

Room Temperature Aging Properties of Some Solder Alloys

Sn-Pb and Sn-Pb-Sb alloys undergo a loss in shear strength and hardness during 1st 30 days of storage after soldering, and some alloys require 30-60 days of aging to stabilize their mechanical properties and microstructure although post-solder annealing at 200 F for 80 hours effectively stabilizes the mechanical properties of 50Sn-47Pb-3Sb

BY B. T. LAMPE

ABSTRACT. Tin-lead and tin-lead-antimony alloys were found to age-soften during storage at room temperature. Some alloys experienced greater than a 20% loss in shear strength and hardness during the first 30 days of storage after soldering. The loss in strength which is accompanied by structural changes in the alloys is attributed to the precipitation of β -tin out the supersaturated lead-rich phase. The presence of antimony reduces the precipitation rate and prolongs the age-softening process in addition to refining the grain structure.

Some alloys required 30 to 60 days of aging before their mechanical properties and microstructure stabilized. The mechanical properties and aging characteristics were found to be sensitive to prior thermal treatment. A post-solder anneal was found effective in stabilizing the properties of the alloys.

Introduction

The term "solder" has become synonymous with the tin-lead alloy system. Tin-lead solders are relative-

ly inexpensive, have desirable electrical properties, and can be used to join most metals. The mechanical strength of tin-lead solder, however, is extremely low compared with the metals which they are generally used to join. When the solder joint must carry a load, the joint must be designed to avoid dependence upon the strength of the solder.

The strength of a solder joint is strongly dependent upon the joint gap or the clearance between the soldered interfaces. Joint strengths far exceeding the strength of the bulk solder can be obtained with very small (less than 0.001 in. or 0.025 mm) joint gaps. Joint gaps exceeding 0.005 in. (0.13 mm), however, generally produce joint strengths approaching that of the bulk solder. Tin-lead solders also have characteristically low creep strengths, especially at elevated temperatures. Alloying elements such as antimony, copper, and silver are commonly added to tin-lead solders to improve their creep strength.

A production requirement called for a low (less than 400 F or 204 C) melting point solder with good shear strength and creep strength. A tin-lead-antimony solder (50Sn-47Pb-3Sb) was selected, but solder joints made with this alloy were found to lose considerable strength during storage. It appeared that the solder was undergoing some type of "age-

softening" transformation at room temperature.

The mechanical properties of many low melting alloys change gradually with time at room temperature because of minute changes in structure. This aging at room temperature is sometimes referred to as room temperature recrystallization or annealing. Aging sometimes has the effect of increasing the hardness and strength of the alloy, but it can also have the opposite effect. For example, a chill-cast quaternary eutectic of tin, bismuth, cadmium, and lead shows an increase in strength of about 34% after 16 weeks of aging at room temperature (Ref. 1).

Lead-antimony alloys exhibit the same age-hardening property. If heated above their solid solubility temperature and then quenched, they show a marked increase in hardness on aging, the extent of which is dependent on the amount of antimony present and the rate of cooling (Ref. 2). Tin-antimony-cadmium alloys containing 7-14 wt-% antimony and 0-2 wt-% cadmium also age-harden when tempered at 100 C (212 F) after water quenching from above 200 C (414 F) (Ref. 3). This hardening is attributed to the dispersion of the SnSb intermetallic in the matrix. Tin-antimony alloys containing less than 7% antimony age-soften when tempered at 100 C (212 F). Softening occurs in two stages: first

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Paper presented at the Fifth International AWS Soldering Conference held in St. Louis, Missouri, May 11-13, 1976.

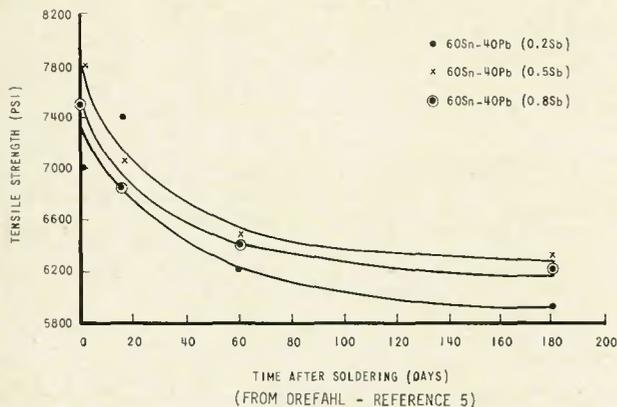
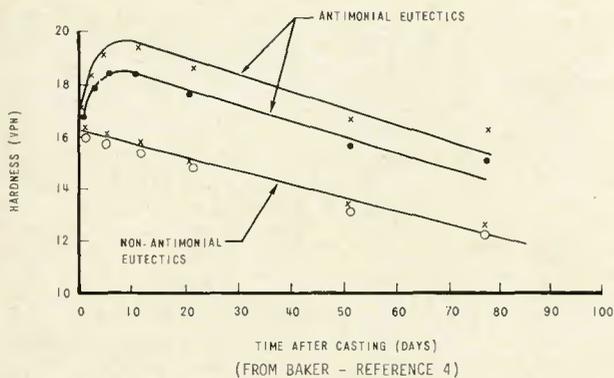


Fig. 1 — Age-softening characteristics of chill-cast eutectic solders

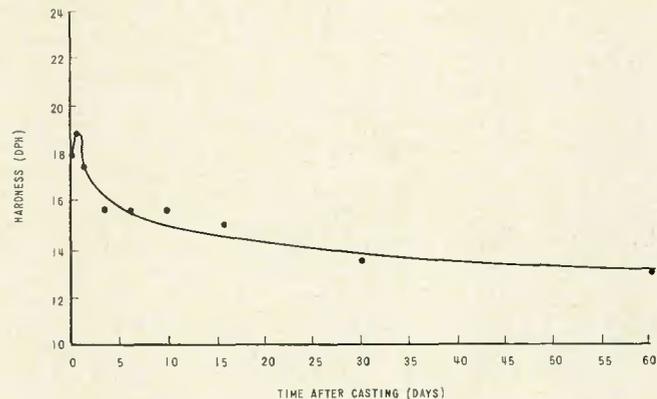
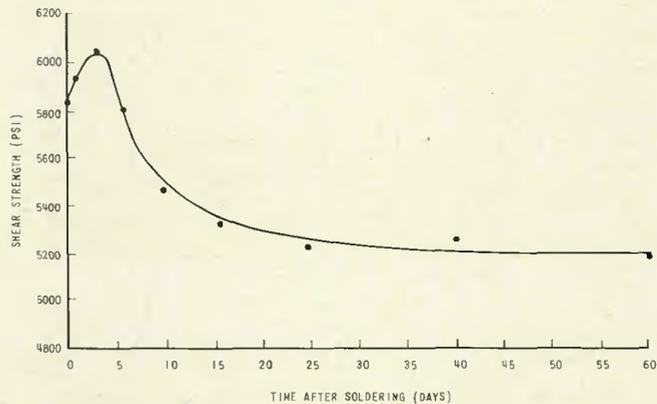


Fig. 2 — Room temperature aging of 50Sn-47Pb-3Sb alloy

very rapid softening during the first 20-100 hours (h), followed by a much longer period of very gradual softening.

Other soft solders are subject to age-softening at room temperature as illustrated in Fig. 1. The upper plot shows the steady decrease in hardness with time at room temperature of some chill-cast eutectic solders. The antimonial solders (55Sn-41.5Pb-3.5Sb) exhibited slight age-hardening during the first few days after casting which was followed by a prolonged age-softening. The nonantimonial eutectics (63Sn-37Pb) age-softened continuously at room temperature. These alloys appeared to reach a stable hardness after aging for 100-150 days at room temperature. The original hardness could be restored by annealing at high temperatures, followed by quenching or fast air-cooling. It was observed by Baker (Ref. 4) that the hardness after annealing was directly related to the annealing temperature, making it likely that the hardness of the alloys was determined by the amount of tin retained in the lead-rich phase. The alloys were also found to age-soften more rapidly at 176 F (80 C) than at room temperature.

Eutectic tin-lead solders containing 0.2-0.8 weight percent (wt-%) antimony undergo age-softening at room

temperatures as shown in the lower plot of Fig. 1. The tensile strength of these solders is reduced by up to one-third as compared to their strength in the homogenized poured condition. The loss in strength is attributed to tin precipitating from the supersaturated lead-rich solid solution (α) during storage at room temperature. The formation of a globular precipitate during aging was observed using an electron microscope. Formation of the intermetallic SnSb was not detected.

