Influence of Flux, Substrate and Solder Composition on Solder Wetting

Equipment and method are described for optimizing several soldering variables

BY J. F. SHIPLEY

ABSTRACT. Equipment capable of measuring the rate at which solder wets a substrate is the basis for a method to optimize the materials of a soldering system. The equipment is essentially a sensitive weight-versus-time recording device. In operation, a substrate specimen is hung from an electrobalance and a pot of molten solder is carefully raised until contact occurs. The increase in weight per unit length of time is a measure of wettability and spreading.

The dependence of wettability on each of several variables is measured by maintaining all variables constant except the one under investigation. By this method the influence of various flux formulations, substrate materials and solder compositions can be optimized for a given soldering system.

Introduction

In his survey of the scientific principles related to wetting and spreading, Milner (Ref. 1) says, "In a survey such as this, which purports to deal with scientific principles, a difficulty is encountered when treating the subject of fluxes. It would in fact be no great exaggeration to dismiss the subject out of hand, on the grounds that scientific principles which govern the behavior of fluxes are not known." This was a challenging statement to those engaged in work related to development of flux materials for the soldering process. Perhaps lack of "scientific principles" referred to the fact that quantitative test methods for flux evaluation had not been developed. What test methods are available to explain or describe what makes a material act as a flux in the soldering process? And, what can be done to chemically optimize a flux?

Harding (Ref. 2) described test methods for flux evaluation which include: area of solder spread, equilibrium contact angle measurement between solder and substrate, and capillary rise of solder in small diameter tubing. These are static measurements, taken after the wetting process has occurred. Dynamic solder-substrate wetting methods include high speed movies of the solder spreading process in measuring advancing solder-substrate contact angle, substrate immersion tests, and molten solder-flux interfacial surface tension measurement. The latter approach, as described by Semenchenco (Ref. 3) has been studied through the maximum bubble pressure method.

Immersion testing as described by Earle (Ref. 4) is an extension of the Wilhelmy slide method for measuring surface tension in which flux is added to the substrate as a third component. Budrys and Brick (Ref. 5) extend this method utilizing a strain gage balance to continuously monitor substrate weight change as it is immersed in molten solder. They showed that the rate of solder wetting on tin plate increased with increasing temperature.

Technical Discussion

A solder flux formulation combines fluxing agents (activators) with other chemicals chosen for the particular soldering operation and process requirement. These may include solvents, varying in boiling point and evaporation rate from methanol to glycerine; surfactants, to reduce flux surface tension and aid surface wetting; colorants, to visibly observe surface coverage; foam and viscosity control agents. Fluxing agents, used within the electronics industry, include organoamine hydrochlorides for their chelation with metal ions, carboxylic acids, rosin and, in few instances, inorganic acids. Not only do activators vary in chemical type from one flux composition to another but also their percent composition varies.

Since a molten tin-lead solder will spontaneously wet onto copper substrate in a reducing atmosphere, one role of a flux material must be to reduce surface metal oxides in preparing metallurgically clean surfaces. This reduction of metallic oxide to base metal is a chemical reaction and should therefore be subject to chemical kinetic analysis. In order to apply such analysis to the soldering process, however, one must first accept that solder wetting onto a substrate is controlled by metallurgical surface preparation; namely, surface oxide reduction, and secondly, establish a method for monitoring the reduction reaction in the presence of solder, substrate and flux.

Solder wetting onto a surface, during the time in which that surface is "being prepared", can be monitored by a substrate weight increase...
method as solder, flux, and substrate are initially brought into contact and solder metallurgically wets onto the surface. Because the rate of substrate weight increase is a measure of the combined reaction rate for oxide reduction and metallurgical wetting, it follows that values of solder wetting rate, $R_{sw}$, are indications of flux reactivity in reducing metal oxide.

