Assessment of Low-Temperature Fluxes

The subject of this paper is the evaluation of the wetting balance as a technique for studying the flux activity of newly developed low-temperature solder paste fluxes. The most effective configuration of the wetting balance was the standard configuration with only one change: the PbSn eutectic solder was replaced with a eutectic solder alloy with a melting point of 58°C. Since 58°C is significantly less than the proposed activation temperatures of the solder fluxes, wetting curves as a function of temperature could be studied for each of the fluxes. The resulting data was used to rank the fluxes in terms of their activation requirement.

by Hubert A. Vander Plas, Russell B. Cinque, Zequn Mei, and Helen Holder

Solder alloys with melting temperatures between 110°C and 160°C are currently under evaluation within Hewlett-Packard. An investigation of the mechanical properties of these solders has indicated that a suitable alloy can be found in the ternary or binary subsets of the BiInPbSn system (see *Article 10*). However, alloy selection is only the first step in developing a low-temperature soldering process. A suitable flux must be chosen for use in a solder paste and the alloy-flux interaction must be studied. Thus, the ability of fluxes to activate at temperatures 20 to 30°C below the melting point of the alloy must be evaluated. In the case where different solder metallurgies have similar mechanical properties, the optimal metallurgy for a low-temperature process may be determined by the availability of the appropriate flux chemistry.

For the flux selection phase, there is no standard procedure for testing the activity of a solder flux. The degree of wetting in a system (solder, substrate, atmosphere, flux) may be characterized with a sessile spread test or by a wetting force measurement. (The sessile spread test is often simply called a spread test.[1]) The two tests are complementary. Each of the tests involves a balancing of surface tensions at a three-phase junction. For an assessment of flux activity, a dynamic measurement is more appropriate than a static measurement. Thus, the wetting force measurement is preferred to the sessile spread measurement.

The wetting balance was developed to test the solderability of component leads in a wave solder process. The technique has been adapted to characterize the solderability of surface mount component leads.[2] The focus of this paper is the evaluation of the wetting balance as a technique for studying the flux activity of newly developed low-temperature solder paste fluxes. Specifically, the Multicore MUST System II wetting balance was modified to evaluate flux activity at lower temperatures. Sample preparation and testing procedures were adapted to compare the wetting of various low-temperature solder alloy/flux combinations.

Review of the Wetting Balance

A wetting balance measures the force produced by the solder meniscus when a solid test specimen is partially immersed into a molten solder. The force is plotted as a function of time to produce a wetting curve. The measured force, F, is the sum of two components: a wetting force F_w, and an Archimedes buoyant force F_b.

$$F = F_w + F_b$$

$$= p\gamma_{lv}\cos\theta - \rho gV.$$

(1)

where p is the sample perimeter, γ_{lv} is the liquid-vapor interfacial energy, θ is the liquid contact angle, ρ is the solder density, g is the gravitational acceleration, and V is the submerged volume of the solid. Fig. 1 shows the relationship between the solder meniscus and the wetting curve. The buoyant force, shown as a dashed horizontal line in Fig. 1, is determined by the immersed volume. Since this remains constant throughout the test, the evolution of the wetting curve reflects changes in wetting force as the solder meniscus rises. The act of immersion (Figs. 1a, 1b) causes the meniscus to curve downward, producing a negative wetting force. As the meniscus rises (Fig. 1c) and becomes horizontal, the wetting force tends to zero. If solder wets the specimen, the meniscus will climb above the level of the bath, producing a positive wetting force. Eventually, the solder meniscus reaches its equilibrium configuration (Fig. 1d) and the wetting curve comes to an equilibrium value.