Experimental Procedure

Materials

The room temperature aging properties of nine soft solder alloys were studied. The list included two of the most widely used tin-lead solders and a commonly used tin-lead-antimony solder. Other alloys were specially made to evaluate the effects of minor alloying elements of copper, silver, and antimony. The alloys were purchased in the form of 0.005 in. (0.13 mm) thick ribbon which had been cold rolled to final form from vacuum cast, high purity materials. The alloys studied are listed below.*

1. 47Sn-47Pb-6Sb.

*Alloy compositions are given in weight percent (wt-%)

2. 58.5Sn-37Pb-4.5Sb.
3. 50Sn-49Pb-1Sb.
4. 50Sn-50Pb.
5. 50Sn-47Pb-3Sb.
6. 50Sn-49.6Pb-0.35Ag-0.05Cu.
7. 60Sn-37Pb-3Sb.
8. 63Sn-37Pb.
9. 60Sn-38.6Pb-1.0Sb-0.4Ag.

Lap Shear Test

It was desired to measure the shear strength of those soft solder alloys and minimize the effects of joint gap and alloying from the base metal. A lap shear specimen was designed with a 0.008 in. (0.2 mm) gap (distance between soldered surfaces). The lap shear specimens were prepared from copper panels. Two 0.375 (9.5 mm) by 0.5 in. (13 mm) preforms of 0.005 in. (0.13 mm) thick solder foil were placed between the panels along with two lengths of 0.008 in. (0.2 mm) diameter copper wire to control the joint spacing. The overlap was maintained at 0.375 in. (9.5 mm). Several drops of rosin-base flux were swabbed on each panel before assembly. The assembled lap joint was clamped together and then immersed for 25 seconds (s) in a hot peanut oil bath maintained at 480 \pm 10 F (249 \pm 5.6 C). Time at soldering temperature was 15 s.

Hardness Test

The relative low hardness of these solder alloys required the use of a microhardness tester. Fifty-gram samples of the various alloys were melted in a stainless steel crucible and chill-cast from a temperature (unless otherwise specified) of 575 ± 10 F (301.7 ± 5.6 C) by placing the crucible in a reservoir of running tap (60 F or 15.6 C) water. The cast solder slugs were ground and polished to less than a 1 micrometer sur-

face finish. Polishing was done in such a way to minimize any heating of the specimen. Diamond pyramid hardness measurements were made using a 100 g load.

Metallography

Metallographic specimens similar to the hardness test specimens were prepared for each of the nine alloys by chill-casting from 575 F (301.7 C). These specimens were carefully polished and etched to reveal the microstructure. The following etching procedure was used.

1. Etchant: 10 parts concentrated nitric acid; 10 parts glacial acetic acid; 80 parts glycerin.
2. Time: 10-30 s.
3. Application: Cotton swab.

Structure changes occurring in the samples during aging were recorded by making X1000 photomicrographs of the etched specimens at regular intervals using a metallograph. After the photomicrographs were taken, the chemical etch was removed by light polishing with an aluminum oxide-water slurry. At the end of each aging interval, the specimens were re-etched.

Aging Tests

The lap shear joints, hardness specimens, and metallographic specimens were stored at room temperature (70 ± 10 F, or 21.1 ± 5.6 C) and tested at intervals of 30 minutes (m), 24 h, and then 3, 6, 10 16, 24 40, and 60 days (d). Some aging tests were conducted at 200 ± 10 F with the 50Sn-47Pb-3Sb alloy. Each slotted point on the hardness and shear strength curves of Figs. 2, 4, 7, 9, 12, 14 and 16 represents an average of five values.

Results

50Sn-47Pb-3Sb Alloy

This alloy was found to initially age-harden with time at room temper-

ature and then undergo a prolonged age-softening as shown in Fig. 2. The shear strength increased during the first three days from about 5830 psi (40.2×10^6 Pa) to a little over 6000 psi (41.4×10^6 Pa) and then decreased rapidly until it leveled off after about 30 days at 5200 psi (35.9×10^6 Pa). The hardness vs. aging time curve showed the same characteristic except it started to decrease at about 24 h after casting.

Structural changes were observed in the alloy during aging. These changes are shown in the series of photomicrographs in Fig. 3. The structure immediately after chill-casting from 575 F (301.7 C) shows large dark crystals of the lead rich solid solution (α) interspersed in a matrix of very fine grained eutectic. The eutectic consists of a mixture of very fine crystals of α and β (tin-rich solid solution).

Within 4 h after casting, the eutectic starts to coarsen. After about 3 d, a white precipitate begins to form between the α and β crystals in the eutectic and in the grain boundaries of the large primary α -crystals.

With further aging, the eutectic continues to coarsen and the white precipitate grows in size. The nucleation of the precipitate appears to be spontaneous and the particles appear to grow at the expense of other particles rather than by a continuous nucleation and growth process. Spheroidization appears to take place, i.e., the precipitate particles increase in size and decrease in number as their shape becomes more nearly spherical.

47Sn-47Pb-6Sb Alloy

This high antimony solder was found to have aging characteristics similar to those of the 50Sn-47Pb-3Sb alloy.

As shown in Fig. 4, the alloy undergoes initial age-hardening followed by prolonged softening at room temperature. The degree of softening is not

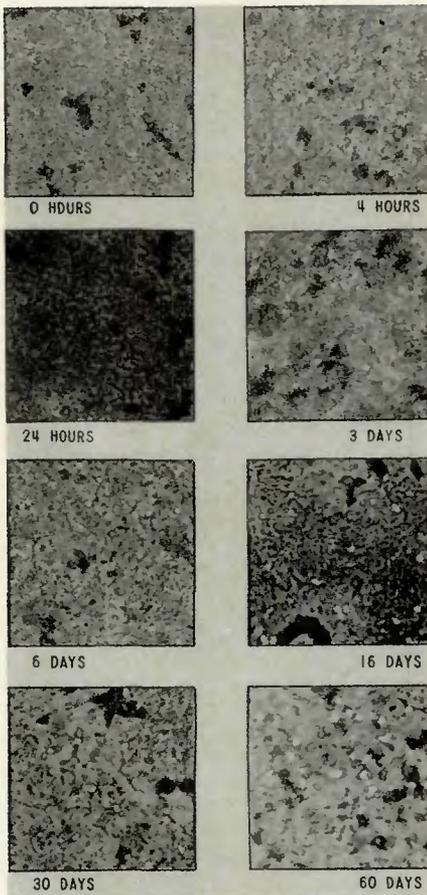


Fig. 3 — Structural changes in alloy 50Sn-47Pb-3Sb during aging at room temperature. X1000 (reduced 48% on reproduction)

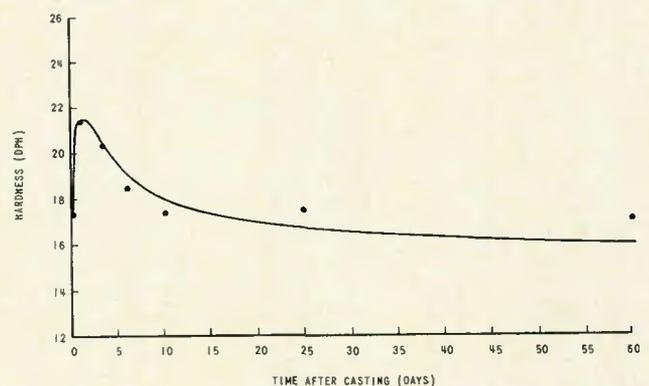
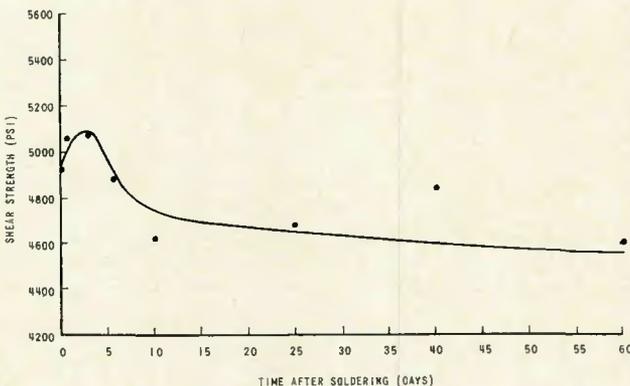


Fig. 4 — Room temperature aging of 47Sn-47Pb-6Sb alloy

as great, however, as for the previous alloy. The shear strength drops from a maximum of about 5100 psi to around 4600 psi (35.2×10^6 to 31.7×10^6 Pa) during aging which is about a 500 psi (3.4×10^6 Pa) decrease as compared to a total decrease of about 850 psi (5.9×10^6 Pa) for the 50Sn-47Pb-3Sb solder alloy. The hardness increases a couple of points during the first 24 h and then drops off to a little below the initial value. The shear strength and hardness curves stabilize after about 10 d at room temperature.

Structural changes occurring in this alloy during aging are shown in Fig. 5. The antimony content of this alloy is 12.8% of the tin content which is well above the reported (Ref. 1) solubility limit of 7% antimony in tin.

