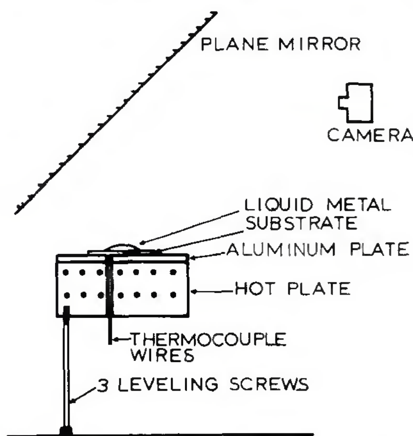


Fig. 1 — Schematic of apparatus for spreading of lead-tin alloys

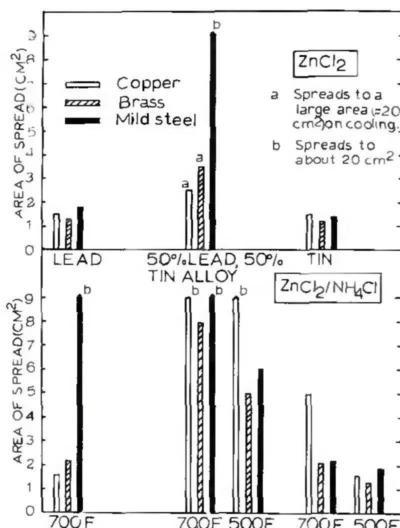


Fig. 2 — Effects of substrate material, flux composition, alloy composition and temperature on area of spread. Volume of drop = 0.1 cm³; amount of flux = 4 g; time of heating = 10 min

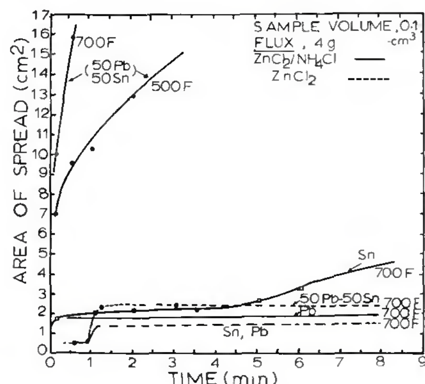


Fig. 3 — Area of spread versus time for liquid lead, tin and 50% lead-50% tin alloy on copper substrate

Ueda et al (Ref. 17) showed that the concentration of $ZnCl_2$ in the flux should be greater than 45% if it is to produce acid and that $ZnCl_2$ is effective only below 200 C (392 F) in removing oxide from an iron plate. It was also demonstrated that addition of NH_4Cl to $ZnCl_2$ resulted in an increase of more than two orders of magnitude in the rate of reaction between the flux and the base metal, iron, at 350 C (662 F). It was concluded that a $ZnCl_2$-nNH_4Cl flux decomposed into $ZnCl_2nNH_3$ and HCl at temperatures above 300 C (572 F).

In the present investigation, available thermodynamic data are used to predict the nature of these chemical and electrochemical reactions. The spreading of lead, tin and an alloy of 50% Pb-50% Sn on copper, brass and mild steel substrates was studied as a function of time and temperature when the substrates had been treated by $ZnCl_2$ and $ZnCl_2$-NH_4Cl fluxes. The probable reactions occurring between the phases were verified by weight loss determinations, electrochemical cell measurements, microprobe analysis, and experiments in which strips of copper or steel were simply dipped into various fluxes.

Experiments

Materials and Preparation

High purity lead and tin (ACS specification: impurity content less than 0.02 wt%) were used to make samples of pure lead, pure tin and 50-50% Pb-Sn alloy. The liquid metal was sucked into 7 mm Pyrex tubing and cylindrical samples were cut and weighed to give a volume of 0.1 cm³; sample masses were accurate to 0.005 g. The samples were washed in alcohol before use.

The $ZnCl_2$, NH_4Cl, $SnCl_2 2H_2O$, $PbCl_2$, CuCl and $FeCl_2$ used were reagent grade. The eutectic mixture of $ZnCl_2$ and NH_4Cl was made by dissolving 3 parts of $ZnCl_2$ and 1 part of NH_4Cl (by weight) in distilled water, boiling off the water and drying in a desiccator.

Copper substrates and strips were cut from 1/16 in. thick OFHC copper sheet. Brass substrates and strips were cut from 1/16 in. thick, half-hard, 70% copper-30% zinc commercial sheet. Mild steel substrates and strips were cut from 0.04 in. thick commercial sheet.

Before use, all substrates and strips were degreased in hot sodium carbonate solution, polished with 500 grade emery cloth, pickled in an acid solution for 2 min, washed in running water and dried.

Procedure and Results

"Area of Spread" Experiments

Approximately 4 g of the desired flux were melted on a substrate in contact with a controlled temperature hot plate (Fig. 1). The liquid flux first boiled and then became quiescent after 1 min. The alloy sample was then placed at the center of the substrate and the top view of the liquid drop was photographed using a 35 mm camera and a plane mirror inclined at 45 deg above the plate. From the photographs, the area of spread was measured by a planimeter. After about 10 min of heating the substrate was carefully removed to a cold aluminum slab, the flux was washed off in running water and the area of spread was again determined. The final areas of spread are shown in Fig. 2 as functions of temperature, flux composition, substrate material and alloy composition. The areas of spread as functions of time on copper and steel substrates are plotted in Figs. 3 and 4, respectively. A number of other important observations were made in these experiments and they are summarized below for each flux.

