

Corrosion of Solders in Automobile Coolant Systems

Tests indicate corrosion resistance of different soldering systems in water and commercial solutions

BY W. L. FALKE, A. E. SCHWANEKE AND A. Y. LEE

ABSTRACT. Corrosion experiments were conducted on three high lead and two zinc base solders in commercial antifreeze coolant solutions, in a rust inhibitor solution, and in corrosive water. The experiments were made to compare the corrosion resistance of presently used soldering systems with that of new systems that can be used for assembling automotive radiators. The high lead solders, 70Pb-30Sn, 95Pb-5Sn, and 95Pb-3.8Sn-1.2Ag, are similar to those used to make automobile radiators. The zinc base solders (95Zn-5Al and 89Zn-7Al-4Cu) were developed for possible use in automobile radiators. Glassware corrosion tests were conducted on each of the soldering alloys for periods of 336 hr at temperatures of 165 and 200 F. A limited number of in-service tests were performed by introducing the sample bundles into the cooling system of two automobiles for 10,000-mile tests. Results are presented as the corrosion weight loss in milligrams for each specimen of (1) bulk solder, (2) solder coated copper, and (3) solder coated brass. Corrosion resistance of the soldering alloys and of the solder coated copper and brass proved to be more dependent on coolant solution type and temperature than on solder alloy composition, whether high lead or zinc base type solders. Increased corrosion occurred for both soldering systems in corrosive water; however, the amount of increase was much greater for the zinc base system. With the exception

of the zinc base bulk solders, the rust inhibitor solution offered little protection to the solder systems tested.

Introduction

The objective of the research reported herewith was to compare the corrosion resistance of presently used soldering systems with that of new systems (Refs. 1, 2) that can be used for assembling automotive radiators. Although manufacturers of automobile antifreezes have performed numerous corrosion tests in the laboratory and in automobile coolant systems, most data are proprietary and few reports of this nature have been published (Refs. 3, 4). These experiments have been designed primarily for the development of corrosion inhibiting antifreeze solutions that would be compatible with the standard copper-brass, lead-tin soldered automobile radiator. The experiments reported herewith were designed to evaluate corrosion resistance of several different soldering systems in already accepted commercial corrosion inhibiting coolant solutions.

Initial corrosion experiments were performed in laboratory glassware apparatus. These glassware corrosion tests use a simple beaker system for evaluating the effects of engine coolant solutions on metal test specimens representative of those found in an automobile cooling system.

The method used was similar to that described in ASTM D1384-70 (Ref. 5). Specimens of typical metals used in automotive cooling systems were totally immersed in radiator coolant solutions at different temperatures for a certain period of time. Included with these specimens were bulk solder, and solder coated copper and brass samples. The corrosion resistant properties of the specimens were evaluated on the basis of the weight changes incurred during the test. The method will generally

distinguish between soldering systems that have unacceptable corrosion resistance, and those that would be suitable for further testing and evaluation.

Subsequent corrosion tests were performed with the soldering materials inserted in actual automobile coolant systems. The procedure was similar to that described in ASTM D-2847-69 (Ref. 6). For these tests, metal corrosion specimens were mounted in special holders and installed in the coolant flow system of test vehicles for extended periods of time. The data obtained were used to provide added significance to the data obtained from the glassware corrosion tests. These tests also provide a fairly solid basis for evaluating the performance of a soldering system in actual service.

Experimental Procedure

Glassware Corrosion Tests

The glassware corrosion test procedure used conforms closely to that described in ASTM Standard Method D1384-70, "Glassware Corrosion Test for Engine Antifreezes." This procedure was developed specifically for evaluation of engine coolant solutions, such as antifreezes, rust inhibitors, etc. However, for this work, the effect of accepted coolant solutions on different solders and solder coated copper and brass specimens was to be evaluated. Consequently, some slight modifications were made in the ASTM standard procedure.

A designated set of metal coupons, 2 × 1 in. (50.8 mm × 25.4 mm) with a 1/16 in. (1.59 mm) thickness, were bolted together through a drilled center hole along with metal conducting and insulating spacers in specified order. The bundle was then immersed in aerated coolant solutions, heated to either 165 F (74 C) or 200 F (93 C), and allowed to corrode for 336 hr (2 weeks). Aeration was used to circulate the coolant solutions

W. L. FALKE is Research Chemist, A. E. SCHWANEKE is Supervisory Research Physicist and A. Y. LEE is Chemical Engineer at Rolla Metallurgy Research Center, Bureau of Mines, U.S. Dept. of the Interior, Rolla, Mo.