Metallurgical wetting $R_{mw}$, of one composition onto another follows the electromotive series and can be represented by its own specific reaction rate kinetics at conditions of constant temperature in a total reducing atmosphere. When the effectiveness of this reducing atmosphere changes (as in the case where different flux materials are used), and their rate of oxide reduction, $R_{or}$, is lower, allowing surface oxides to interfere with metallurgical contact, then values of metallurgical wetting are lowered. It follows then that values of solder wetting rate, $R_{sw}$, are indications of flux reactivity with metal oxide according to the expression,

$$R_{sw} = R_{mw}(1 - 1/R_{or})$$  

where values for metallurgical wetting rate, $R_{mw}$, are constant and reduced by the rate of surface oxide reduction, $R_{or}$, for the flux materials used in the soldering process.

Using this rate of solder wetting, the Arrhenius equation,

$$K = S \exp(-\Delta H_{a}/RT)$$  

might therefore be applied, which in logarithmic form,

$$\log K = (-\Delta H_{a}/RT) + \log S$$

predicts a straight line when logarithm reaction rate is plotted versus reciprocal absolute temperature. This now provides a method to quantitatively describe soldering materials and processes.

Keeping substrate and solder composition constant and varying only the flux used, changes in solder wetting rate are attributed to flux reactions at the solder-substrate interface. This procedure was used to study effects of chemical type of flux activator and concentration within the flux composition. By maintaining substrate and flux materials constant, varying only solder metallurgy, changes in the rate solder wets onto the substrate are attributed to wettabiltiy of the solder metallurgy, which establishes a test method for evaluating solder materials. Similarly, while maintaining solder metallurgy and flux materials constant, varying only substrate materials, changes in solder wetting rate can be attributed to substrate materials.

**Apparatus**

Solder wetting rate measurement is a modification of the Wilhelmy slide method for measuring surface tension wherein the liquid is molten solder and the slide is copper substrate onto which a third component, flux, is applied. The molten solder level is gradually raised until it first touches the hanging substrate which is suspended from an electrical output analytical balance. The rate which solder metallurgically wets onto the substrate, monitored by substrate weight increase versus time, is measured as a function of solder temperature.

Figure 1 shows the laboratory apparatus used to measure solder wetting rate. Component parts include:
- Cahn Model RG Electrobalance
- Cahn Electrobalance Controller
- Strip chart recorder
- Oscilloscope/light beam recorder
- Temperature controlled solder reservoir
- Digital thermocouple
- Variable transformer
- Alignment block and slide
- Movable lift support
- Electrically driven micrometer head and switch

**Experimental Procedure**

Substrates are die punched from 5 mil copper foil to a dimension 0.25 in. wide, 1 in. long with a 0.030 in. diameter hole at one end. After solvent cleaning and drying, substrates are suspended from the weighing arm of the electrobalance by means of thread and hook connections, as shown in Fig. 2. Flux is applied onto the substrate and the temperature controlled liquid solder is raised until in close proximity to the substrate. The electrical drive is then actuated, raising the solder at a rate of 0.0015 in./s until contact is made. In some applications this operation is done by hand without using the electrical drive.
A typical solder-substrate wetting curve for weight increase versus time is shown in Fig. 3. Wetting rate is obtained from the slope of the line for initial substrate weight increase. Depending upon rate of wetting and recording system response rate, either the strip chart or oscilloscope is used to record substrate weight change with time. At least five replicate tests are conducted for each test temperature. Calculations specify solder wetting rate onto the test substrate in milligrams of solder per second per 1/4 in. of substrate width, which is then converted to the more appropriate terminology of dynes/cm/s. Least square regression analysis of these data is used to provide straight line equations for expression of reaction rate kinetics. Correlation coefficients for test data fit are high, usually above 0.95.