$ZnCl_2$-NH_4Cl Flux:

1. When $ZnCl_2$-NH_4Cl was used as a flux on a brass substrate at 700 F, copious fumes were evolved and the brass substrate turned reddish. The same flux on a mild steel substrate at 700 F changed color from yellow to brown and then black, and, as the

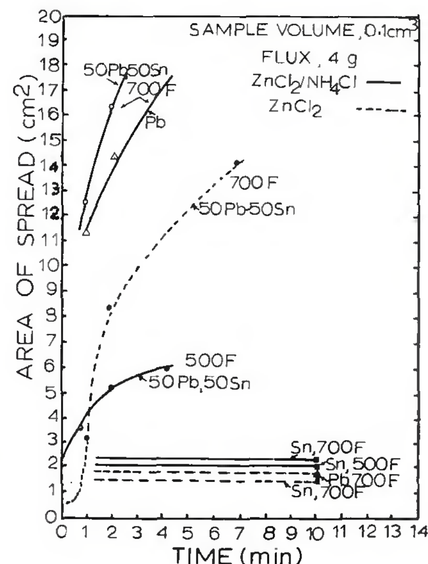


Fig. 4 — Area of spread versus time for liquid lead, tin, and 50% lead-50% tin alloy on mild steel substrate

color changed, the flux became more viscous and eventually contained solid particles. The flux did not fume and remained clear on a copper substrate at 700 F.

2. Upon melting, lead, tin and 50-50 Pb-Sn alloy samples wetted all the substrates instantaneously. On the mild steel substrate at 700 F, the spread area of the 50-50 Pb-Sn alloy was dull and brittle, and the alloy was readily removed when the substrate was washed in running water. However, if the flux was heated for about 5 min prior to placing the alloy sample on the substrate, the spread area was bright and the alloy adhered to the substrate even after washing in running water. Similar behavior was observed when a pure lead sample was heated on the mild steel substrate at 700 F where extensive spreading occurred (areas of spread greater than 20 cm^2).

3. A gray band appeared at the edges of both tin and 50-50 Pb-Sn alloy drops on the copper substrate at 700 F. On the mild steel substrate, a white band of 1 to 2 mm width was seen at the edge of the tin drop.

4. At 500 F, only a small amount of fuming was observed with brass and steel substrates and the flux remained clear. The widths of the gray band on the copper substrate at the edge of the tin drop were also smaller than at 700 F.

$ZnCl_2$ Flux:

1. Molten zinc chloride remained clear on all substrates at 700 F. The samples of lead, tin, and 50-50 Pb-Sn alloy floated on the flux, after melting, for 15 to 30 s before making contact and subsequently wetting the metallic substrate.

2. The area of spread of the 50-50 Pb-Sn alloy on copper and brass substrates increased during cooling. $ZnCl_2$ solidifies at 542 F while the alloy starts solidifying at 420 F. Thus, when the flux solidified the alloy was still molten and it spread rapidly beneath the solidified flux.

3. On the copper substrate, the area of spread was about 2.5 cm^2 for the 50-50 Pb-Sn alloy at 700 F and did not change with time. (See Fig. 3.) When the substrate was cooled rapidly (by placing on a cold aluminum slab) the alloy solidified in about 2 min and the final area of spread was 3.7 cm^2. When the copper substrate was cooled slowly on the hot plate by turning off the power, the alloy solidified in 15 to 20 min and the final area of spread was greater than 20 cm^2. The liquid alloy was observed to be moving as a very thin layer over the substrate beneath the solidified flux.

4. The occurrence of rapid spreading beneath the solidified zinc chloride flux was verified by depositing a layer of flux on the copper substrate. The layer was then broken at one spot and a 50-50 Pb-Sn alloy sample was placed at that point. The substrate, the flux and the alloy sample were then heated to 500 F on the hot plate. The flux did not melt but the alloy sample melted in less than 1 min and spread to an area of more than 20 cm^2 underneath the solid flux. Similar experiments with the brass and mild steel substrates were unsuccessful since the molten alloy did not wet the substrate. Oxidation of the surface at the point where the flux was broken through prevented the wetting action.

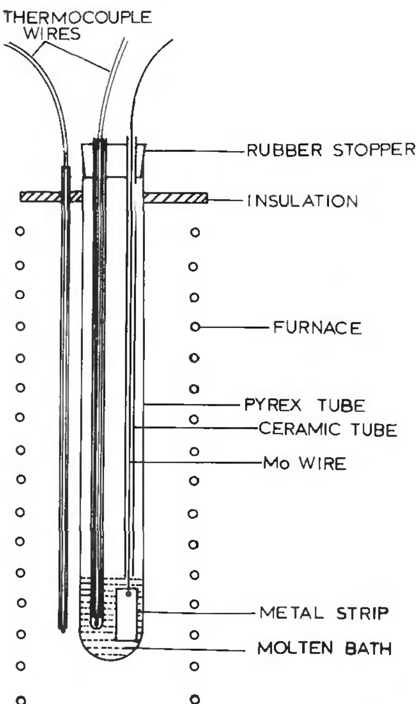


Fig. 5 — Schematic of the apparatus for the weight loss determinations

Weight-Loss Determinations

These experiments were carried out to determine whether the substrates dissolved in or reacted with the flux.

About 25 g of flux were melted in a Pyrex tube inside a furnace maintained at a fixed temperature (Fig. 5). A copper or mild steel strip was weighed before dipping in the flux for the desired length of time. The strip was then removed from the flux, washed in running water, dried and reweighed. The results of such weight loss determinations are plotted in Figs. 6 and 7.