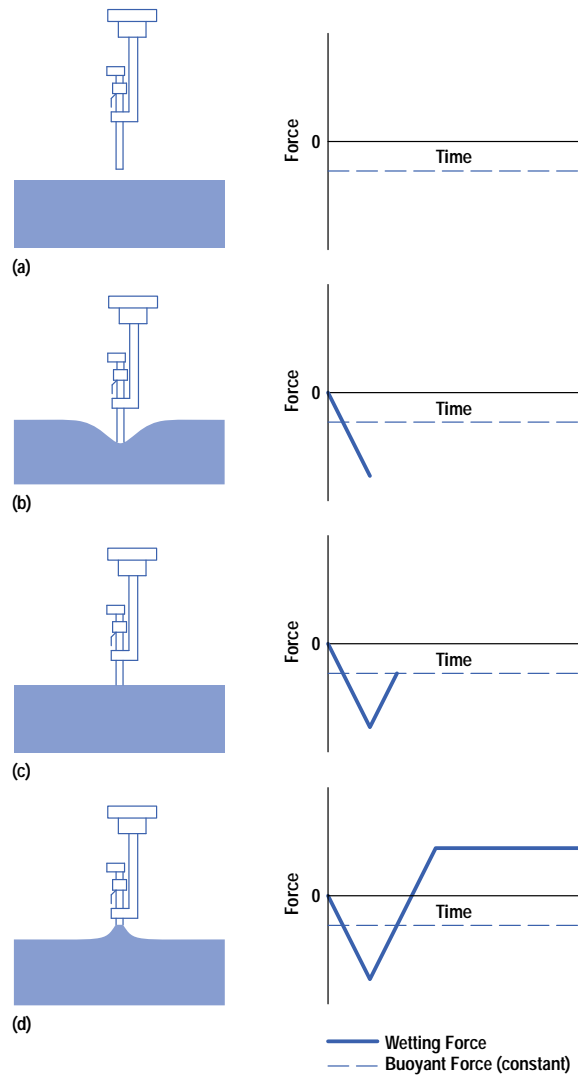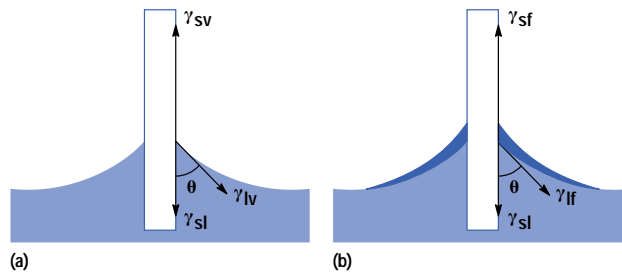*Fig. 1. Relation between the solder meniscus and the wetting curve.*

Fig. 2. The balance of surface energies at the three phase junction. (a) Basic system. (b) More complex system with flux forming a viscous ring around the solid.

When using wetting force measurements to study flux efficacy, it is essential to understand how fluxes may affect wetting curves. There are essentially only two points of comparison for wetting curves: the equilibrium wetting force and the rate of wetting. From equation 1, it can be seen that the wetting force is proportional to the cosine of the solder contact angle θ. The equilibrium wetting force is, therefore, proportional to the cosine of the equilibrium contact angle θ_{eq}. For simple systems, as shown in Fig. 2a, the equilibrium contact angle is given by Young's equation:[3]

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv}\cos\theta_{eq} \qquad (2)$$

where γ_{sv} is the solid-vapor interfacial energy, γ_{sl} is the solid-liquid interfacial energy, and γ_{lv} is the liquid-vapor interfacial energy. By combining equations 1 and 2, the equilibrium wetting force $F_{w,eq}$ is determined by the difference in the

solid-vapor and solid-liquid surface energies:

$$F_{w,eq} = p(\gamma_{sv} - \gamma_{sl}). \tag{3}$$

Thus, fluxes may improve the wetting force by increasing solid-vapor surface energies or by lowering solid-liquid surface energies. Notice that the liquid-vapor surface energy does not appear in equation 3.

The system becomes more complex when flux forms a viscous ring around the solid. As shown in Fig. 2b, flux replaces vapor at the original three-phase junction, altering the surface energies, which determine the wetting force. Furthermore, the mass of flux and the creation of two additional three-phase junctions may alter the wetting force by distorting the shape of the solder meniscus. Despite these complications, measurement of the wetting force should still provide useful information that reflects the efficacy of the flux.