Results

Flux Materials

Straight line regression analysis of data taken for tin-lead eutectic solder wetting rate onto copper substrate between 190-380°C is plotted as log solder wetting rate versus reciprocal absolute temperature in Fig. 4 for a rosin flux containing dimethylamine-hydrochloride (DMA.HCl), a glycerine flux containing DMA.HCl and for DMA.HCl alone as the flux material. Correlation coefficients for data fit were 0.96, 0.94 and 0.99 respectively. From the slope of these straight lines, energies of activation are calculated and used to describe differences between flux materials.

The comparison in wetting rate and temperature dependence for these flux materials shows that while specific solder wetting rate may depend on flux composition (3260 dynes/cm/s at 260°C for DMA.HCl reduced to 2480 dynes/cm/s at 260°C for either glycerine or rosin containing DMA.HCl), activator material controls temperature reactivity of the flux independent of carrier material (4647 cal per mole compared to 5175 and 4908). This is shown more clearly in Fig. 5 where the activation energy 5175 cal per mole for rosin containing 0.7% DMA.HCl is closer to that of DMA.HCl, 4647 cal per mole, than it is for rosin, 10624 cal per mole. Reduction in wetting rate when carrier resins are contained within the flux formula may be due to high temperature oxidation or polymerization reactions occurring within these carrier resins.

The effectiveness of various "flux activators" were studied and included amine hydrochlorides, dicarboxylic and monocarboxylic acids. A compilation of data for all organic acids evaluated is shown in Table 1 for comparison. Attempts to correlate flux effectiveness, either energy of activation or specific wetting rate, with individual acid ionization constant or chemical structure were unsuccessful. Solder wetting characteristics for four dicarboxylic acids as the flux are compared, in Fig. 6, to solder wetting for DMA.HCl as the flux. As shown in Fig. 7, the three chemical types of flux material can be illustrated categorically by their ability to allow solder wetting to occur, with the amine hydrochloride being the most active of the flux materials in reducing surface oxides, the dicarboxylic acids second most active and the monocarboxylic acids the least active of the three chemical types evaluated.

Flux Concentration

Activator concentration within the flux formula also plays a role in reducing metallic oxides and causing metallurgical wetting.

To illustrate this, weight percent dimethylamine-hydrochloride in glycerine was varied between 0.001 and 0.7% in DMA.HCl. A decrease in wetting rate with a 0.7% increase in DMA.HCl indicated a decrease in the ability of the flux to wet solder. Correlations in effectiveness of various "flux activators" were studied and included amine hydrochlorides, dicarboxylic and monocarboxylic acids. A compilation of data for all organic acids evaluated is shown in Table 1 for comparison. Attempts to correlate flux effectiveness, either energy of activation or specific wetting rate, with individual acid ionization constant or chemical structure were unsuccessful. Solder wetting characteristics for four dicarboxylic acids as the flux are compared, in Fig. 6, to solder wetting for DMA.HCl as the flux. As shown in Fig. 7, the three chemical types of flux material can be illustrated categorically by their ability to allow solder wetting to occur, with the amine hydrochloride being the most active of the flux materials in reducing surface oxides, the dicarboxylic acids second most active and the monocarboxylic acids the least active of the three chemical types evaluated.

Effects of gravitational acceleration and solder density are neglected.

Fig. 3 — Solder-substrate wetting curve

Fig. 4 — Regression analysis plots for tin-lead eutectic solder on copper substrate indicating energies of activation

Fig. 5 — Regression analysis comparison for fluxes with and without DMA.HCl indicating energies of activation (tin-lead eutectic solder, copper substrate)
Table 1 — Properties of Organic Acids as Fluxes for Tin-Lead Eutectic Solder on Copper Substrates