White cubic crystals of the intermetallic compound SnSb can be seen in all the photomicrographs of Fig. 5. Noticeable structural changes are observed in this alloy during room temperature aging. A white precipitate begins to appear after about 3 d and grows with time and appears to reach a stable size after 30-60 d of aging.

In some of the photomicrographs of Fig. 5, clusters of small cubic intermetallic crystals can be seen. They appear to be in a process of coalescing into the larger cubic crystals. The precipitate crystals can be distinguished from the crystals of SnSb because they have a spherical shape rather than cubic.

58.5Sn-37Pb-4.5Sb Alloy

The aging characteristics for this alloy are very similar to those of the previous tin-lead-antimony alloys. The shear strength and hardness of the alloy appear to stabilize after 10-15 d at room temperature.

Structure changes occurring during aging are shown in Figure 6. Cubic crystals of SnSb intermetallic are

present since the antimony content (7.7% of tin content) exceeds the solubility limit of antimony in tin. The matrix is essentially a eutectic structure with a few primary α lead-rich crystals present along with the large cubic crystals of SnSb. The eutectic structure coarsens with aging time and a white precipitate becomes visible after about 3 d and grows with further aging time. As in the previous alloys, the nucleation of the precipitate appears to be spontaneous with

the precipitate crystals growing at the expense of others during the aging process.

60Sn-37Pb-3Sb Alloy

The aging curves for this alloy are shown in Fig. 7. The shear strength vs. aging time curve does not exhibit the initial age-hardening characteristic of the previous tin-lead-antimony alloys, although the hardness curve does. The shear strength of the alloy

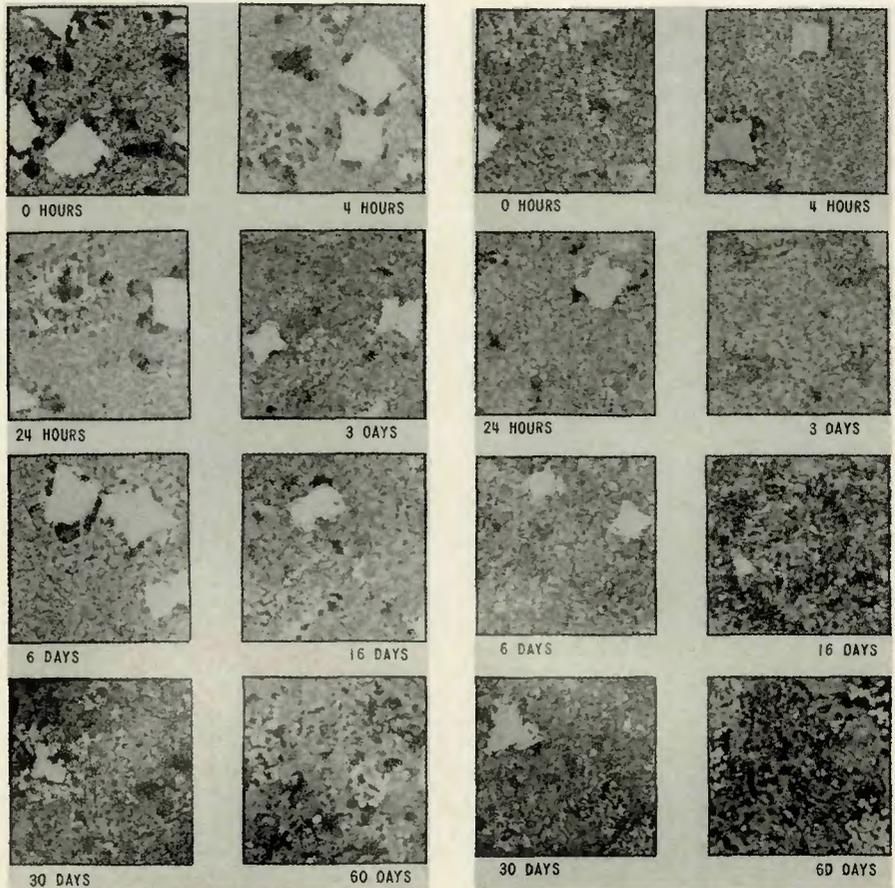


Fig. 5 — Structural changes in alloy 47Sn-47Pb-6Sb during aging at room temperature. X1000 (reduced 48% on reproduction)

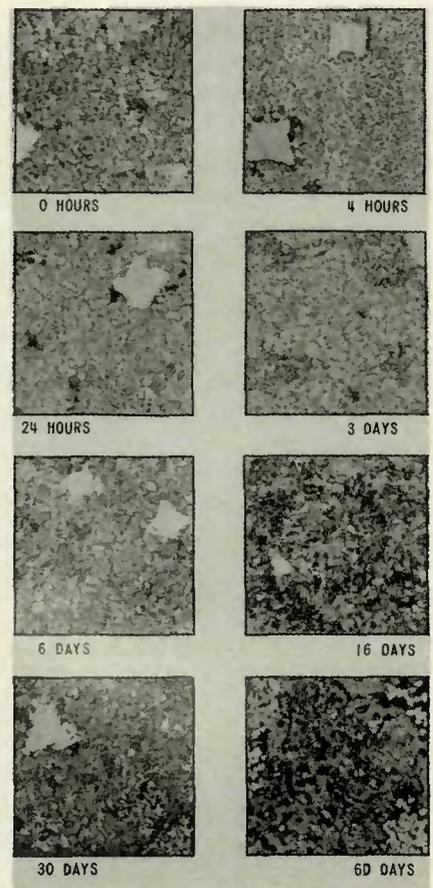


Fig. 6 — Structural changes in alloy 58.5Sn-37Pb-4.5Sb during aging at room temperature. X1000 (reduced 49% during reproduction)

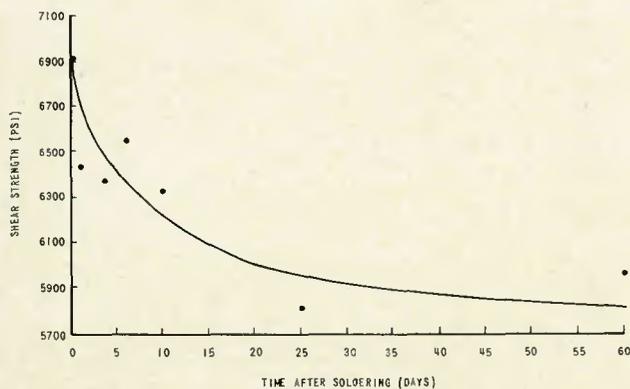
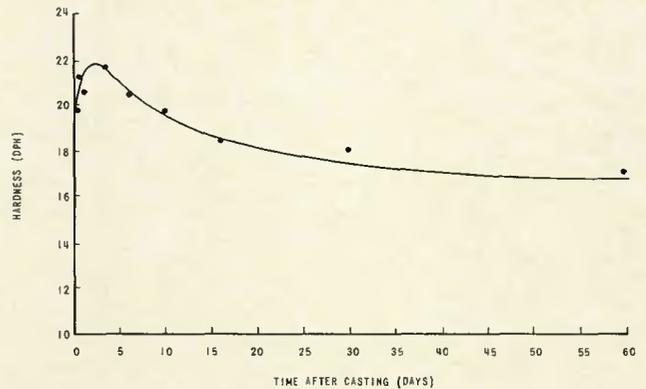


Fig. 7 — Room temperature aging of 60Sn-37Pb-3Sb alloy



decreases more than 1000 psi (6.98×10^6 Pa) during the first 25 d after soldering while the diamond pyramid hardness (DPH) only drops about 4 points. The strength and hardness appear to stabilize after about 25-30 d.

Structural changes during room temperature aging are shown in Fig. 8. The structure is basically a laminar eutectic structure which coarsens during aging. A white precipitate becomes visible in the boundaries of the

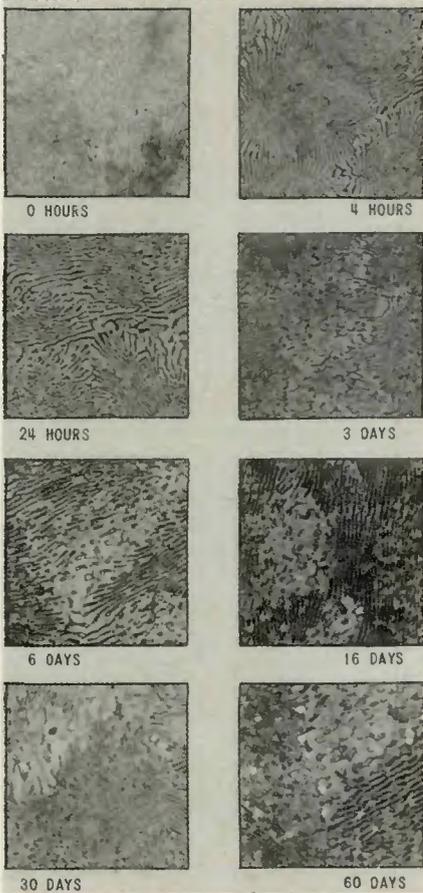


Fig. 8 — Structural changes in alloy 60Sn-37Pb-3Sb during aging at room temperature. X1000 (reduced 48% during reproduction)

dark lead-rich (α) lamellae of the eutectic after 3 d. The precipitate grows with time, with some of the precipitate crystals growing completely across the width of the lamellae. The lead-rich lamellae also coarsen during aging. The structure appears to stabilize after about 60 d at room temperature.