The results show that only very small weight losses occur in the $ZnCl_2$ flux. Much larger weight losses are obtained in the $ZnCl_2$-NH_4Cl flux. With this flux the weight losses depend strongly on temperature and NH_4Cl concentration. Above 600 F some of the NH_4Cl in the bath sub-

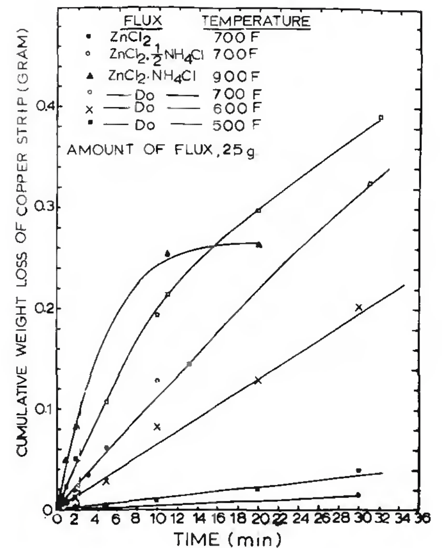


Fig. 6 — Results of weight loss experiments for copper strips, 1 × ½ × 1/16 in. in various fluxes

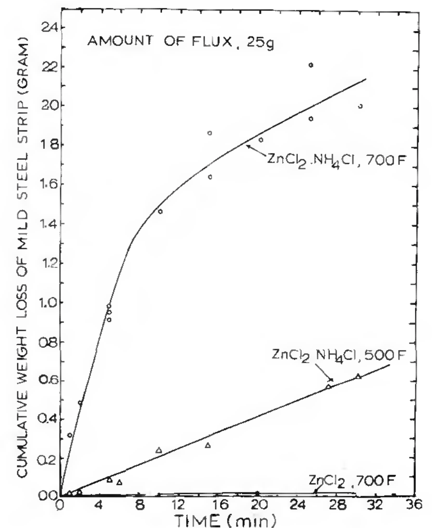


Fig. 7 — Results of weight loss experiments for mild steel strips, 1 × 0.5 × 0.04 in. in various fluxes

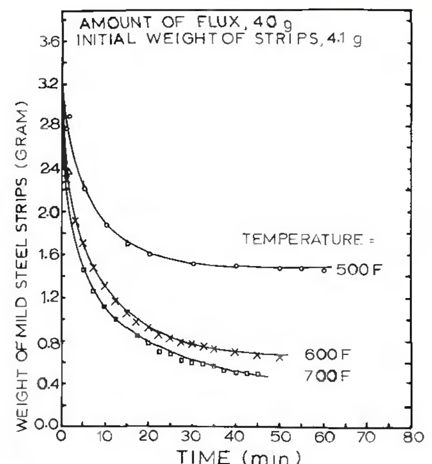


Fig. 8 — Weights (while in the flux) of three ⅝ × ⅜ × 0.04 in. mild steel strips versus time of immersion in molten $ZnCl_2$-NH_4 Cl flux

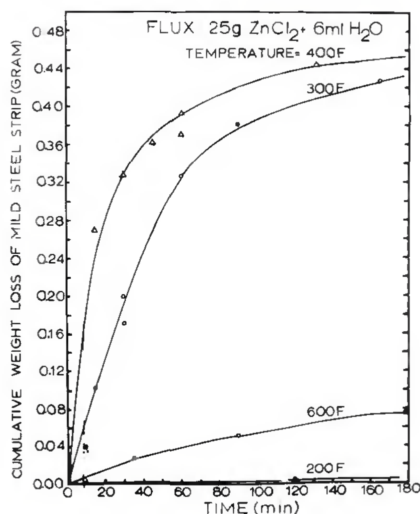


Fig. 9 — Weight loss of mild steel strips, 5/8 × 3/8 × 0.04 in. in liquid $ZnCl_2$-H_4O flux

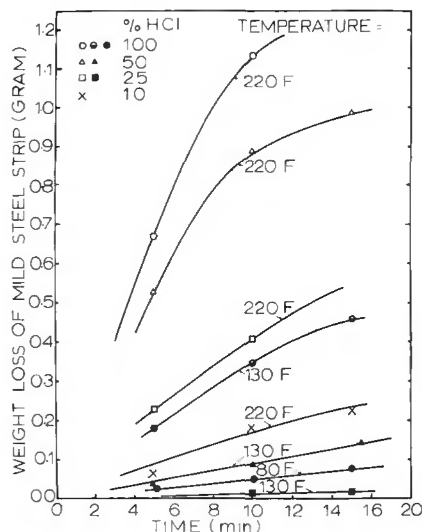


Fig. 10 — Weight loss of mild steel strips, 5/8 × 3/8 × 0.04 in. in 20 ml HCl -H_2O solution

Table 1 — Results of Dipping Experiments at 700 F

Composition of molten bath	Color of coating on strip surface: Copper	Mild steel
$ZnCl_2$	No coating	No coating
$ZnCl_2$+20%$SnCl_2$	Gray	White
$ZnCl_2$+20%$SnCl_2$ +20%CuCl	No coating	Reddish
$ZnCl_2$+20%$PbCl_2$	No coating	White
$ZnCl_2$+20%$PbCl_2$ +20%CuCl	No coating	Reddish
$SnCl_2$	Gray	White
$SnCl_2$+1%CuCl	Gray	
$SnCl_2$+5%CuCl	Part gray, Part red	
$SnCl_2$+10%CuCl	No coating	
$ZnCl_2$ above liquid tin	No coating	No coating
$ZnCl_2$ above liquid lead	No coating	No coating
$ZnCl_2$+25%NH_4Cl above liquid tin	Gray	Black
$ZnCl_2$+25%NH_4Cl above liquid lead	No coating	Black
$ZnCl_2$+25%NH Cl	No coating	Black

limes and its concentration is lowered; thus, smaller final weight losses are observed for copper strips in the flux at 900 F. At a fixed temperature and NH_4Cl concentration, mild steel suffers more attack than copper.

Further experiments on mild steel strips were conducted on specimens suspended from a continuous weighing balance. These experiments were designed to show whether the flux reached saturation with substrate material. The results are plotted in Fig. 8, the weights being determined during immersion. At 500 F, the *actual* final weight of strips of initial weight 4.1 g was 2.1 g, so equilibrium appears to be reached when 2 g of the strip material has dissolved in 40 g of flux. If NH_4Cl is not lost from the flux and the iron dissolves as $FeCl_2$, the final composition of the flux will be 28.8 g of $ZnCl_2$, 4.5 g of $FeCl_2$ and 7.4 g of NH_4Cl.