The second point of comparison for wetting curves is the rate of wetting. This can be reasonably defined in a number of ways. In this paper, the rate of wetting will be taken as the time to reach the buoyant force ($\theta = 90°$). In the standard mode of operation, the heat for flux activation is supplied when the specimen is immersed into the solder bath. In this case, progress of wetting may be limited by the rate at which flux reduces the surface oxide of the specimen. The time to wet, t, normally follows the exponential form expected for an activated process:

$$t = t_0 e^{Q/kT},$$

where t_0 is a constant, k is Boltzmann's constant, T is the temperature of the solder bath, and Q is an activation energy. It follows that higher temperatures and more active fluxes will produce more rapid wetting. The situation is altered when a furnace preheat is used for flux activation. In this case, oxide reduction and the rate of wetting will depend on the time at high temperature in the furnace. If the flux works properly the surface oxide will have been reduced before initiation of the wetting test.

Procedure

The activation requirements of low-temperature fluxes and the effects of flux alloy interaction were investigated using a Multicore Universal Solderability Tester (MUST II). All tests were conducted in air using a standard copper wire as the test specimen. Standard samples consisting of 1-mm-diameter copper wire were prepared by etching the as-received wire to remove all surface oxides. These samples were aged at 100°C for one hour in air to produce a uniform, repeatable oxide coating on the samples.

Fluxes were applied in one of two ways. First, when the flux was in liquid form, the specimen was dipped into the liquid to produce an even coat. The liquid fluxes (Actiec 5, Actiec 2, and SM/NA) are standard fluxes provided by Multicore with the MUST II system. Second, when the flux was part of the solder paste flux vehicle, a uniform weight of flux vehicle (approximately 4 to 5 mg) was evenly spread on the surface of the Cu wire.

Since the goal was to evaluate each flux as a component of a solder paste, all of the experimental fluxes were obtained as part of the solder paste flux vehicle, that is, the solder paste without the solder. All of the fluxes—flux 1, flux 2, and flux 3—evaluated in this program were low-temperature flux systems under development. The performance of the developmental fluxes was compared to a flux vehicle developed for use with eutectic PbSn solder.

The Multicore wetting balance was set up in the three different configurations shown in Fig. 3.

- Standard configuration (Fig. 3a). This is the normal mode of operation for the Multicore MUST II. The copper wire is dipped into a large volume (6 cm in diameter by 5 cm deep) of molten solder. Two different solder alloys were used in the large bath: eutectic PbSn, which melts at 183°C, and 49Bi21In18Pb12Sn, a quaternary eutectic alloy (the numbers are the percentages by weight of the four components of the alloy) that melts at 58°C. Heating the sample occurs when it is dipped into the molten solder.

Fig. 3. *The three configurations of the wetting balance studied. (a) Standard configuration. (b) Furnace preheat configuration. (c) Microbath configuration.*
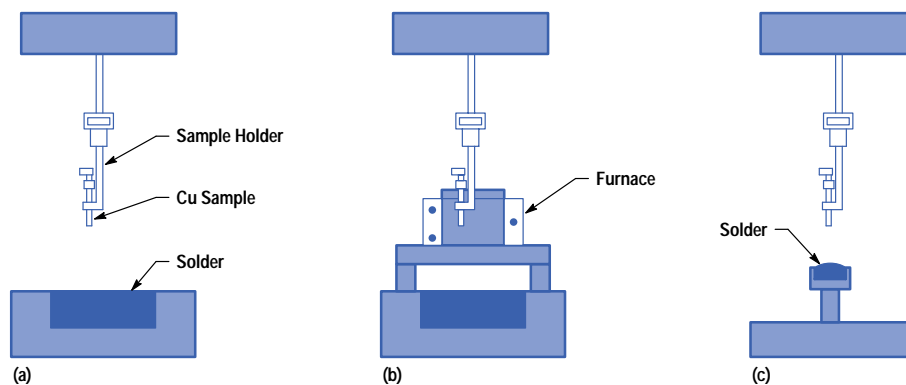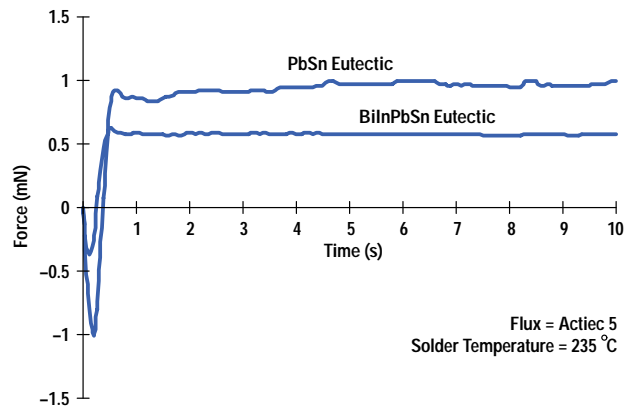
Fig. 4. *The effect of solder composition on the equilibrium wetting force.*