50Sn-49Pb-1Sb Alloy

The aging curves of Fig. 9 indicate that this alloy undergoes a prolonged age-softening process at room temperature but does not exhibit the initial age-hardening characteristic of the previous tin-lead-antimony solders. The shear strength decreases about 500 psi (3.5×10^6 Pa) during the first 25 d after soldering, and the DPH hardness drops about 4 points during the first 10 d and then levels off.

Structural changes that occur during aging are shown in Fig. 10. The structure coarsens with time, but no precipitate can be observed as was the case in the previous alloys which contained a greater amount of antimony. The dark crystals of α lead-rich solid solution within the eutectic matrix grow in size and become more spherical in shape during aging, reaching a stable size after about 60 d. No large crystals of the primary α -phase were observed in the microstructure.

50Sn-50Pb Alloy

The aging characteristics of this common tin-lead solder were studied for comparison purposes. They are very similar to those of the 50Sn-49Pb-1Sb alloy, except the age-softening occurs at a faster rate. The shear strength appears to stabilize after about 10 d and the hardness after about 5 d at room temperature. The total decrease in strength and hardness for both this alloy and the previous alloy containing 1% antimony is about the same.

Structural changes occur in the 50Sn-50Pb alloy during room temperature aging as shown in Fig. 11. The microstructure consists of large dark α (lead-rich solid solution) crystals in an eutectic matrix. The eutectic structure has a "salt and pepper" appearance with small dark α -crystals dispersed in a light β -tin matrix. The small α -phase crystals coarsened and became more spherical in shape during aging. Small white crystals were observed to form within the large primary α -crystals within the first 4 h after chill casting and increased in size during aging. These white crystals were not identified but are presumed to be the tin-rich β -phase. The overall structure coarsened during aging.

63Sn-37Pb Alloy

This eutectic tin-lead solder undergoes an age-softening process at room temperature similar to that of the 50Sn-50Pb alloy as shown by Fig. 12. The shear strength decreases about 800 psi (5.5×10^6 Pa) during the first 20 d of aging with most of the decrease occurring within the first 10 d. The decrease in hardness is not as pronounced as the decrease in shear strength, dropping only about 3 points during the same aging period. Changes in the eutectic structure during aging are shown in Fig. 13. The structure coarsens with time at room temperature reaching what appears to be a stable microstructure after about 30 d. No precipitate could be detected in the small α -phase crystals.

60Sn-38.6Pb-1.0Sb-0.4Ag Alloy

Figure 14 shows the aging characteristics of the alloy. Similar to the high-antimony solders, this alloy exhibits initial age-hardening followed by prolonged age-softening at room temperature. This alloy showed the greatest decrease in shear strength (1300 psi, or 8.9×10^6 Pa)

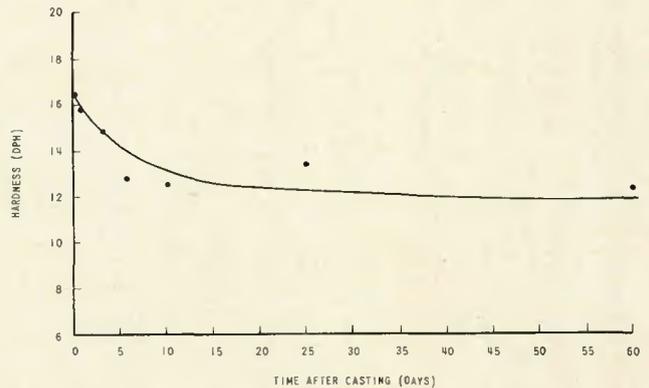
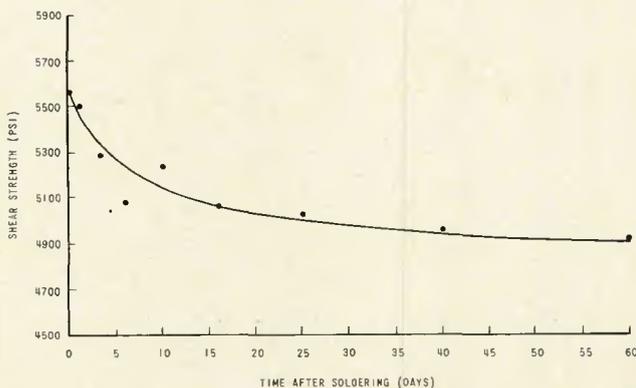


Fig. 9 — Room temperature aging of 50Sn-49Pb-1Sb alloy

of any of the alloys tested. Its DPH hardness also decreased significantly (5 points) during aging. Softening occurs at a rapid rate and the shear strength of the alloy does not appear to stabilize during the testing period of 60 d. The hardness, however, appears to level out after about 30 d.

The structure of this alloy is essentially a fine-grained eutectic structure that coarsens during aging as shown in Fig. 15. The dark lead-rich lamellae of the eutectic grow in size during aging and tend to become spherical in shape. Structural changes occurred throughout the 60-day aging period. The structure of the alloy did not appear stabilized at the end of the 60-day aging period.

50Sn-49.6Pb-0.35Ag-0.05Cu Alloy

This alloy exhibited a very high shear strength immediately after soldering but age-softened rapidly during the first 10 d of aging at room temperature as shown in Fig. 16. The hardness also drops off rapidly during the first 5 days of aging. Both the shear strength and hardness appear to stabilize in about 10-20 d.

Structural changes occurring in this alloy during aging are shown in Fig. 17. The basic microstructure consists of large α lead-rich crystals in an eutectic matrix (light). Small white precipitate crystals are observed to form within the large α grains after about 4 h at room temperature. With further aging, the precipitate grows in size, accompanied by a general coarsening of the overall structure. The structure appears to stabilize after about 30 d.

Effect of Thermal History on Aging Characteristics of 50Sn-47Pb-3Sb

The aging characteristics of the 50Sn-47Pb-3Sb soft solder were found to be dependent upon the thermal history of the alloy. The effects of casting temperature and cooling rate

are shown by the hardness vs. aging time curves of Fig. 18. The faster cooling rate produced higher hardnesses at all aging times.

The cooling rates specified in Fig. 18 represent average cooling rates from the casting temperatures. Chill-casting from 480 F (249 C) produced much lower hardnesses than chill-casting from 600 F (316 C). The hardness aging curve for specimens

chill cast at the lower temperature (480 F, 249 C) did not exhibit initial age-hardening which is characteristic of this alloy.

Aging curves based on the shear strength of lap joints soldered at this temperature and cooled at a somewhat slower rate (see Fig. 2) show a very significant age-hardening during the first 3 d of aging at room temperature.