To check these equilibrium conditions, a fresh batch of flux of this exact composition was made and the loss in weight of an immersed strip of mild steel was determined. At 500 F, the loss in weight was only 0.021 g in 30 min while at 600 F, the loss was 0.74 g in 30 min. However, at higher temperatures, losses of NH_4Cl to the atmosphere are appreciable and the density of the molten bath changes as the flux reacts with the metallic strip. Thus continuous measurements of the weight of the metallic strip immersed in the bath are not reliable.

The possibility that $ZnCl_2$ hydrolyzes to form HCl, which then dissolves the strip material, was examined by carrying out weight-loss experiments in $ZnCl_2$-H_2O solutions at different temperatures. The results are summarized in Fig. 9. Mild steel suffered appreciable weight loss in a $ZnCl_2$-H_2O flux maintained at 300 F or 400 F but not at 200 F. The boiling point of H_2O is increased when $ZnCl_2$ is dissolved in it so that the flux remained liquid for about 48 h at 300 F and for about 8 h at 400 F. However, all the H_2O (or HCl formed by hydrolysis) evaporated, leaving behind a solid residue, before a temperature of 500 F would be reached. At still higher temperatures, $ZnCl_2$ melted but the attack on mild steel was slow. The results are thus analogous to those with the $ZnCl_2$-NH_4Cl flux except that the evaporation of NH_4Cl occurs at a higher temperature, around 900 F.

The results of a few weight loss experiments in HCl-H_2O solutions showed that the rates of the chemical reactions depended strongly on temperature and HCl concentration (Fig. 10). Corresponding experiments with copper strips showed very small weight losses, e.g., 0.005 g compared to 1.1 g for mild steel. Weight losses for copper in the $ZnCl_2$-H_2O solution were negligible.

Dipping Experiments

These experiments were carried out to observe changes in the appearance of copper and mild steel strips as a result of chemical reactions with the flux. Fresh salt and fresh strips were used for each experiment. After dipping in the molten salt for 1 min, the strips were washed in running water and examined for any color changes at the surface. Some experiments were carried out by adding molten lead or molten tin to the flux and inserting the strip without touching the liquid metal. The results are summarized in Table 1.

A copper surface turns gray when dipped in a salt containing $SnCl_2$. The surface of a mild steel strip becomes whiter when dipped in a salt containing $PbCl_2$ or $SnCl_2$. The presence of sufficient CuCl in the salt prevents the formation of a gray coating on the surface of a copper strip but produces a reddish coating of copper on a mild steel strip.

Electrochemical Cell Measurements

The possibility of electrochemical deposition of tin on copper in the presence of molten fluxes was examined by setting up the cell shown in Fig. 11. The cell consisted of two vertical Pyrex tubes A and B connected by a horizontal Pyrex tube C. Flux of the desired composition was melted in the cell to a level above tube C. The conductivity of the molten salt was determined by measuring the resistance with a conductivity

bridge between two copper wires dipped into tube A and tube B. The specific conductance of molten $SnCl_2$ at 700 F is known to be 1.5 ohm^{-1} cm^{-1} (Ref. 14) and the specific conductance of any other salt may be determined by comparing the measured resistances.

The electrodes were liquid tin or lead in tube B and a copper strip in tube A. Insulated copper wires were used to make contact with the electrodes. A third electrode of liquid metal was placed in the bottom of tube A. The electrical circuit was designed to allow simultaneous measurements of open circuit voltage between electrodes 1 and 2 and short circuit current between electrodes 2 and 3. (See Fig. 11.) It was also possible to measure the open circuit voltage and short circuit current separately between electrodes 1 and 2 or between 2 and 3. A dual-beam storage oscilloscope was used to measure voltage and current as functions of time. The current was obtained by measuring the voltage across a standard 1 ohm resistance between the electrodes.

Open circuit voltage and short circuit current responses recorded on the oscilloscope are shown in Fig. 12 for the tin/salt/copper system and in Fig. 13 for the lead/salt/copper system. The voltage and current rise to high values as soon as the copper strips are added to the cell. After these initial high readings, the voltage and current then decrease to constant values. These constant values of open circuit voltage and short circuit current, together with the resistance and specific conductance of the electrolyte are given in Table 2.

The open circuit voltage was found to be independent of the spacing between the two electrodes while the short circuit current increased with decreasing distance between the two electrodes. This was checked by measuring the open circuit voltage and short circuit current separately between electrodes 2 and 3 and between electrodes 1 and 2. For the same distance between the two electrodes, the short circuit current values increased with an increase in the open circuit voltage of the cell or with an increase in the specific conductance of the molten salt (see Table 2). These results seem to indicate that measurements of the current merely conform to Ohm's law; they do not provide any additional information about the nature of the reactions in the cell.

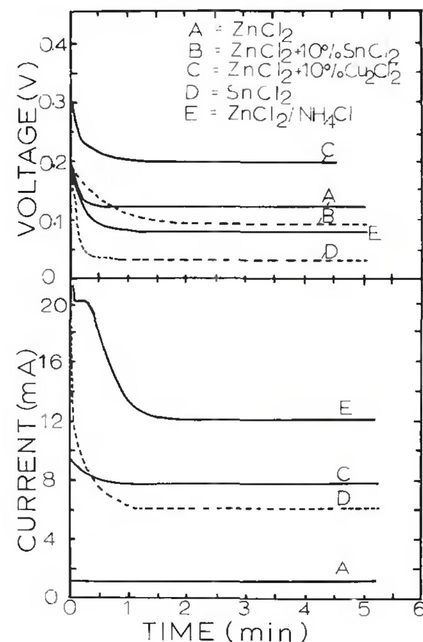


Fig. 12 — Open circuit voltage and short circuit current versus time after inserting copper strip in tin/salt/copper cell at 700 F