Paper was presented at the 2nd International Soldering Conference held in Chicago on April 3, 1973.



Fig. 1 — Glassware corrosion test apparatus

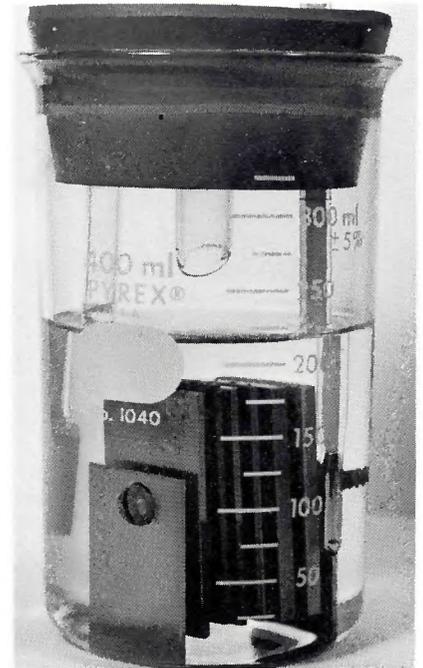


Fig. 2 — Glassware corrosion test unit

Table 1 — Test Coolant Solutions

Coolant solution	Present in additive	Type of solution
A	Boron Phosphorus Sodium	50-50 commercial antifreeze-corrosive water
B	Boron Phosphorus Potassium Silicon	50-50 commercial antifreeze-corrosive water
C	Boron Calcium Sodium	50-50 commercial antifreeze-corrosive water
D	—	Commercial rust inhibitor-corrosive water
E	—	Corrosive water

and maintain the oxygen concentration. Figure 1 shows the corrosion test apparatus with 12 specimen bundles under test. Figure 2 is a close-up of one of the test beakers showing the metal test specimen bundle, thermometer, aerator, and reflux condenser outlet.

The metal test specimens were comprised of bulk solder, solder coated copper and brass, steel, cast iron, and cast aluminum. The copper, brass, steel, cast iron, and cast aluminum test specimens are the types prescribed in the ASTM standard test. The soldering alloys investigated were three high lead types (70Pb-30Sn, 95Pb-5Sn, and 95Pb-3.8Sn-1.2Ag) and two zinc base solders (95Zn-5Al and 89Zn-7Al-4Cu). The copper and brass specimens were coated (½ surface area) by dipping in the test solders in order to determine

the effect of solder in contact with substrate materials, as they would be under actual operating conditions.

The test specimen bundle was made up on a brass screw and supported on two brass legs. The pieces were assembled in the following order: brass leg, solder coated copper, bulk solder, solder coated brass, steel, cast iron, cast aluminum, and brass leg. The specimens were cleaned and prepared for testing according to the procedure prescribed in the ASTM method.

The assembled specimen bundles were placed in 400 ml tall form beakers and submerged in the test coolant solution. A gas dispersion tube and thermometer were inserted into the test solution, and a water reflux condenser was added to prevent loss of solution during testing. Test temperatures were 165 and 200 F for

the 336 hr test. Temperature was maintained to within ± 3 F during the test periods. Aeration rate was 100 ± 10 ml per minute dry air. The aerator tube was located in such a way as to avoid direct contact of air with the test specimens.

The five different coolant solutions used to test the solders for their corrosion resistance are shown in Table 1. Coolant solutions A and B were made with corrosive water and antifreeze manufactured by the same company; solution B was made with a new product called "silicon type" antifreeze. Solution C was made with an antifreeze supplied by a different manufacturer. Solution D contained corrosive water with the prescribed amount of an anti-rust product. Solution E was 100 percent corrosive water with no antifreeze or rust inhibitor additives. The corrosive water was a solution containing 100 ppm each of sulfate, chloride, and bicarbonate ions in distilled water. This "synthetic" corrosive water is standard for the ASTM test.