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structure (dibasic)</th>
<th>Activation energy, cal/mole</th>
<th>Wetting rate, dynes/cm/s. @ 233 C</th>
<th>Ionization PKa = -logKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic</td>
<td>HOOC-(CH₂)₅-COOH N=0</td>
<td>3160</td>
<td>1888</td>
<td>1.23</td>
</tr>
<tr>
<td>Malonic</td>
<td>HOOC-(CH₂)₄-COOH N=1</td>
<td>2675</td>
<td>1891</td>
<td>2.83</td>
</tr>
<tr>
<td>Succinic</td>
<td>HOOC-(CH₂)₃-COOH N=2</td>
<td>3383</td>
<td>1178</td>
<td>4.19</td>
</tr>
<tr>
<td>Glutaric</td>
<td>HOOC-(CH₂)₂-COOH N=3</td>
<td>3873</td>
<td>1274</td>
<td>4.35</td>
</tr>
<tr>
<td>Adipic</td>
<td>HOOC-(CH₂)₁-COOH N=4</td>
<td>10240</td>
<td>436</td>
<td>4.43</td>
</tr>
<tr>
<td>Pimelic</td>
<td>HOOC-CH₂-COOH N=5</td>
<td>7791</td>
<td>930</td>
<td>4.68</td>
</tr>
<tr>
<td>Suberic</td>
<td>HOOC-CH₂-COOH N=6</td>
<td>3039</td>
<td>1892</td>
<td>4.52</td>
</tr>
<tr>
<td>Azelaic</td>
<td>HOOC-CH₂-COOH N=7</td>
<td>4432</td>
<td>930</td>
<td>4.53</td>
</tr>
<tr>
<td>Sebacic</td>
<td>HOOC-CH₂-COOH N=8</td>
<td>9577</td>
<td>888</td>
<td>4.60</td>
</tr>
<tr>
<td>Fumaric</td>
<td>HOOC-(CH₂)₅-COOH</td>
<td>2937</td>
<td>1069</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Wetting rate. dynes/cm/s. @ 233 C
1988 1891 1178 1274 456 930 1892 930 456 930 456 930

Substrate Metallurgical wetting is dependent not only on the flux materials used to reduce surface oxides but also upon metallurgy involved in the reaction. This is shown in Fig. 9 where regression analysis plots of logarithm solder wetting rate for tin-lead eutectic solder versus reciprocal temperature are plotted for nickel, copper foil, pyrophosphate copper plating and an immersion tin on copper foil. Energies of activation are 6828, 5175, 297, and 351 cal per mole respectively and 100 percent and tin-bismuth eutectic solder wetting rate onto copper foil at 170 C was measured using these flux formulations. Results are shown in Fig. 8 and indicate that significant reduction in solder wetting rate occurs below a concentration of 0.7% DMA.HCl in glycerine and that above this concentration, rate of change in wetting rate is less for increasing amounts of activator.

Fig. 6 — Regression analysis comparison for several dicarboxylic acids and DMA.HCl as fluxes (tin-lead eutectic solder, copper substrate)

Fig. 7 — Solder wetting comparison for three chemical families of flux materials (tin-lead eutectic solder, copper substrate)

Fig. 8 — Solder wetting rate versus concentration of flux activator for tin-bismuth eutectic solder on copper substrate at 170 C

Fig. 9 — Solder wetting rate comparison of four substrates (tin-lead eutectic solder, rosin flux containing DMA.HCl)
Table 2 — Wetting Rate Comparison for Several Solders on Copper Substrates with Rosin + DMA.HCl Flux

<table>
<thead>
<tr>
<th>Solder</th>
<th>Symbol</th>
<th>Composition</th>
<th>Activation energy, cal/mole</th>
<th>Temp., C</th>
<th>Wetting rate at liquidus +50 C, dynes/cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>—</td>
<td>2112</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tin/Silver/+</td>
<td>Sn/Ag</td>
<td>95/3.5/+</td>
<td>3660</td>
<td>271</td>
<td>3552</td>
</tr>
<tr>
<td>Tin/Lead</td>
<td>Sn/Pb</td>
<td>63/37</td>
<td>5175</td>
<td>233</td>
<td>1930</td>
</tr>
<tr>
<td>Tin/Lead/Indium</td>
<td>Sn/Pb/In</td>
<td>54/26/20</td>
<td>5088</td>
<td>195</td>
<td>660</td>
</tr>
<tr>
<td>Tin/Indium</td>
<td>Sn/In</td>
<td>50/50</td>
<td>6178</td>
<td>117</td>
<td>618</td>
</tr>
<tr>
<td>Tin/Bismuth</td>
<td>Sn/Bi</td>
<td>42/58</td>
<td>7246</td>
<td>188</td>
<td>328</td>
</tr>
<tr>
<td>Tin/Lead/Bismuth</td>
<td>Sn/Pb/Bi</td>
<td>16/32/52</td>
<td>9842</td>
<td>150</td>
<td>50</td>
</tr>
</tbody>
</table>