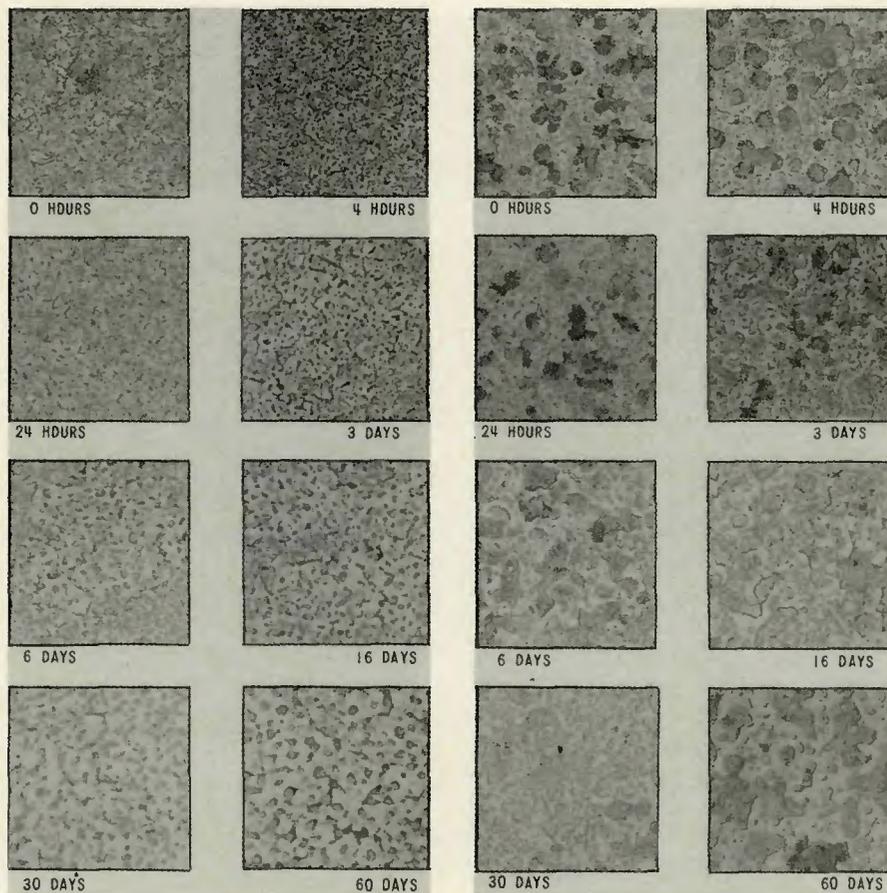


Fig. 10 — Structural changes in alloy 50Sn-49Pb-1Sb during aging at room temperature. X1000 (reduced 48% on reproduction)

Fig. 11 — Structural changes in alloy 50Sn-50Pb during aging at room temperature. X1000 (reduced 48% on reproduction)

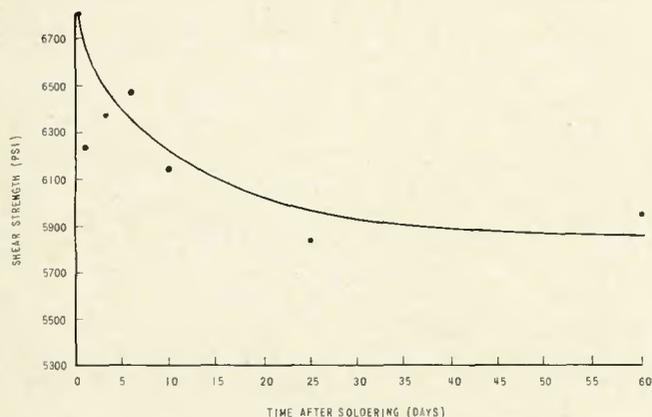
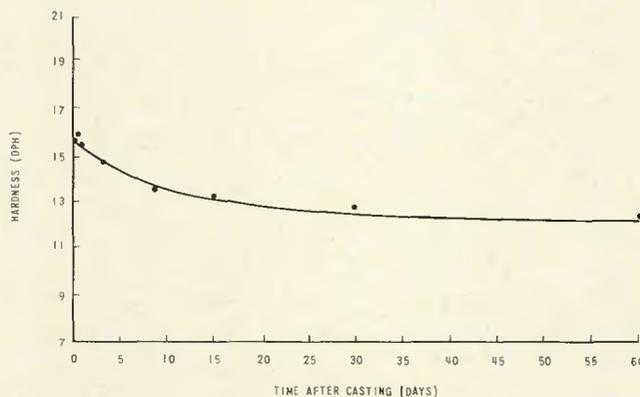


Fig. 12 — Room temperature aging of 63Sn-37Pb alloy



Effect of Aging at Elevated Temperatures

Figure 19 shows the effects of elevated temperature storage on the aging characteristics of the 50Sn-47Pb-3Sb solder alloy. The specimens were placed in an oven immediately after soldering and aged at 200 F (93 C) for the desired time. The aging curves for specimens stored at 200 F (93 C) have the same general shape as the curves for samples stored at room temperature (Fig. 2). This indicates that the aging process in this alloy is the same at 200 F (93 C) as it is at

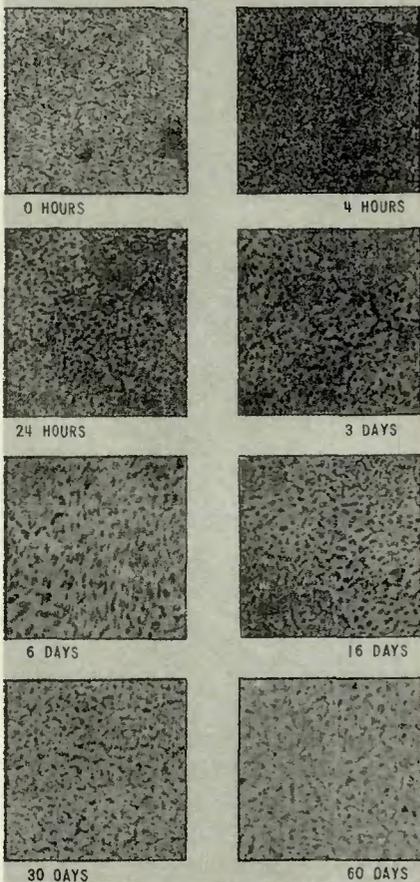


Fig. 13 — Structural changes in alloy 63Sn-37Pb during aging at room temperature. X1000 (reduced 48% on reproduction)

room temperature, except that the aging process at the elevated temperature is much faster. The shear strength vs. annealing time curve levels out after about 80 h at 200 F (93 C) as does the hardness curve.

Discussion Aging Characteristics

The results of this investigation indicate that tin-lead soft solder undergo a prolonged age-softening process at room temperature after soldering. This softening process is accompanied by structural changes in the alloys. Tin-lead alloys containing more than 1% antimony undergo an initial age-hardening process during the first three days after soldering, followed by prolonged age-softening. This was also characteristic of the eutectic tin-lead alloy containing 1% antimony and 0.4% silver. However, in this alloy, the onset of the softening began after only 24 h at room temperature. The aging characteristics of these tin-lead solders were identified by changes in the shear strength and hardness of the alloys with time at room temperature.

Structural changes were observed in all the alloys during aging. Considerable coarsening of the overall microstructure was invariably observed. For the tin-lead-antimony alloys containing more than 1% antimony, a white precipitate formed in the grain boundaries of the lead-rich (α) solid solution. This precipitate was analyzed and found to be a solid solution containing 98 wt-% tin and 2 wt-% antimony. The precipitate became microscopically visible at X1000 magnification after about 3 d aging at room temperature, which corresponded with the end of age-hardening and the onset of age-softening in these alloys. The precipitate grew and became spherical with further aging at room temperature. The nucleation of the precipitate appeared to be spontaneous with the precipitate particles increasing in size and de-

creasing in number as they became more spherical in shape. No precipitate formation was observed in the 50Sn-49Pb-1Sb alloy.

The eutectic structure of the widely used solder alloy 63Sn-37Pb coarsened considerably during the first 6 d after chill-casting and approached a stable structure after about 30 d. The period of the greatest structural change corresponded to the period of greatest decrease in the mechanical properties (shear strength and hardness). This was true for all the alloys. In the 50Sn-50Pb alloy, formation of a second phase was observed within the large crystals of lead-rich α solid solution immediately after casting and grew in size during aging. The second phase was not identified but was assumed to be β -tin. In the noneutectic tin-lead alloy containing small additions of copper and silver, a similar second phase was observed in the dark α crystals. However, it did not become visible until after 4 h of aging.

The aging curves for 50Sn-50Pb and 50Sn-49Pb-1Sb alloys are very similar. The shear strength and hardness values at the start and at the end (60 d) of the aging cycle for both alloys are about the same. However, the softening process occurs more rapidly in the tin-lead alloy without the antimony. Apparently, the antimony slows down and prolongs the softening process. The antimony appears to have an even greater effect on the microstructure. The structure of the 50Sn-49Pb-1Sb alloy is much finer grained than that of the 50Sn-50Pb alloy, with no large crystals of primary α -phase evident. In addition, no second phase formation was observed in the crystals of the antimony-containing alloy.