After the corrosion experiments were completed, test specimens from the high lead solder tests were cleaned, and the oxide deposit removed according to procedures prescribed in the standard. In those corrosion experiments in which the zinc base solders were used, the standard test cleaning procedures were followed on the steel, cast iron, and cast aluminum specimens. The bulk solder and solder coated copper and brass were cleaned with a soft bristle brush and fine scouring powder, rinsed in distilled water followed by acetone, allowed to dry thoroughly, and then

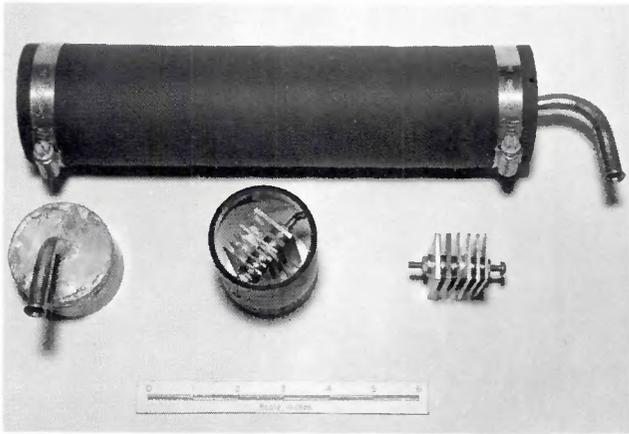


Fig. 3 — In-service corrosion test components

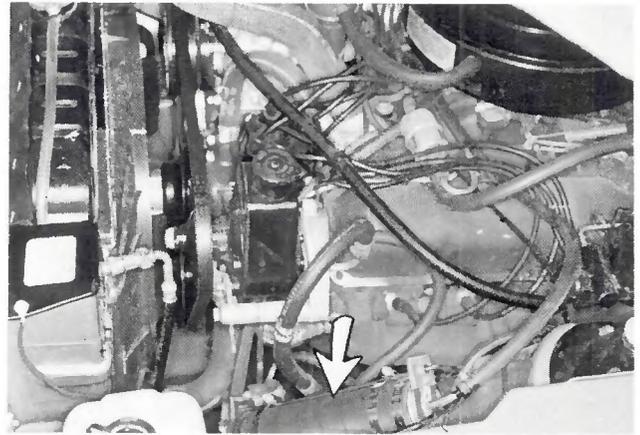


Fig. 4 — Underhood arrangement in-service corrosion test (arrow points to corrosion capsule)

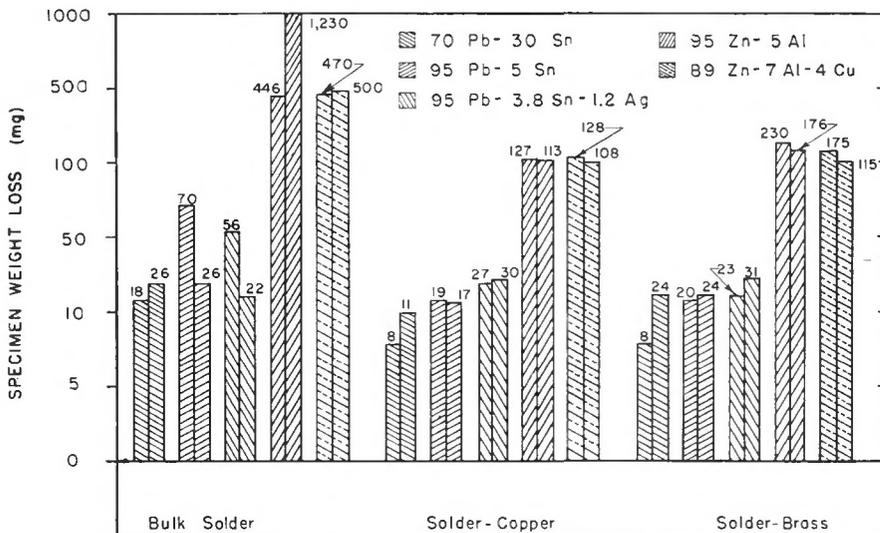


Fig. 5 — Glassware corrosion tests — weight loss vs. solder composition and temperature — coolant E (left side of each bar shows 165 F weight change; 200 F on the right)

weighed. The corrosion weight losses or (in some cases) gains of each specimen are reported to the nearest 1 milligram. The results are given as averages for at least three tests in every case. A weight loss of over 300 milligrams for the bulk solder samples, and about 200 milligrams for the solder coated copper and brass coupons, would probably be unacceptable for in-service use (Ref. 3).

In-Service Corrosion Tests

Because glassware corrosion experiments indicated no special problems should arise during in-service testing, capsules containing specimen bundles were inserted in the coolant circuit of two 1972 model passenger automobiles. The metal corrosion specimen bundles were prepared in the same way as for the glassware corrosion tests, except that the brass supporting brackets were not included. Three identical

specimen bundles were used for each test. Each bundle was mounted in a rigid plastic tube, and three of these tubes were inserted in a capsule (automotive hose, 2¼ in. ID), connected between the heater supply and return lines of the automobile cooling system. Figure 3 shows the method of assembly of the corrosion specimen bundles in the sleeves and capsule, and Fig. 4 shows the capsule location in the test automobiles.