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It is apparent from the combined plot of solder wetting rate at 50 C above liquidus and energy of activation versus percent tin in the solder, as shown in Fig. 12, that tin content of the solder plays a large role in the overall surface wettability of a solder. Rate of wetting is maximum and temperature dependence minimum at maximum tin percent composition.

**Conclusion**

The influence of flux, substrate and solder composition on the wetting of solders is shown through the use of a laboratory test method for solder wetting rate measurement. It is a fast, dependable, and consistent analytical procedure for laboratory optimization of materials used within the soldering process. Reactivity rate between solder, substrate and flux materials is the basis for quantitative expression.

**Acknowledgments**

The author wishes to thank W. Albrecht for his continued technical encouragement during the course of this work and to L. Balan and J. Sirsen for their laboratory support in conducting many of the tests.

**References**


**Correction**

In the paper, "Performance of the MnO-SiO₂-CaO System as a Welding Flux" (July 1975), Fig. 6, page 213-s, does not show the dark circle mentioned in the caption. The coordinates of the dark circle are 0.74 arc penetration and 75% MnO.

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**WRC Bulletin 203**

**February 1975**

"Niobium and Vanadium-Containing Steels for Pressure Vessel Service"

by J. N. Cordea, Armco Steel Corp.

The effects of niobium (Nb) and vanadium (V) additions on the properties of plain carbon (C) steel have been well known for some years now. Recently, through refinements and processing technology, very effective use has been made of relatively small amounts of Nb or V (up to 0.2 wt-%) to significantly increase yield strength and improve notch toughness. These improvements have resulted through optimization of Nb and V carbonitride precipitation hardening, ferrite grain size refinement, and a reduction in C content. The latter item also significantly improves weldability.

Nearly all of the industrialized countries of the world have taken advantage of the economy of producing higher strength steels with a minimum of extra alloying cost. This is especially true for structural applications where weight saving is so important. Many countries have also made effective use of these steels for pressure vessel applications. Although the United States is very active in high-pressure line-pipe development, very little activity has been directed toward using Nb and V steels for pressure vessels and other containers. The principal reason is that allowable-stress calculation as specified by the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code is usually governed by tensile strength. While yield strength is increased significantly by Nb and V additions, there is a relatively small effect on tensile strength. Consequently, no direct advantage can be gained in pressure vessel design by an increase in yield strength.

It is the purpose of this report to summarize the state of the art of Nb- and V-containing C-Mn steels for pressure vessel applications and to identify areas needing further research. Specifically, this report covers low-alloy steels with an upper yield-strength range of about 75 ksi (53 kg/mm²). A brief summary of the pressure vessel codes around the world is presented in order to provide a basis for important material properties in the design of pressure vessels. Available steels, their mechanical properties and the technology for producing them are covered in detail. Although a few structural grades and pipeline steels from the United States are discussed, the main emphasis is directed toward foreign steels produced for pressure vessel applications. Where appropriate, comparisons are made to similar composition structural grades produced in the United States. Weldability and other important properties necessary for satisfactory fabrication and service are evaluated. This work was initiated and sponsored by the Pressure Vessel Research Committee of the Welding Research Council, Fabrication Division, Subcommittee on Thermal and Mechanical Effects.

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