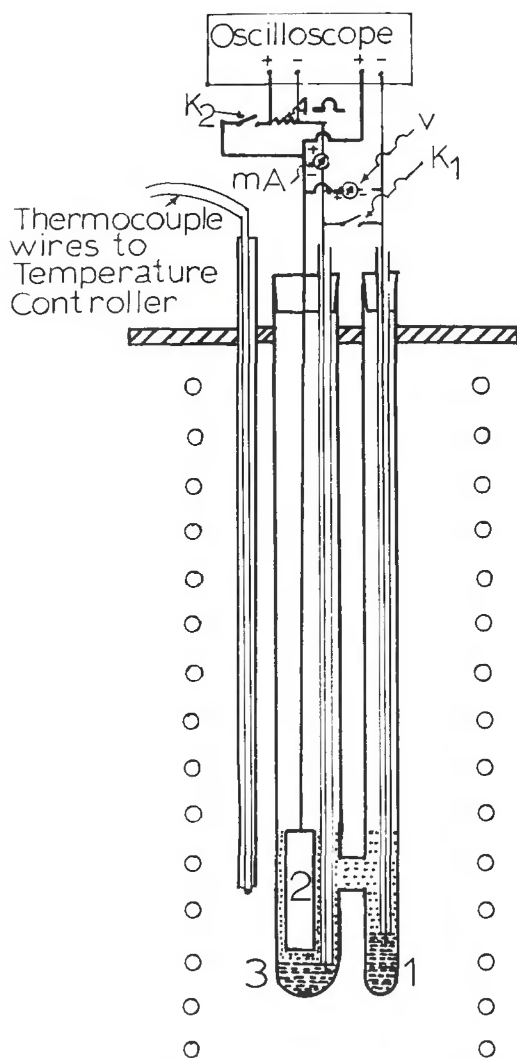


Fig. 11 — Schematic diagram of electrochemical cell

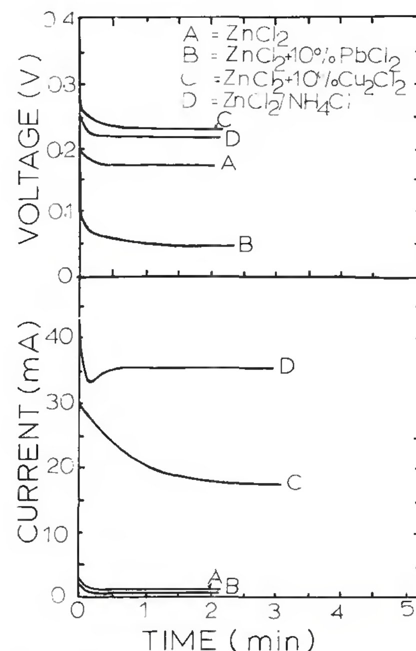


Fig. 13 — Open circuit voltage and short circuit current versus time after inserting copper strip in lead/salt/copper cell at 700 F

Table 2 — Results of Conductivity, Voltage, and Current Measurements on Electrochemical Cell

Electrolyte	Temp., F	Measured resist., ohm	Calc. spec. conductance, ohm cm -1	Open circuit voltage, V	Short circuit current mA
Tin and copper electrodes					
$ZnCl_2$	700	400	0.013	0.13	1
$ZnCl_2$+10wt% $CuCl_2$	700			0.21	8
$ZnCl_2$+10wt% $SnCl_2$	700	90	0.06	0.07	
$SnCl_2$	700	3.5	1.50	0.02	6
$SnCl_2$+10wt% $CuCl_2$	700			0.08-0.03	8.3
$ZnCl_2$ NH_4Cl	700	15	0.35	0.12-0.08	22-12
$SnCl_2$	500	5	1.05	0.05	10
$SnCl_2/NH_4Cl$	500	50	0.105	0.14	8
Lead and copper electrodes					
$ZnCl_2$	700	400	0.013	0.19	2
$ZnCl_2$+10wt% $PbCl_2$	700	290	0.018	0.06-0.03	1
$ZnCl_2$+10wt% $CuCl_2$	700			0.23	20
$ZnCl_2/NH_4Cl$	700	15	0.35	0.22	36

Table 3 — Results of Microprobe Analysis of Gray Band at Edge of 50-50 Pb-Sn Alloy Drop on Copper Substrate with $ZnCl_2$-NH_4Cl Flux

Material	Lead counts	Tin counts
Pure tin	2,880	60,000
75Sn-25Pb	3,330	51,900
50Sn-50Pb	6,320	30,500
25Sn-75Pb	11,670	10,760
Pure lead	13,430	1,680
Clean copper	2,044	109
Gray band I	2,280	12,850
Gray band II	2,240	15,800
Gray band III	2,100	12,300

Microprobe Analysis

An electron microprobe analyzer was used to determine the chemical composition of the band which appeared at the edge of a molten 50-50 Pb-Sn drop on a copper substrate with molten $ZnCl_2$-NH_4Cl flux. The method involved simultaneous determination for two elements (lead and tin) of the number of counts in a fixed time interval. Lead-tin alloys of known composition (samples containing 0, 25, 50, 75 and 100% lead) and clean copper were also analyzed on the probe to provide suitable standards.

Table 3 gives results for the analysis of the gray band at the edge of a 50-50 Pb-Sn alloy drop on copper, using a $ZnCl_2$-NH_4Cl flux. Three arbitrary locations on the gray coating were chosen for the analysis. The results indicate that the band contained tin but no lead.