Before adding the capsules to the automobiles, the coolant systems were thoroughly flushed with water and the test coolant solution. Coolant solution A was used for the experiments. The solders investigated were 95Pb-3.8Sn-1.2Ag, 95Zn-5Al, and 89Zn-7Al-4Cu. Specimens were left in the test automobiles for approximately 10,000 miles before removal. This distance was chosen because, for normal running time of a passenger automobile, the accepted average

speed of 30 miles per hour would result in about 336 hr of operation for 10,000 miles. The operating temperatures of the test vehicles ranged from 180 to 230 F depending on ambient temperature, speed, and accessories, such as air conditioning and heater operation. Test severity was about the same for each of the solders tested, because the test vehicles were usually driven under similar conditions. The procedure used for cleaning and weighing the corrosion specimens after testing was the same as that used in the glassware corrosion test.

Results

Glassware Corrosion Experiments

The results of corrosion tests, employing the five different solders, with corrosive water (coolant solution E) are illustrated in Fig. 5. Weight losses for the solders either as bulk coupons or as coated on copper and brass are shown for corrosion tests at 165 and 200 F. The corrosion weight loss for the bulk 70Pb-30Sn solder was very small. A small amount of crusty corrosion was noted on the outer edges of the bulk samples for the 95Pb-5Sn and 95Pb-3.8Sn-1.2Ag solders, in tests made at 165 F, but the corrosion weight losses were still small. One anomalous effect was that less corrosion occurred for these two solders as bulk coupons at 200 F than at 165 F. This was evident from both weight loss and close visual inspection of the coupons after testing. The corrosion resistance of the solder coated copper and brass pieces was very good for all three of the high lead solders. Figure 6 shows 95Pb-3.8Sn-1.2Ag bulk solder and solder coated copper and brass specimens before (a) and after testing in (b) corrosive water and (c) coolant.

The zinc base solders corroded extensively at both temperatures in the

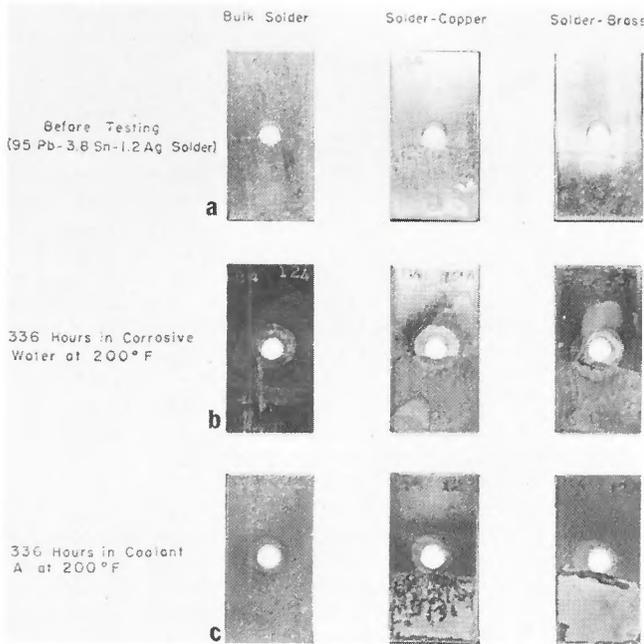


Fig. 6 — Test coupons: 95Pb-3.8Sn-1.2Ag bulk solder coated copper and brass before and after glassware corrosion tests