- Furnace preheat configuration (Fig 3b). A separate heater is attached on top of the solder bath in the standard configuration. This allows the sample to be heated before immersion into the molten solder. The preheat temperature can be controlled independently of the solder bath temperature.
- Microbath configuration (Fig. 3c). The volume of molten solder is reduced to 0.6 cm in diameter by 0.5 cm deep. This configuration minimizes the amount of each solder alloy that is required to do the tests.

When the quaternary eutectic alloy is used in the standard configuration, the bath temperature can be set to investigate the activation as a function of temperature for the low-temperature fluxes. The furnace preheat technique is a variation of the standard test that was developed to imitate more closely the thermal cycle of a standard surface mount soldering process. The furnace, mounted directly above the solder bath, provides control of the specimen temperature independent of the solder bath temperature. Finally, the microbath was used to investigate the effects of flux-alloy interaction for a variety of alloys. The microbaths are aluminum containers that were machined to sit atop the MUST II globule heater. The baths, which hold less than 10 grams of solder, minimize the amount of solder required for testing. The microbath setup yielded more reproducible results than the standard globule tests provided by Multicore.

Results

Equilibrium Wetting Force. Differences in equilibrium wetting force can be produced either by varying the solder bath composition or by varying the flux composition. Fig. 4 shows the differences in the equilibrium wetting force produced by varying the solder composition. In this test, both the PbSn eutectic solder and the BiInPbSn quaternary eutectic solder were used with the standard configuration and a bath temperature of 235°C. One flux, Actiec 5, is plotted for both alloys and clearly shows the difference in the equilibrium wetting force.

Fig. 5 shows the differences in the equilibrium wetting force that can be produced by changing the flux composition. Flux 1 and flux 2 are two different experimental low-temperature fluxes. They were both used with the eutectic quaternary alloy and a bath temperature of 190°C in the microbath configuration. Tests conducted using flux 2 exhibit a consistently greater equilibrium wetting force.

Rate of Wetting. Differences in the rate of wetting can be produced by varying the flux composition or by varying the bath temperature. Fig. 6 shows the difference in wetting rate as the hydrochloric acid content (flux composition) is varied from 0 to 5% using the standard liquid fluxes supplied by Multicore. These tests used the standard configuration with PbSn eutectic