Discussion

In order to explain the experimental observations, it is necessary to consider the factors which, in theory, govern wetting and spreading. The area of spread, A, is related to the contact angle, θ , between the liquid alloy of volume, V, and substrate as follows (Ref. 15).

$$A = 3.7 (V/\theta)^{2/3} \quad (1)$$

provided that the liquid drop is small enough to be regarded as spherical. If

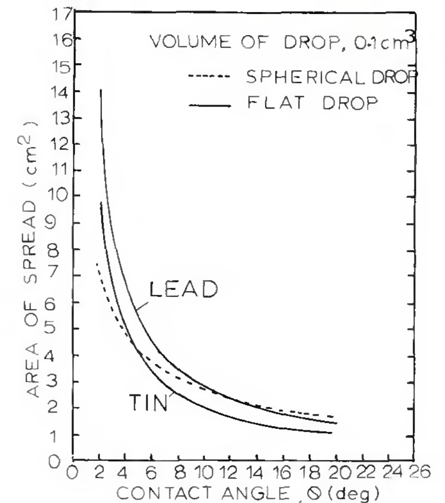


Fig. 14 — Area of spread versus contact angle for 0.1 cm³ of liquid lead and tin

the drop is large enough to be regarded as flat on the top surface, the relation is (Ref. 10):

$$A = V/H = \left[\frac{1}{2}\ \frac{g}{\gamma_{L/F}}\left(\frac{\rho_l - \rho_f}{1-\cos\theta}\right)\right]^{1/2} V$$

where H is the height of the drop, ρ_l the liquid alloy density, ρ_f the flux density, $\gamma_{L/F}$ the liquid alloy-flux interfacial tension and g the acceleration due to gravity.

The contact angle, θ , is determined by the equilibrium between the three interfacial tensions at the liquid-flux, solid-flux and solid-liquid phase boundaries, i.e. (Refs. 4, 7):

$$\gamma_{L/F} \cos\theta = \gamma_{S/F} - \gamma_{S/L} \quad (2)$$

When the contact angle is less than 10 deg, the area of spread depends markedly on contact angle, (Fig. 14). Slight changes in the values of the interfacial tensions due to flux reactions may therefore result in substantial changes in the extent of spreading. It would also follow that, unless flux composition, substrate surface preparation, and temperature are closely controlled, the results of different investigators may be expected to show discrepancies.

For example, the present work is in agreement with that of Raman et al (Ref. 16) and Latin (Ref. 10) in showing that the area of spread on a copper substrate is greater at higher temperatures. On the other hand, Bailey and Watkins (Ref. 3) report that, for lead-tin alloys spreading on a copper substrate, the area of spread decreases at higher temperatures. In all cases, a zinc-ammonium chloride flux was used and the contact angles were less than 5 deg.

As another example of discrepancies between various investigators, the present work shows that sub-

stantial spreading of pure tin on copper could occur after a period of 3-4 min at 700 F. Bailey and Watkins (Ref. 3) did experiments for 1½ min only and therefore did not observe significant spreading of pure tin.

Another phenomenon encountered in the present work but not reported in the literature is the spreading of the liquid alloy on copper and brass substrates beneath a solidified $ZnCl_2$ flux. The solidified flux does not adhere well to the substrates and thus provides a channel for capillary penetration of the liquid alloy.

Substantial spreading of soldering alloys cannot occur unless the contact angle between alloy and solid substrate is low. As Eq. (2) shows, factors which increase the difference between $\gamma_{S/F}$ and $\gamma_{S/L}$ or decrease the value of $\gamma_{L/F}$ favor low contact angles. Removal of oxide from the substrate by fluxes may be expected to increase $\gamma_{S/F}$ but significant decreases in $\gamma_{S/L}$ can also be expected with reactive fluxes which allow deposition of an alloy constituent, e.g., Sn, at the periphery of the drop. $ZnCl_2$-NH_4Cl is such a reactive flux.

As shown by experiment, fumes are evolved, brass substrates change color and the flux becomes dark and viscous in contact with a steel substrate. Weight-loss experiments confirm that NH_4Cl is the reactive constituent. With this flux, gray or white bands appear at the periphery of tin and alloy drops placed on copper and steel substrates. Microprobe analyses show that the gray band at the periphery of the alloy drop on copper contains tin but not lead. It is of interest, therefore, to consider the likely flux reactions which would lead to such deposition reactions.

Data on the standard free energies of formation of metal chlorides have been compiled by Kellogg (Ref. 17) and Reid (Ref. 18). For the metals of interest in the present study, Fig. 15 shows the standard free energies of formation of the chlorides as functions of temperature. The data for ammonium chloride have been calculated from standard heats of formation, entropies, and heat capacities (Refs. 19-20).

It is clear that zinc chloride is stable in the presence of iron, lead, tin or copper over the complete temperature range of interest. On the other hand, ammonium chloride is stable at room temperature but, with respect to these same metals, becomes unstable as the temperature increases and at 700 F (371 C) is readily decomposed by iron, lead, tin and copper. The equilibrium constants for such reactions at 700 F (371 C) is given in Table 4. These comments apply to the standard free energy changes, but the fluxes used here contain ammonium chloride at less than unit activity. Correspondingly, the reaction products, for example iron chloride or copper chloride which are produced by reaction between flux and substrate material, are soluble in the flux and will be present initially at a very low activity.

Thus the reactions will proceed quite readily, though one would expect a dependence of the extent of reaction on the concentrations of ammonium chloride and the reaction product in the flux. The results of weight loss experiments, in which mild steel or copper strips are suspended in the flux, show that the rate and extent of reaction depend strongly on temperature and the ammonium chloride concentration of the flux. From the weight loss curves, the initial rate of loss may be obtained and the logarithm of this quantity is plotted against reciporcal temperature in Fig. 16. A straight line is obtained for both mild steel and copper corresponding to an activation energy of about 18 kcal. This value would seem to be of the correct order for a process controlled by diffusion and convection in the liquid flux though this evidence cannot be considered to be decisive.