The noneutectic tin-lead alloy containing 0.35% silver and 0.05% copper exhibited a very high shear strength immediately after soldering but age-softened rapidly during the first few days at room temperature. During the first 10 days of aging, the

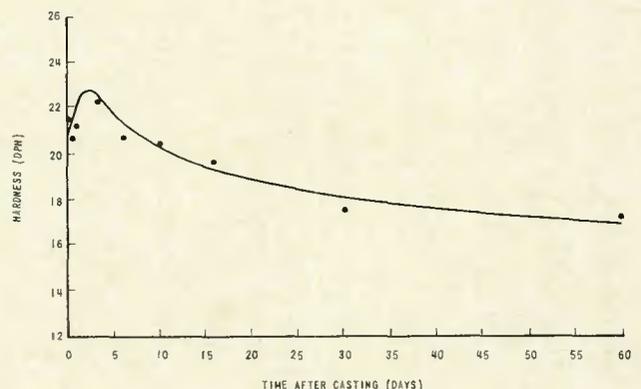
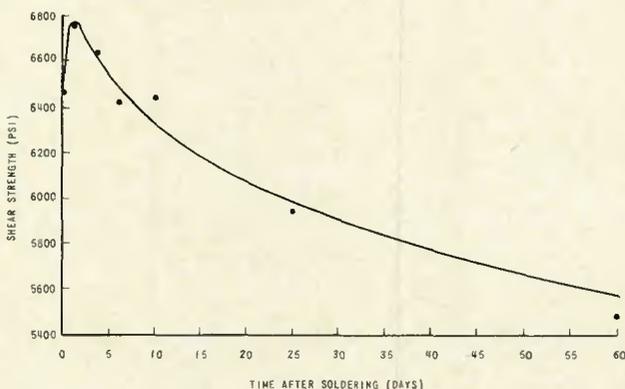


Fig. 14 — Room temperature aging of 60Sn-38.6Pb-1.0Sb-0.4Ag alloy

shear strength decreased more than 1200 psi. The hardness decreased rapidly also, but the magnitude of the decrease was not as great. The small copper and silver additions apparently have a profound strengthening effect on the tin-lead alloy, but the effect is short-lived and unstable. The shear strength of the alloy after 25 days aging time approaches that of the 50Sn-50Pb solder. There is some permanent strengthening (400 psi at 60 days) but the effect is not as great as first indicated immediately after soldering.

There was little difference between the microstructure of this alloy and that of the pure tin-lead alloy, indicating that the minute additions of silver and copper were not very effective in refining the grain structure. The tin-lead solder with the antimony and silver additions (60Sn-38.6Pb-1.0Sb-0.4Ag) exhibited aging characteristics similar to those of the high antimony alloys (i.e., initial age-hardening followed by prolonged age-softening); however, the rate of softening is more rapid.

When compared to the 63Sn-37Pb eutectic solder, the 60Sn-38.6Pb-1.0Sb-0.4Ag alloy actually softens to a lower shear strength value although its final (60-day) hardness is greater. If compared to the 60Sn-37Pb-3Sb alloy, the maximum shear strengths and hardnesses are about the same but this alloy softens at a somewhat faster rate. The results suggest that 0.4 wt-% silver and 1.0 wt-% antimony added in combination are about equivalent to 3.0 wt-% antimony with respect to the strengthening effect on eutectic tin-lead solder. However, the strengthening effect from the silver and antimony is less stable as evidenced by the more rapid rate of age-softening.

The two solder alloys containing antimony additions in excess of the 7% solubility limit of antimony in the exhibited similar aging characteris-

tics. Both showed initial age-hardening followed by extended softening. It is interesting to note that the shear strength values for both the 47Sn-47Pb-6Sb and 58.5Sn-37Pb-4.5Sb alloys are lower than comparable values for the 50Sn-47Pb-3Sb alloy. The reverse is true for the hardness values. One would expect the alloys containing the higher antimony additions to have greater strength and hardness due to the presence of the intermetallic SnSb.

The initial shape of the shear strength aging curve (Fig. 12) for the 63Sn-37Pb eutectic alloy is open to question because of the wide scatter in the data points. In drawing the curve to fit the data, it was assumed that shear strength of this alloy would follow the same general trend during aging as does the hardness.

Mechanism of Age Softening

Tin-Lead Alloys. Binary tin-lead alloys solution-harden when quenched or fast-cooled from near or above their eutectic temperature due to the retention of supersaturated lead-rich solid solution (α) at room temperature. At a temperature just below the eutectic temperature (361 F, or 182.8 C), a 50 wt-% tin and 50 wt-% lead alloy will consist of primary α crystals suspended in a eutectic matrix ($\alpha+\beta$).

As shown in the tin-lead equilibrium phase diagram of Fig. 20 the primary α -phase consists of 81% lead and 19% tin. As the temperature decreases, the solubility of tin in lead decreases until, at room temperature, the equilibrium composition of α is about 97% lead and 3% tin.

If the 50Sn-50Pb alloy is quenched (fast cooled) from just below the eutectic temperature, the elevated temperature α -phase (81Pb-19Sn) is retained at room temperature. The alloy exists in a metastable condition consisting of supersaturated α crys-

tals in a eutectic matrix. The alloy is much harder in this state than in its equilibrium state. However, the alloy tends to revert to its equilibrium state at room temperature by the precipitation of β -tin from the supersaturated α solid solution. Precipitation of tin from the α -phase softens the alloy. The same process occurs in soldering, whether it be a chill-cast solder slug or an air-cooled lap joint. The cooling rate is fast enough to retain a significant amount of super-

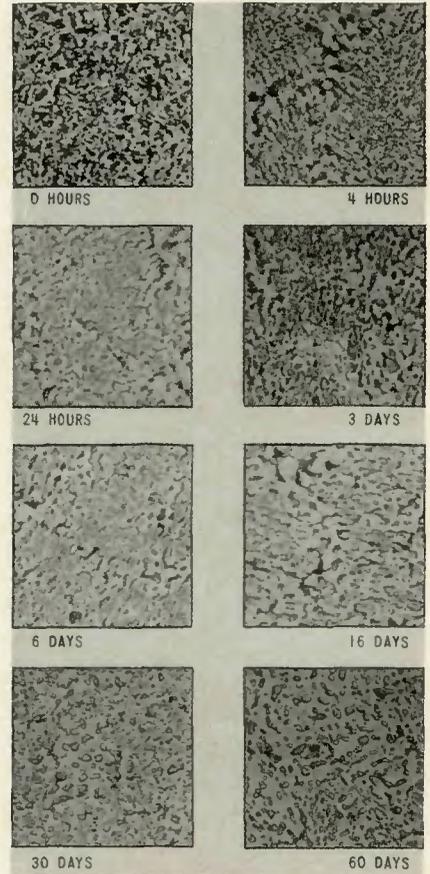


Fig. 15 — Structural changes in alloy 60Sn-38.6Pb-1.0Sb-0.4Ag during aging at room temperature. X1000 (reduced 49% on reproduction)

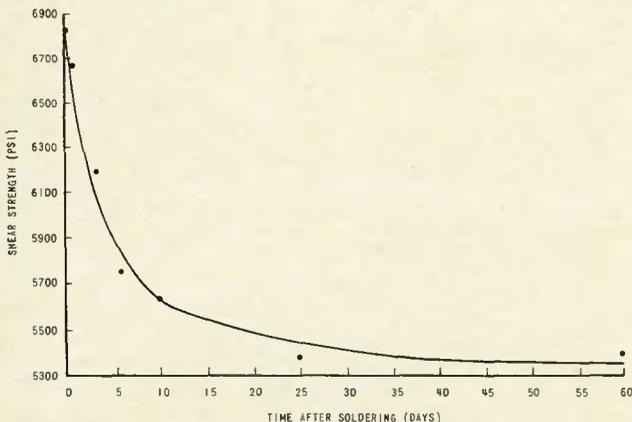
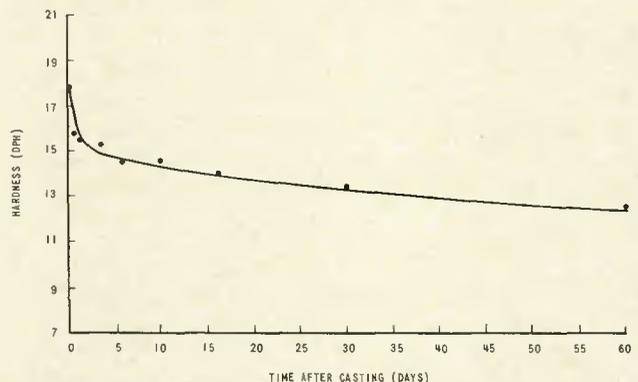


Fig. 16 — Room temperature aging of 50Sn-49.6Pb-0.35Ag-0.05Cu alloy



saturated α -phase at room temperature. During storage, the solder softens as it transforms to its equilibrium state.