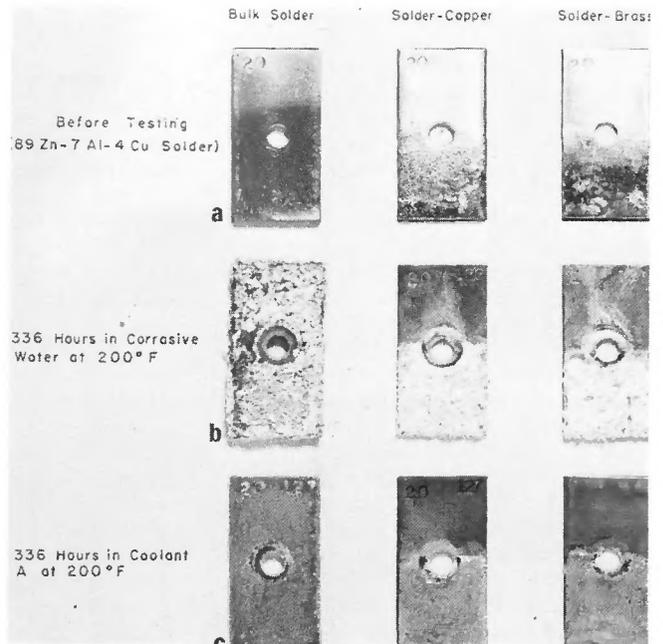


Fig. 7 — Test coupons: 89Zn-7Al-4Cu bulk solder and solder coated copper and brass before and after glassware corrosion tests

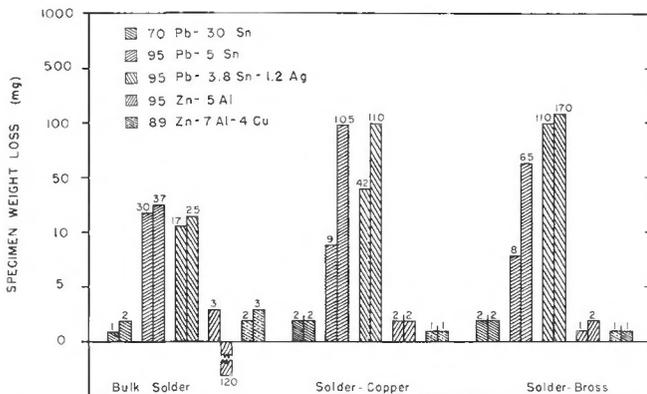


Fig. 8 — Glassware corrosion tests — weight loss vs. solder composition and temperature — coolant A (left side of each bar shows 165 F weight change; 200 F on the right)

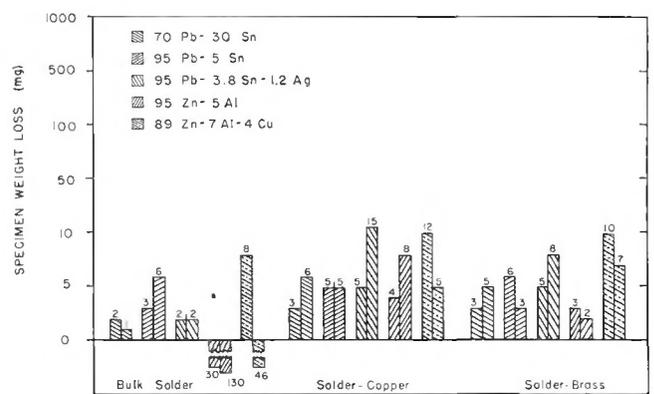


Fig. 9 — Glassware corrosion tests — weight loss vs. solder composition and temperature — coolant B (left side of each bar shows 165 F weight change; 200 F on the right)

corrosive water solution, with the 95Zn-5Al solder losing over 1,200 milligrams weight at 200 F. For the 89Zn-7Al-4Cu solder, weight loss of the bulk coupon was 500 milligrams at the same temperature. The acceptability of copper coupons coated with the zinc solders and tested in corrosive water was questionable, but the corrosion of the solder coated brass was definitely extensive.

In both cases the solder coated portion of the coupons was the most corroded. The bulk solder and solder coated copper and brass coupons for the 89Zn-7Al-4Cu soldering system are shown in Fig. 7 before (a) and after testing in corrosive water (b) and coolant (c). The coupons shown in Figs. 6 and 7 were only flushed with water after testing. The discoloration around the center holes re-

sulted from brass washers used in the assembly. For the high lead solder tests, the steel, cast iron, and cast aluminum coupons that were part of the specimen bundles were heavily corroded. In the zinc base solder tests the cast aluminum showed excessive corrosion but the steel and cast iron coupons showed very little.

Figure 8 shows the corrosion weight losses obtained for the five solders tested in coolant solution A at 165 and 200 F. The 70Pb-30Sn and the 89Zn-7Al-4Cu solders exhibited outstanding corrosion resistance with practically no weight loss occurring for either the solders or solder coated copper and brass. Coupons from the 89Zn-7Al-4Cu tests at 200 F are shown in Fig. 7 before and after testing. For the 95Zn-5Al solder

only the bulk solder coupon corroded in the 200 F test. Here a weight gain rather than a weight loss was obtained with corrosion evident in the form of tiny cracks along the edge of the specimen. No corrosion of either bulk solder or solder coated copper and brass was observed for the rest of the 95Zn-5Al solder coupons.