It is clear, therefore, that the ammonium-chloride-zinc-chloride flux can chemically etch brass, iron or copper substrate materials. This may not in itself be sufficient to induce extensive spreading. However, the flux will, according to the thermodynamic data, also react with lead and tin in the soldering alloy. The lead-chloride or tin-chloride formed in the flux by such reaction may in turn react with the substrate material resulting in the deposition of lead or tin on the substrate.

The values of $\Delta G°$ and log K at 700 F (371 C) for the reactions between substrates of iron or copper and $SnCl_2$ or $PbCl_2$ dissolved in the flux are given in Table 5. The form of the equilibrium constant is, e.g.:

$$K = \frac{a_{FeCl_2} \cdot a_{Sn}}{a_{SnCl_2} \cdot a_{Fe}}$$

Inspection of the values in Table 5

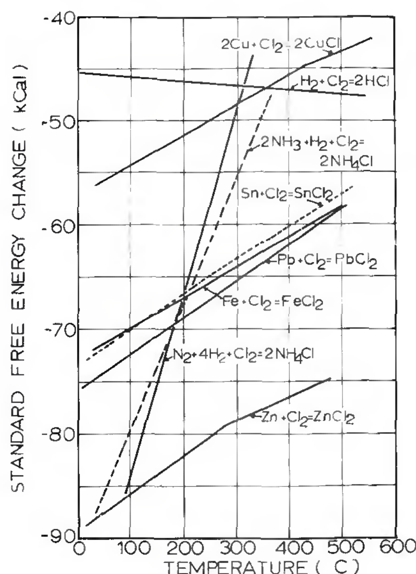


Fig. 15 — Standard free energy of formation versus temperature for chlorides of interest in the present study

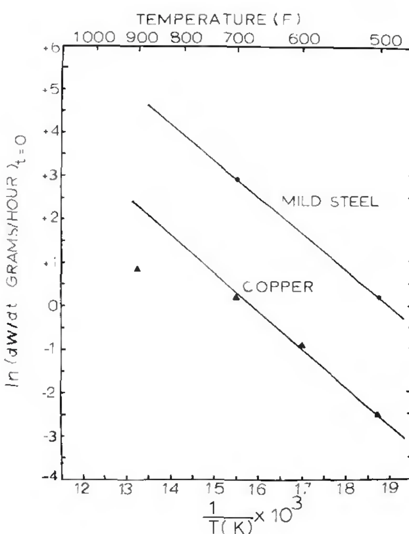


Fig. 16 — Logarithm of initial rate of weight loss in $ZnCl_2$-NH_4Cl flux versus reciprocal of absolute temperature

Table 4 — Standard Free Energy Changes and Equilibrium Constants for Reactions with NH_4Cl at 700 F (371 C)

Reaction	$\Delta G°$ kcal	Log K
$2Cu + 2NH_4Cl = 2CuCl + 2NH_3 + H_2$	+1.0	−0.34
$Fe + 2NH_4Cl = FeCl_2 + 2NH_3 + H_2$	−15.5	+5.25
$Zn + 2NH_4Cl = ZnCl_2 + 2NH_3 + H_2$	−30.0	+10.2
$Pb + 2NH_4Cl = PbCl_2 + 2NH_3 + H_2$	−16.5	+5.6
$Sn + 2NH_4Cl = SnCl_2 + 2NH_3 + H_2$	−14.5	+4.9

shows that it is possible to deposit pure Sn or Pb on an iron substrate if the ratio of the activities, $FeCl_2/SnCl_2$ is close to unity (a_{Fe} the substrate, being assumed to be unity). For copper as substrate, however, the corresponding ratio must be very low and, practically speaking, the deposition of pure Sn or Pb would seem to be impossible. However, tin readily forms intermetallic compounds, such as Cu_3Sn and Cu_6Sn_5, with copper, in which the activity of Sn is very much less than unity.

It should be noted that a gray coating formed on copper strips dipped in a flux containing $SnCl_2$ with 1% CuCl, but not if the flux contained 10% CuCl. Lead does not form intermetallic compounds with copper and hence lead cannot be deposited on the substrate by any such displacement reaction, in agreement with the microprobe analyses and results of dipping experiments.

In addition to such displacement reactions, electrochemical reactions are possible between soldering alloy and substrate material, with the flux acting as electrolyte. With an $SnCl_2$ electrolyte, tin may be transferred from the alloy to substrate by the following mechanism:

- Anodic half-cell reaction: Sn' (liquid alloy) = $Sn^{2+} + 2e^-$
- Cathodic half-cell reaction: $Sn^{2+} + 2e^- =$ S'' (substrate)

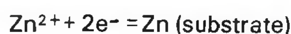
Tin ions are transferred through the flux by diffusion and convection with electrons being transferred through the alloy and metallic substrate. Since the sum of the half-cell reactions is the transfer of tin from a higher to a lower activity, the electrochemical mechanism can only be operative if a_{Sn}'' is less than a_{Sn}'. Tin cannot, therefore, deposit as the pure metal on the substrate but must be alloyed with it (as, e.g., in intermetallic compounds).

The experiments using $SnCl_2$ as electrolyte and pure copper and liquid tin as electrodes show that copper becomes the cathode. The EMF (open-circuit) is presumably given by

$$E = \frac{-RT}{2F} \ln \frac{a_{Sn}''}{a_{Sn}'}$$

Initially, a_{Sn}'' is zero so the cell voltage is very high and soon drops to a value characteristic of the activity of tin in the particular Cu-Sn compound formed.