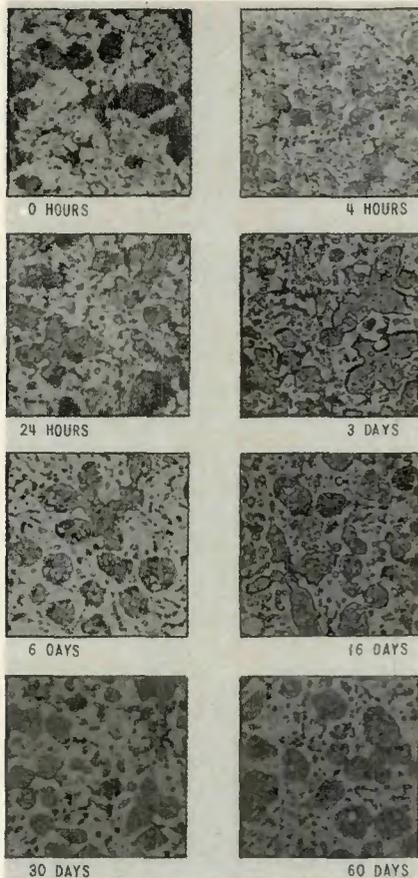


Fig. 17 — Structural changes in alloy 50Sn-49.6Pb-0.35Ag-0.05Cu during aging at room temperature. X1000 (reduced 49% on reproduction)

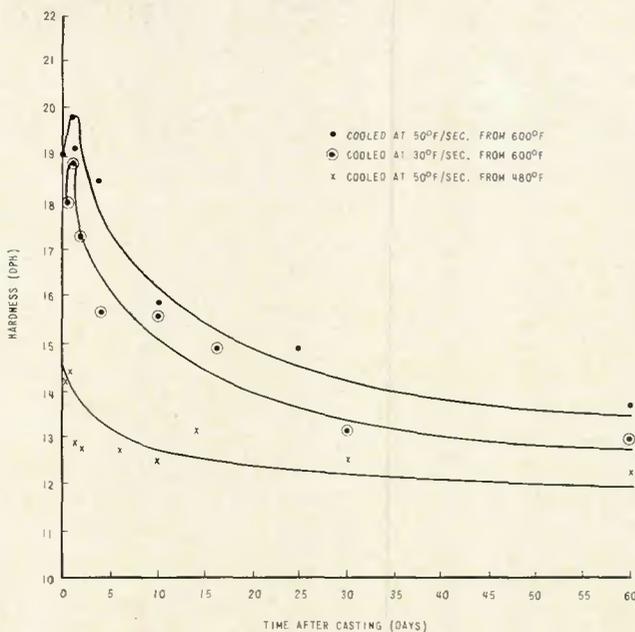


Fig. 18 — Effect of cooling rate and casting temperature on aging characteristics of 50Sn-47Pb-3Sb alloy

The curve of hardness vs. aging time for the 50Sn-50Pb solder alloy illustrates this softening process in tin-lead solders. The alloy has its maximum hardness immediately after chill casting. During the first 10 d of storage, the hardness decreases significantly. This decrease in hardness is accompanied by significant structural changes in the alloy. Small white globules of β -tin form within the large dark crystals of the primary α -phase. The globules of β -tin appear immediately after casting and reach a stable size at about the time the hardness curve starts to level off.

At this point in time (6-10 d), the 50Sn-50Pb alloy appears to be close to equilibrium.

No further significant changes in hardness or microstructure are noted. The shear strength of the alloy behaves in a similar fashion and appears to level out after about 20 d aging time at room temperature. If the alloy is reheated to a temperature close to the eutectic temperature (361 F, or 183 C) and quenched, the original high hardness is restored and the softening process starts over again.

The eutectic tin-lead alloy (63Sn-37Pb) undergoes the same type of softening process after chill-casting from the soldering temperature. The aging curves for this solder indicate that the softening process takes about 10-20 days at room temperature. The

microstructure of eutectic tin-lead solder is unique and consists of a finely dispersed mixture of lead-rich α (dark) and tin-rich β (light) solid solutions. As seen in Fig. 13, the α crystals are very small initially but coarsened during the aging process. No β -tin globules can be observed within the α crystals. The β -tin which precipitates from the supersaturated α -phase apparently is indistinguishable from the existing β -phase.

According to Turnbull *et al* (Refs. 6-9), β -tin precipitates from the supersaturated lead-rich (α) solid solution in two stages. The first stage involves a discontinuous precipitation process which proceeds at a rapid rate and drains about 60% of the excess tin from solution. Only 10-30 min are required a complete 50% of the precipitation process. The remaining 40% comes out by a much slower reaction (about 2 orders of magnitude slower than the fast reaction).

Precipitation occurs by the nucleation and growth of cells. These cells of transformed material (β) nucleate at the beginning of the precipitation process mostly in the vicinity of grain boundaries and grow into the grains. The reaction rate of the first stage of precipitation is obviously too fast to account for the relatively slow and prolonged age-softening characteristics observed in the high tin-lead alloys used in the investigation. However, the first stage (fast reaction) only

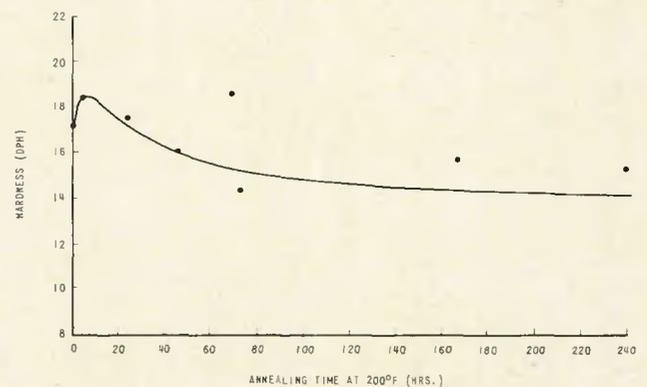
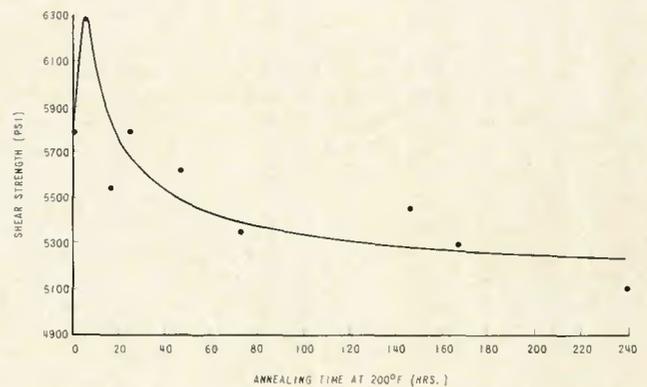


Fig. 19 (right) — Effect of annealing on aging characteristics of 50Sn-47Pb-3Sb alloy

accounts for 60% of the excess tin in the supersaturated α -phase. The much slower second stage reaction accounts for the remaining 40% of the transformation.

It appears that the gradual changes in structure and mechanical properties of the tin-lead alloys studied in this investigation are a result of the second stage precipitation of β -tin from the supersaturated lead-rich α solid solution. Livingston (Ref. 6) in his studies of the second stage process, noted a gradual spheroidization and coarsening of the β -tin precipitate during aging. A similar effect was observed in this investigation with the 50Sn-50Pb alloy.

Effects of Antimony and Other Minor Alloying Elements. Age-softening in tin-lead alloys containing antimony occurs at a reduced rate. The antimony appears to slow down the second stage precipitation of β -tin from the supersaturated lead-rich solid solution. The addition of antimony to tin-lead alloys also has other effects. The composition of β -phase precipitate is altered from essentially pure tin to a solid solution of tin and antimony.

The precipitate in the 50Sn-47Pb-3Sb alloy was identified as a solid solution containing 98 wt-% tin and 2 wt-% antimony. The precipitate particles are smaller and greater in number. In the alloys containing 3% or more antimony, the precipitate did not become visible optically until 3 d after chill-casting from 575 F (302 C). Antimony also serves to refine the grain structure of tin-lead alloys. The antimony-containing alloys were much finer grained than the binary tin-lead alloys.

The alloys containing 3% or more antimony age-harden during the first 3 d of aging at room temperature and then proceed to soften upon further aging. This can be explained in terms of a classical precipitation hardening process. When the tin-lead-antimony alloy is fast-cooled from above its melting temperature, it exists in a metastable condition at room temperature due to the presence of the supersaturated lead-rich phase. The alloy tends to approach its equilibrium condition at room temperature by precipitation of β -tin from the supersaturated lead-rich phase.