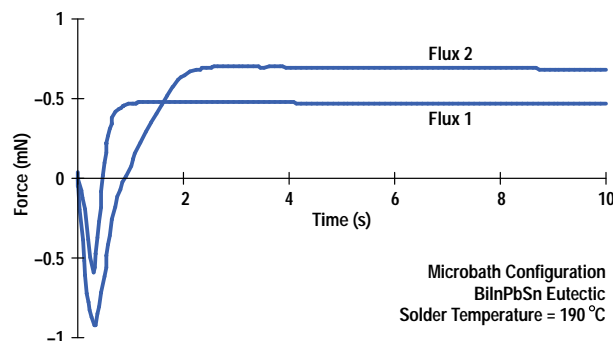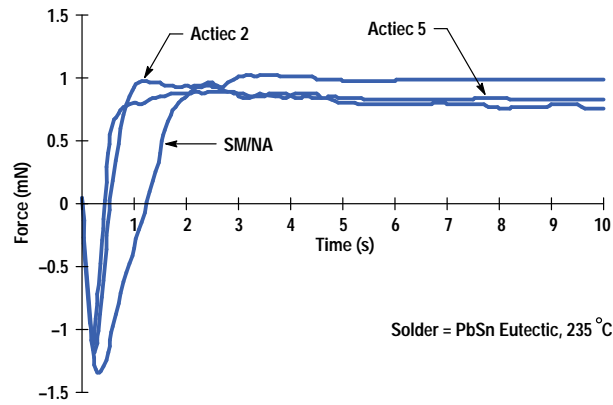**Fig. 5.** *The effect of flux vehicle composition on the equilibrium wetting force.*

Fig. 6. *The effect of flux activity on wetting times.*

Actiec 2 Actiec 5

SM/NA

Solder = PbSn Eutectic, 235 °C

solder and a bath temperature of 235°C. They illustrate that the wetting balance is capable of detecting a change in wetting rate as the flux composition is changed.

Differences in the rate of wetting produced by varying the bath temperature are shown in Fig. 7. These tests were conducted using the standard configuration, the quaternary alloy, and flux 1. The bath temperature was varied from 110°C to 160°C as indicated. Each curve represents the average of two tests. The wetting behavior improves as the bath temperature is raised. At 160°C, the equilibrium wetting force reached its maximum value of 0.5 mN.

Fig. 7. *Wetting curves for flux 1 as a function of solder temperature using the quaternary alloy as the solder bath.*

160 °C   135 °C   110 °C

Solder = BiInPbSn Eutectic
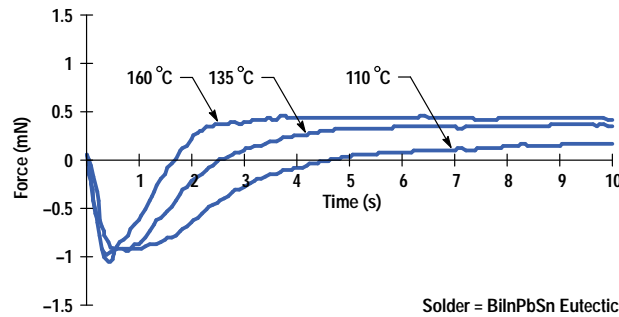
The furnace preheat configuration provided a method of changing the flux activation temperature while maintaining a constant solder bath temperature. For the data presented in Fig. 8, the solder bath temperature was set at a constant value of 100°C using the quaternary eutectic solder. The activation temperature was changed by varying the power to the heater. In each case, the sample was submitted to a short (30 s) preheat at the indicated power setting before immersion into the solder bath. Fig. 9 shows the temperature as a function of time for each power setting. Insertion into the solder bath and the start of the 30-s preheat are at time = 50 s in Fig. 9. As the power is increased from 0 to 60% (~50°C to ~160°C), the rate of wetting improves and the equilibrium wetting force remains constant. The furnace preheat was intended to replicate the flux activation time used in a normal reflow furnace. Thus, preheat times of a few minutes were planned. However, longer preheat times produced a progressive deterioration of the wetting behavior. The low-temperature fluxes were unable to protect the specimens from reoxidizing during the longer preheats. Preheating in a nitrogen atmosphere was considered.