However, the value of the open-circuit voltage is influenced by the electrolyte composition, as Fig. 12 shows. With $ZnCl_2$ flux as electrolyte, tin is still the anode and copper the cathode, but the open-circuit voltage is higher. The cathodic half-cell reaction is then, probably:



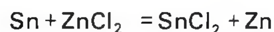
$$Zn^{2+} + 2e^- = Zn \text{ (substrate)}$$

Table 5 — Standard Free Energy Changes and Equilibrium Constants for Reactions Leading to a Deposition of Lead or Tin on the Base Plate

Temperature = 700 F (371 C)

Reaction	$\Delta G°$	Log K. $\Delta G°/2.3RT$
$SnCl_2 + 2Cu = 2CuCl + Sn$	+15.5	-5.25
$PbCl_2 + 2Cu = 2CuCl + Pb$	+17.5	-5.90
$SnCl_2 + Fe = FeCl_2 + Sn$	-1.0	+0.34
$PbCl_2 + Fe = FeCl_2 + Pb$	+1.0	-0.34

The overall reaction is the displacement reaction:



$$Sn + ZnCl_2 = SnCl_2 + Zn$$

for which log K at 700 F is -5.25. The reaction will, therefore, not proceed unless the $SnCl_2$ concentration in the electrolyte is small and, more importantly, a_{Zn} in the copper cathode is small. Addition of 10% $SnCl_2$ to the $ZnCl_2$ results in a mixed EMF intermediate between that characteristic of the tin concentration cell and the chemical cell. Addition of CuCl to the $ZnCl_2$ results in a potential higher than that for the other cells, presumably because Cu ions may discharge at the cathode, reducing the tin and zinc activities.

With NH_4Cl added to the $ZnCl_2$ a low EMF results but interpretation is difficult since both anode and cathode can react chemically with the electrolyte, altering the anode and cathode composition. It is of interest also that the short-circuit current is highest for this electrolyte and smallest for pure $ZnCl_2$. If the electrochemical deposition of tin or zinc is an appreciable factor in wetting, the rate of the electrochemical reaction is highest for the $ZnCl_2$-NH_4Cl flux; this is also the more effective flux in the spreading experiments.

With lead as the anode instead of tin, similar results are obtained, but it must be presumed that chemical cells involving dissolution of lead at the anode and deposition of alloyed zinc at the cathode are the likely contributors. Lead does not alloy with copper so that the contribution of a lead concentration cell is expected to be negligible.

On a mild steel plate, deposition of tin on the plate from the flux gives rise to a white band at the periphery of the liquid tin drop, but extensive spreading of tin does not occur possibly because of the high tin-flux interfacial tension. Similar deposition of lead on the steel plate is possible but the lead-flux interfacial tension is lower and extensive spreading of the lead drop is observed.

If the chloride flux is heated in air, it may absorb moisture and hydrolyze to form hydrochloric acid which, in turn, reacts with the solder and the base metal, enhancing the cleansing action of the flux. Weight loss determinations for copper and mild steel strips in $ZnCl_2$-H_2O and HCl-H_2O solutions show that steel, but not copper strips in $ZnCl_2$ H_2O and HCl-H_2O solu- extent. Further, as the temperature is raised above 400 F, HCl and H_2O boil off leaving $ZnCl_2$ which remains stable in contact with the solder or the base metals. Hydrolyzation of the flux is, thus, limited to lower temperatures and cannot account for the reactions leading to chemical deposition of lead or tin ahead of the advancing liquid solder drop as was postulated by Lewis (Ref. 24). The presence of NH_4Cl in the flux is essential for these reactions to occur.

Conclusions

1. Molten $ZnCl_2$ and $ZnCl_4$-NH_4Cl fluxes effectively remove oxides from copper, brass and mild steel plates by dissolution or chemical reaction, thus producing clean wettable surfaces.

2. NH_4Cl in the binary flux reacts with solder and base metal elements; such reactions are strongly dependent on temperature and NH_4Cl concentration. Lead and tin in the solder form $PbCl_2$ and $SnCl_2$ in the flux by reaction with NH_4Cl and may then be deposited on the base metal. Tin forms intermetallic compounds with the copper and its deposition produces a gray band at the edge of liquid tin or lead-tin alloy drop. Such deposition of tin may also take place by an electrochemical mechanism. Lead does not form compounds with copper and no such band appears at the edge of a molten lead drop.

3. On a mild steel plate, deposition of tin produces a white band at the edge of the molten drop. Similar deposition of lead leads to extensive spreading of the lead drop.

4. A zinc chloride flux shows no visible reaction with copper, brass or steel base plates. In the presence of moisture, the flux hydrolyzes to form hydrochloric acid which attacks a steel plate. As the temperature is

raised above 400 F, HCl and H_2O are boiled off leaving a stable zinc chloride residue.

5. Extensive spreading of 50-50 Pb-Sn alloy occurs on copper and brass plates with a zinc chloride flux during cooling. The solidified flux does not adhere to the base plate and provides a channel for capillary penetration.

Acknowledgements

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Correction

In the paper, "Stress Relaxation and Strain-Age Cracking in Rene 41 Weldments" by J. E. Franklin and W. F. Savage, for September, there are two revisions. On page 381-s, last line of first paragraph under *Introduction*, change "microscopic" to "macroscopic". On page 383-s, change equation (5) to read:

$$\sigma = E(L_t/L_o - \varepsilon_p)$$

WRC BULLETIN No. 189 November 1973

"Hardness as an Index of the Weldability and Service Performance of Steel Weldments"

by R. D. Stout

The idea of specifying a maximum hardness as a simple means of controlling cracking in steel weldments has appealed to many investigators; therefore, a considerable amount of research has been done in the past 35 years, particularly in the US and the UK, and more recently in Japan and Canada, in an attempt to correlate hardness with that elusive parameter "weldability."

The purpose of this report is to examine the evidence available in the literature regarding the fields of usefulness and the limitations that must be recognized in utilizing hardness as a control in welded construction. From this evidence, recommendations are made for the proper use of hardness testing as an aid in producing satisfactory weldments.

Publication of this paper was sponsored by the Interpretive Reports Committee of the Welding Research Council. The price of WRC Bulletin 189 is $3.00 per copy. Orders should be sent to the Welding Research Council, 345 East 47th Street, New York, New York 10017.