During the precipitation process, there are two opposing effects on the mechanical properties of the alloy. One is a softening effect due to the drainage of β -tin out of the supersaturated α -phase. The other effect is a hardening effect due to the formation of precipitate particles in the grain boundaries and along dislocations in the crystal lattice. In pure tin-lead

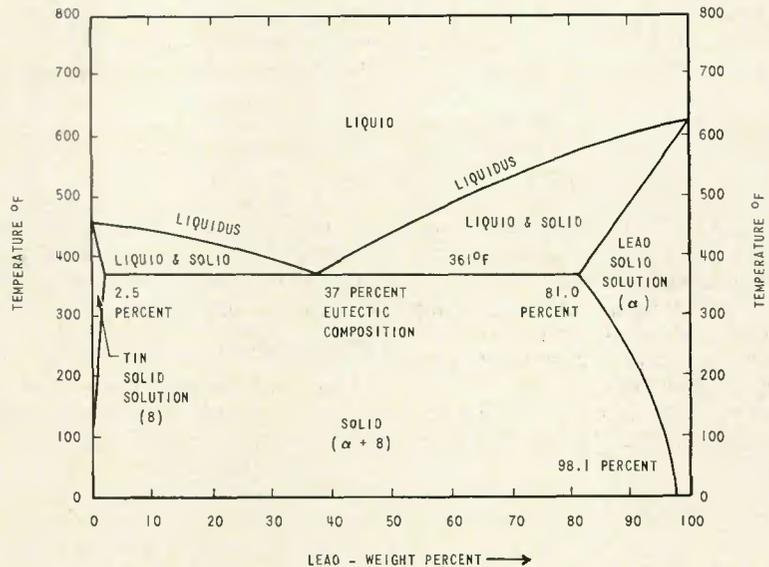


Fig. 20 — Tin-lead phase diagram

alloys, the softening effect overcomes the hardening effect very quickly due to the fast transformation rate. In the antimony-containing alloys, however, the slower transformation rate and the increased number of precipitate particles of smaller size causes the age-hardening effect to be predominant.

During the first three days of aging, a classical age-hardening process takes place, with the precipitate particles too small to be observed by optical microscopy. Hardening continues as the precipitate grows until a critical particle size is reached. At this point the alloy "overages" and the softening process becomes predominant. The critical particle size appears to correspond to the size which can be resolved with the optical microscope. This process might be compared to the typical age-hardening process for copper-beryllium alloys carried out at elevated temperatures. This characteristic is not seen in the pure tin-lead alloys or the tin-lead alloys containing small additions of antimony, copper, or silver because the precipitation rate is too fast and the number of nucleating sites too few to cause effective age-hardening to occur. The alloys "overage" almost immediately.

The presence of 1.0% antimony and 0.4 percent silver in combination produce an aging effect very similar to the effect produced by 3% antimony in eutectic solder alloys. Both alloys undergo initial age-hardening followed by prolonged softening. Both alloys have about the same maximum shear strength and hardness values, but the high-antimony alloy softens at a faster rate. The microstructure of the 3% antimony alloy is a typical laminar pearlitic structure in

which a white precipitate is observed to form after 3 days aging at room temperature. The presence of antimony and silver combined in the eutectic solder destroyed the fine laminar structure and coarsened it considerably. No precipitate was observed in the 50Sn-47Pb-3Sb alloy during aging at room temperature. The structural changes observed during aging were similar to those observed in the binary eutectic (63Sn-37Pb) alloy — a general coarsening of the overall structure.

Adding 1% antimony to a 50Sn-50Pb solder has a permanent hardening effect and acts to prolong the age-softening process. It also serves to refine the grain structure, making the lead-rich α -phase crystals much smaller.

Effects of Thermal Treatment. The aging characteristics of the 50Sn-47Pb-3Sb alloy were found to be dependent upon its prior thermal treatment. Samples chill-cast from 600 F (316 C) at an average cooling rate of 50 F/s (27.8 C/s) had higher hardness values throughout the aging cycle than did samples chill-cast at a slower cooling rate of about 30 F/s (16.7 C/s). The rate of softening for the two samples was about the same, and both aging curves had the same characteristic shape. The faster cooling rate produced a finer grained microstructure.

Samples chill-cast from a lower temperature of 480 F (249 C) had significantly lower hardness values at all aging times. The rate of softening was reduced, and there was no initial age-hardening effect. The casting temperature, cooling rate, and aging temperature also had a great effect upon the resulting structure of the alloy.

Higher casting temperatures and faster cooling rates produce a higher degree of hardening and finer grain structures in this alloy. This is due to a greater degree of supersaturation (more retained β -phase) of the lead-rich α -phase during cooling. This causes greater lattice strain, thereby creating more nucleating sites for precipitation. The precipitate particles are smaller and greater in number, producing a greater hardening effect on the alloy. Slow cooling causes less of the β -phase (tin) to be retained at room temperature producing a softer alloy.

The same effects would also be expected for the other tin-lead alloys in the study.

Effects of Aging Temperature. Samples of the 50Sn-47Pb-3Sb alloy aged at 200 F (93 C) produced the same characteristic aging curves as similar samples aged at room temperature. However, the age-hardening and age-softening processes occurred at a much faster rate. Aging or annealing at 200 F (93 C) causes the alloy to develop its maximum hardness and shear strength after about 10 h aging time as compared to 3 d at room temperature (70 F, or 21.1 C). The higher aging temperature also increases the softening rate, causing the aging curves to level out after about 80 h. This compares to 25 d at room temperature.

An interesting note is that the alloy stabilizes to a somewhat higher shear strength and hardness when aged at 200 F (93 C). This is due primarily to the small amount of solution hardening produced when cooling the samples to room temperature for testing. The solubility of tin in lead at 200 F (93 C) is about 8% compared to 3% at room temperature. Some excess tin in the α -phase is retained causing a small amount of hardening. The alloy could be expected to soften further with time at room temperature even after prolonged aging at 200 F (93 C).

The results of the elevated temperature aging tests indicate that a post-soldering anneal at 200 F (93 C) would be an effective method of stabilizing the strength and structure chill-cast 50Sn-47Pb-3Sb alloy. It is safe to assume that the same would hold true for the other alloys used in this investigation. Annealing the alloy at 200 F (93 C) speeds up the precipitation process, causing the alloy to stabilize after about 80 h compared to about 25 d at room temperature.

Solid Solubility of Antimony in Tin at Room Temperature

The precipitate that formed during aging of the 50Sn-47Pb-3Sb alloy was identified by electron microprobe

analysis to be a solid solution of 98 wt-% tin and 2 wt-% antimony. This supports the work reported by Eyre (Ref. 10) who reported the solid solubility of tin in antimony at room temperature to be in the order of 0.6 wt-% rather than 7% as reported by Manko (Ref. 1).

Although the antimony content (3%) in this alloy represented 6% of the tin content, no evidence of the intermetallic SnSb could be found using optical microscopy.

Conclusions

Tin-lead alloys which are fast-cooled from the melt harden due to the formation of a supersaturated lead-rich solid solution. Upon subsequent storage at room temperature, these alloys tend to approach equilibrium by precipitation of tin out of the supersaturated lead-rich phase. The precipitation process softens the alloys, causing a reduction in shear strength and hardness of up to 20%.

The softening process takes from 6 to 60 d at room temperature, depending upon the tin-lead alloy. Binary tin-lead alloys age-soften rapidly after casting, requiring less than 10 d to reach a stable strength and hardness. The addition of antimony to tin-lead solders slows down the precipitation rate and prolongs the softening process. Small additions (less than 0.5 wt-%) of silver and copper increase the as-cast strength and hardness but have little effect on the age-softening process.

The decrease in shear strength and hardness of tin-lead alloys during storage (aging) at room temperature is accompanied by noticeable structural changes. In all of the alloys tested, a general coarsening of the overall structure was observed. In the 50Sn-50Pb alloy, globules of β -tin were observed to form within the large α -crystals immediately after casting. These globules grew during aging and became spherical in shape. In tin-lead alloys containing 3 wt-% or more antimony, a white precipitate was observed after 3 d aging time. The precipitate particles increased in size and became spherical in shape with further aging. The precipitate was identified as a solid solution containing 98 wt-% tin and 2 wt-% antimony. A precipitate was not observed in the eutectic tin-lead solder or the eutectic alloy containing 1% antimony and 0.4% silver.

In the tin-lead alloys containing 3 wt-% or more antimony, the size and distribution of the precipitate particles were such that age-hardening occurred during the first 3 d of aging. After about 3 d, the particle size exceeded the "critical" size for effective precipitation hardening and the alloys

became "over-aged" and started to soften. The onset of softening corresponded to the time at which the precipitate first becomes visible with a light microscope at X1000 magnification. The addition of 1% antimony and 0.4% silver in combination to tin-lead solder had a similar but less pronounced effect on its aging characteristics.

The mechanical properties and microstructure of the 50Sn-47Pb-3Sb alloy were found to be dependent upon the thermal history of the sample. Higher casting temperatures and faster cooling rates result in higher strengths and hardnesses at all aging times. These conditions also produce a finer grain structure with an increased number of precipitate particles. Slow cooling from the melt produces a typical lamellar eutectic structure which is inherently softer and more stable. Reheating and quenching after prolonged age-softening restores the high original hardness and starts the age-softening process over again.

Annealing at 200 F (93 C) after soldering was found to be effective in stabilizing the structure and strength of the 50Sn-47Pb-3Sb alloy. The mechanical properties stabilized after 80 h at this temperature as compared to 25-30 d at room temperature.

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