Fig. 8. *Wetting curve for flux 2 as a function of furnace preheat power settings.*

60%   40%   30%   No Power

Flux = Flux 2
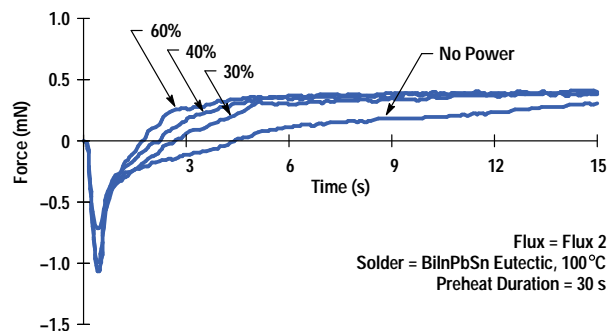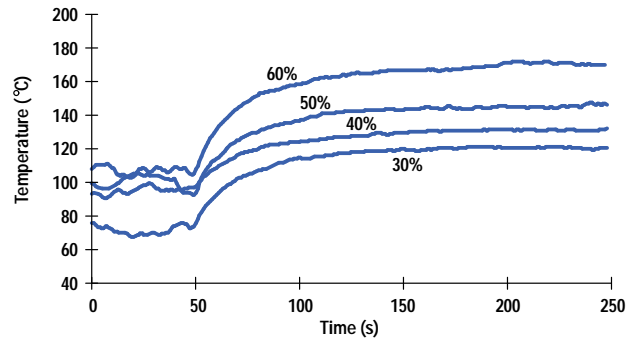Solder = BiInPbSn Eutectic, 100°C
Preheat Duration = 30 s

Fig. 9. *Temperature calibration curves for the preheat furnace.*

However, this option requires a major modification of the equipment that was outside the scope of this project. As a result, the objective of using the preheat configuration to assess flux activation requirements was not accomplished.

Analysis

Equilibrium Wetting Force. Figs. 4 and 5 indicate that the wetting force measurement is able to distinguish the effects of varying the solder alloy and the flux composition on the equilibrium wetting force. From equation 3, the wetting force is reduced by the difference $(\gamma_{sv} - \gamma_{sl})$. For the test shown in Fig. 4, the solid, vapor, and flux are constant. As a result, γ_{sv} should remain constant and the differences in the equilibrium wetting force are produced by variations in γ_{sl}. In Fig. 5, the solid, liquid, and vapor remain constant and the flux is varied. The equilibrium wetting forces produced by flux 2 are consistently greater than those produced by flux 1. This difference is difficult to associate with either γ_{sv} or γ_{sl}. The equilibrium wetting force is a function of both the solid-liquid and the solid-vapor interface. Both of these interfaces may depend on the presence of the flux. The solid-vapor interface will be influenced by the presence of the flux. In addition, different fluxes will remove surface oxides from the solid with different efficiencies. Thus, the observed differences in equilibrium wetting forces are difficult to associate with either interface.

Rate of Wetting. Figs. 6 and 7 indicate that the rate of wetting, defined here as inversely proportional to the time to cross the $F_w = 0$ axis, is a function of both the flux composition and the activation temperature. In Fig. 6, the solid, liquid, and vapor remain constant and the flux is variable. The rate of wetting increases as the acid content of the flux increases. The rate of wetting is dependent on the degree of oxide removal, which is a function of acid concentration and temperature. In Fig. 7, only the temperature was varied. The rate of wetting increases with increasing temperature and the equilibrium wetting force reaches its maximum at 160°C. This indicates that the flux has effectively removed surface oxides within the first three to four seconds at this temperature.

Ranking of Low-Temperature Fluxes

The four plots in Fig. 10 compare the wetting behavior of the three developmental fluxes—flux 1, flux 2, and flux 3—to the control flux formulated for use with eutectic PbSn solder. In each test, the standard configuration was used with the quaternary eutectic alloy. The bath temperature was varied from 110 to 160°C. As expected, the control flux shows no wetting until the bath temperature is 160°C. Flux 3 performs similarly to the control flux and would not be a candidate for use with low-temperature solders. Flux 1 is the most promising of the three developmental flux vehicles. Its wetting times at 110°C are equivalent to the wetting times of flux 2 at 160°C. In addition, the equilibrium wetting force of 0.5 mN is greater than the equilibrium wetting force of flux 2. In summary, the ranking of fluxes in terms of activation requirements is (flux 1 < flux 2 < flux 3 and the control flux).

