Since the mid-sixties, CDA has had a continuing program to improve manufacturing methods for copper and brass auto radiators. The results of this work have been published in a series of CDA technical reports and are briefly summarized in this data sheet. The primary aim of the program has been to improve the reliability of the copper and brass auto radiator and of the soldering processes used to produce it. The results will be useful in other application areas as well.

THE SOLDERING PROCESS

Soldering of copper and its alloys is simple to accomplish, but metallurgically it is quite a complex process as was established early in the ongoing program summarized here. Reliable soldered joints depend on seven major factors:
1. The materials being soldered
2. Solder composition
3. Soldering temperature
4. Time at temperature
5. Degree of solder agitation
6. Flux composition
7. Soldering atmosphere.

These seven factors interact in a complex way to determine the results of the soldering process. The major purpose of CDA’s experimental program has been to analyze and understand the most important of these interactions. To do this it is necessary first to study the soldered joint itself. Test results on bulk solder specimens bear little relation to the properties of actual soldered joints. Testing joints to failure and analyzing them has shown clearly that fractures generally follow the interface between the solder and the base material — that is, along or through the reaction zone which forms during soldering. The reaction zone, which cannot exist in a bulk solder specimen, is the major factor in determining solder joint strength.

Early in the program, the experimental work concentrated on soldered joints in two materials: Copper No. 102 (oxygen-free copper, 99.95 Cu) and Copper Alloy No. 260 (copper brass, 70Cu-30Zn). Some results are summarized in Figure 1. As the figure shows, joints with Alloy 260 were generally stronger for the same solder and soldering temperature, other things being equal. A zinc ammonium chloride flux was used in the preparation of all experimental joints. In all cases, the soldered joints were made with a 5-second exposure to the indicated temperature.

The results demonstrate that joint strength does indeed vary with the workpiece material.

Later work concentrated on Alloy 260, since such joints are the most important ones in copper and brass radiator construction.

Solder Composition

The results summarized in Figure 1 also demonstrate the importance of solder composition in determining joint strength. Although the 85-15 Pb-Sn solder shows the highest joint strength with Alloy 260, it is not necessarily the best solder to use with that alloy. For example, the figure shows that for each solder composition joint strength varies markedly with solder-

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*Listed on last page, References.
TABLE 1. STRENGTH OF SOLDERED JOINTS MADE WITH MODIFIED SOLDER ALLOYS
Tested at Room Temperature

<table>
<thead>
<tr>
<th>Solder Composition</th>
<th>Fracture Initiation Strength, lb per in.</th>
<th>Series</th>
<th>Avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>95Pb-3.85Sn-1.2Ag</td>
<td>124.0</td>
<td>118.0</td>
<td></td>
</tr>
<tr>
<td>95.7Pb-3.85Sn-0.5Ag</td>
<td>112.0</td>
<td>107.0</td>
<td>104.5</td>
</tr>
<tr>
<td>69.9Pb-29.5Sn-0.5Ag</td>
<td>64.4</td>
<td>68.2</td>
<td>73.7</td>
</tr>
<tr>
<td>69.9Pb-29.5Sn-0.5Ag</td>
<td>64.4</td>
<td>68.2</td>
<td>73.7</td>
</tr>
</tbody>
</table>

Soldered at 680 F
95Pb-3.85Sn-1.2Ag  124.0  118.0
95.7Pb-3.85Sn-0.5Ag 112.0  107.0
69.9Pb-29.5Sn-0.5Ag 64.4  68.2
69.9Pb-29.5Sn-0.5Ag 64.4  68.2

Soldered at 850 F
95Pb-3.85Sn-1.2Ag  124.0  118.0
95.7Pb-3.85Sn-0.5Ag 112.0  107.0
69.9Pb-29.5Sn-0.5Ag 64.4  68.2
69.9Pb-29.5Sn-0.5Ag 64.4  68.2

Agitation
Comparing joints made with and without agitation of the solder bath showed that the reaction between solder and workpiece proceeds three to four times more rapidly when the bath is agitated violently. Since the reaction zone contains brittle intermetallic compounds, it is important to minimize its thickness therefore agitation of the bath should be avoided for maximum joint strength.

Flux Composition
Fluxes and their action are probably the least understood aspect of soldering. This may account for the proliferation of commercial fluxes available. The general requirement for a flux is that it produce a tarnish-free surface and be removed in the

Time at Temperature
Tests to determine the effect of time at soldering temperature on fracture initiation strength showed that little could be gained from detailed study of exposure times longer than 5 seconds, thus a standard exposure time of 5 seconds was used throughout the program.

The thickness of the reaction zone between the solder and the workpiece material does increase as exposure time lengthens. This reaction zone contains a brittle intermetallic compound and there is a tendency for joint failure to occur preferentially along this zone, according to detailed metallographic study and microprobe analysis. Metallographic and microprobe analysis shows how the alloy and solder constituents are distributed across the reaction zone between the solder and the brass (Figure 4).

Figure 2. Effect of temperature and solder composition on fracture strength of soldered joints in Copper Alloy No. 260. Soldered at 850 and 680 F.

Figure 3. Comparison of fracture initiation strengths of joints made with modified silver-bearing solder and standard silver-bearing solder.

Soldering Temperature
The effects of soldering temperature on the fracture initiation strength are shown in Figure 1. The data indicate that each material and each solder alloy has its own optimum soldering temperature, based on fracture initiation strength. And, as is pointed out in the discussion below on the effect of flux composition, a change in flux material will also change the optimum temperature for soldering.

Figure 4. Composition gradients across reaction zone between solder and Alloy 260 brass.

Figure 5. Effect of flux composition and soldering temperature on fracture initiation strength of joints made with two solders.
soldering process. Figure 5 shows the profound differences in solder joint strength resulting from different fluxes. It compares three commercial fluxes and a laboratory-compounded zinc ammonium chloride flux.

The results of further experiments demonstrate how changes in flux composition should be accompanied by an adjustment in processing temperatures (Figure 6). Three fluxes were tested: a commercial “low residue” flux, a flux compounded of temperature is fixed, a flux can be formulated to provide maximum joint strength. Conversely, if other considerations dictate the use of a given combination of flux and solder, then the processing temperature can be adjusted to provide optimum joint strength.

CDA’s experimental work on fluxes leads to these conclusions: 1. Fluxes can be formulated for optimum processing with a given solder over the temperature range from 650 to 1100 F. Commercial fluxes do not appear to be available which give best results at the extremes of this range. 2. The combination of solder, workpiece material and flux which is optimum for one set of conditions may not be best when processing conditions are changed. 3. Flux selection based on considerations other than joint strength, including cost, may be risky.

Protective Atmospheres

No flux can provide perfect protection against surface oxidation of the workpiece during soldering. Atmospheric oxygen can dissolve in the flux and re-oxidize metal surfaces. As part of the CDA experimental program, argon was used to protect the solder bath and limit the availability of oxygen to the workpiece. The result: less surfacecrossing of the solder, less workpiece oxidation, more uniform solder fillet formation, more consistent joint strength, and in one instance, considerably stronger joints, as shown in Table 2.

Protective atmospheres other than argon can also be used. Nitrogen has been found effective, and carefully controlled burnt gas has given good results.

TABLE 2. EFFECT OF AN ARGON ATMOSPHERE ON THE STRENGTH OF EXPERIMENTAL SOLDER JOINTS

<table>
<thead>
<tr>
<th>Flux and Atmosphere</th>
<th>Fracture Initiation Strength, lb per in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Ammonium Chloride Flux</td>
<td></td>
</tr>
<tr>
<td>Without Argon</td>
<td>71.9</td>
</tr>
<tr>
<td>With Argon</td>
<td>72.9</td>
</tr>
<tr>
<td>Commercial Flux F1</td>
<td></td>
</tr>
<tr>
<td>Without Argon</td>
<td>32.2</td>
</tr>
<tr>
<td>With Argon</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Values are averages of three tests with 97.5Pb-1Sn-1.5Ag solder, Cooper No. 102 strip, exposed 5 sec@850 F.

The commercial flux plus a 10% addition of zinc ammonium chloride, and a 100% zinc ammonium chloride flux. As is clear from the figure, for each flux composition there is a different soldering temperature for maximum joint strength.

To further demonstrate the importance of flux selection, experiments were done to determine whether maximum joint strength for a given solder could be maintained over a broad range of soldering temperatures by matching flux composition to processing temperature. Three experimental fluxes were formulated; the results are summarized in Figure 7. They show that by choosing flux materials with appropriate melting temperatures, the same solder joint strength can be achieved at soldering temperatures across the range from 650 to 1100 F. These laboratory flux materials are not likely to be appropriate for commercial use. The results show, however, that if the process

Figure 8. Effect of coolant and solder composition on blooming corrosion of washed specimens made using a low-residue commercial flux. Specimens are solder in cups made of Alloy 260 about 1.5 inches in diameter by 0.25 inches deep. Solder amount in cup is about 20 grams.
CORROSION EVALUATION

Service performance is the ultimate test of the soldered joint in an automobile radiator. No evaluation of the soldering process for radiators is complete without an investigation of the relationship between soldering process variables and the phenomenon known as “blooming corrosion.” Blooming corrosion describes what occurs in service when a coolant attacks and corrodes soldered joints in an auto radiator. When it occurs the corrosion products are voluminous and can block coolant passages and reduce radiator performance.

Blooming corrosion tests using four solders, three fluxes, and three different soldering temperatures were carried out in three coolant solutions rated as corrosive, marginally corrosive and non-corrosive by the Union Carbide Consumer Products Laboratory, who did the corrosion testing in the CDA program. Some of the results are summarized in Figure 8.

The dominating factor in the corrosion test was the coolant. Regardless of solder, flux, etc., the “corrosive” antifreeze produced a large weight loss and a highly visible corrosion bloom, as shown in the figure.

Flux formulation also affected blooming corrosion. Furthermore, the experiments showed that some fluxes are more difficult to wash away than others. For example, the washed zinc ammonium chloride samples experienced less blooming corrosion than a washed commercial flux. Unwashed zinc ammonium chloride fluxed specimens resulted in more blooming corrosion than the other fluxes.

Up to now the conventional belief has been that blooming corrosion can be prevented or minimized in auto radiators by using solder with a high tin content. Some radiator manufacturers specify a minimum tin content in solder for that reason. The CDA test program has shown that even a high tin content will not prevent blooming corrosion when a corrosive coolant is present in the radiator. The tests did indicate that high-tin solders do have an advantage when the coolant is “mildly corrosive.”

CONCLUSIONS

The results of the CDA experimental program summarized above and presented in detail in the references below have improved the understanding of the complex interrelationship between copper alloy, solder composition, flux formulation, and process parameters. Clearly, careful consideration of the interrelated effects of all these soldering variables is needed if superior joints are to be produced.

Finally, it is also possible to extend radiator operating temperature and pressure capabilities by joining with plasma-arc welding techniques, and this has been investigated. The results, presented in the final reference below, indicate that the process is a feasible alternative to soldering for the fabrication of high-performance automotive radiators.

REFERENCES