Conclusions

The wetting balance as a method to discriminate the wetting behaviors of various solder alloys and fluxes has been generally successful. Replacing the standard eutectic PbSn solder with a low-temperature solder alloy in the standard configuration was the most effective method for evaluating the low-temperature fluxes. Operating in the standard configuration with a low-melting-point quaternary eutectic alloy, the wetting balance was able to rank the fluxes in terms of activation requirement (flux 1 < flux 2 < flux 3 and the control flux). The results illustrate the usefulness of wetting force measurements in the characterization of low-temperature fluxes.

Fig. 10. *Wetting curves comparing the wetting behavior of flux vehicles. The BiInPbSn eutectic solder was used for each test. The label for each curve is the solder bath temperature.*
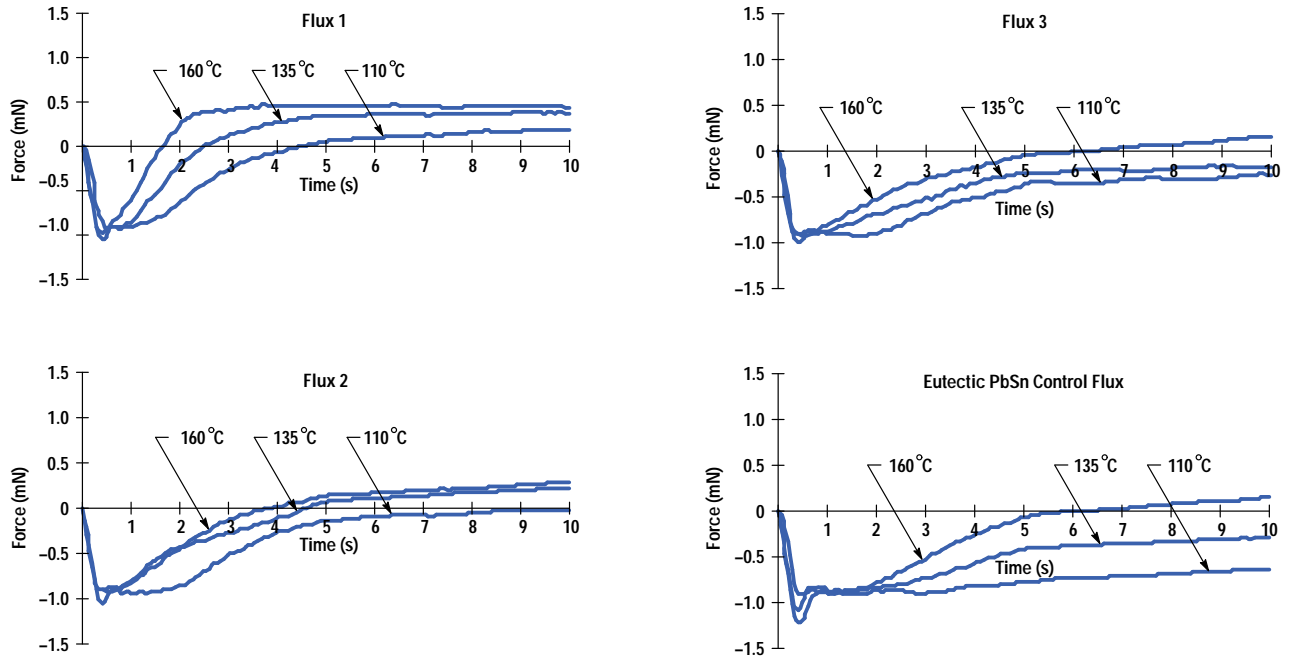
Acknowledgments

References

1. F.G. Yost, F.M. Hosking, D.R. Frear, editors, *The Mechanics of Solder Alloy Wetting and Spreading*, Van Nostrand Reinhold, 1993, pp. 215-216.
2. *Ibid*, pp. 16-17.
3. *Ibid*, p. 146.