Relatively small corrosion weight losses were obtained with the bulk 95Pb-5Sn and 95Pb-3.8Sn-1.2Ag solder coupons in coolant solution A. For the latter solder this is visibly evident in Fig. 6. At 165 F very little corrosion occurred on the 95Pb-5Sn solder coated copper and brass coupons. At 200 F the amount of corrosion increased considerably, even to the point where more corrosion weight loss was obtained than with corrosive water.

The same was true for the copper and brass pieces coated with 95Pb-3.8Sn-1.2Ag solder, since weight losses here were considerably higher at both temperatures than those obtained in corrosive water. This fact was also visibly evident as shown in Fig. 6 when comparing coupons after testing in corrosive water and in coolant solution A. The bulk of the corrosion occurred on the solder portion of the coupons. Very little corrosion of the steel, cast iron, and cast aluminum samples was noted for all the soldering systems in coolant A.

Very little corrosion occurred for most of the five solders either in the bulk form or as coated on copper and brass in coolant solution B (Fig. 9). Weight gains were observed for bulk 95Zn-5Al solder at 165 and 200 F, and for 89Zn-7Al-4Cu solder at 200 F. However, very little corrosion was visible except for 95Zn-5Al solder at 200 F, where again minute cracks were observed on the edge of the bulk solder coupon. Copper and brass coupons coated with the same 95Zn-5Al solder lost almost no weight during testing, and showed no visible evidence of corrosion or cracking at either 165 or 200 F.

Slightly more corrosion was exhibited by the steel, cast iron, and cast aluminum coupons for all solders in coolant solution B than with A. However, corrosion weight losses were still very small (1 to 15 milligrams).

Weight losses for corrosion tests in coolant solution C are illustrated in Fig. 10. For all five solders in bulk, very little corrosion occurred at both test temperatures with the exception again of the 95Zn-5Al solder at 200 F. Small edge cracks and some blisters were noted, and a weight gain of 230 milligrams was measured after cleaning. All the other bulk solder coupons showed very little evidence of corrosion after testing.

Copper and brass coupons coated with the two zinc base solders exhibited very little corrosion in solution C. The same was true for the 70Pb-30Sn and 95Pb-5Sn solders at 165 F, but at 200 F the weight losses of the coated plates were more than twice that at 165 F. The weight changes approached those obtained at 200 F in corrosive water. Corrosion of the solder portion of the copper and brass coupons coated with 95Pb-3.8Sn-1.2Ag was severe in coolant solution C just as it was with solution A — more than in the corrosive water tests.

Corrosion of the steel and cast iron coupons was negligible in coolant solution C. A slightly higher degree of corrosion was noted for the cast aluminum with this solution as indicated by weight losses of 10 to 26 milligrams, depending on the solder system being investigated.

The effects of solution D (rust inhibitor compound in corrosive water) on the various solder combinations are shown in Fig. 11. Tests were made at 200 F only. The bulk zinc base solders exhibited much less weight loss in this solution over that for corrosive water alone — 1 mg versus 1230 for the 95Zn-5Al solder, and 2 mg versus 500 mg for the 89Zn-7Al-4Cu solder. Weight changes were about the same for the copper and brass coupons as they were in corrosive water. The weight losses of all the lead base solders, including the coated copper and brass plates, were either the same or higher than they were with corrosive water. In every case the visible corrosion occurred on the solder coated half of the copper and brass plates.

Solution D offered little protection for the cast iron and cast aluminum plates associated with the high lead solders. The aluminum plates were heavily pitted. The steel coupons with

these same tests showed negligible corrosion. In the tests with the zinc base solders in solution D, the steel and the cast iron were only slightly affected, but the aluminum plates were, again, severely pitted with deep holes.

The pH of coolant solutions A, B, and C (antifreeze solutions), and D (rust inhibitor solution) decreased during the corrosion tests. Table 2 lists pH for the coolant solutions before and after tests at 165 and 200 F. For coolant solution A only a slight reduction in pH occurred, but this coolant solution initially had a low pH. The pH values before and after the tests were very close to the same (± 0.1), independent of the solder alloy being tested.

Spectrographic analyses were also made on all the coolant solutions before and after corrosion tests. The analyses were made to determine whether the solder constituents were dissolved rather than oxidized by the coolant solutions. When the high lead solders were tested in coolant solutions A and C at 200 F, lead appeared in the analyses. This was the only time a solder cation was found in any of the spent coolant solutions.

In-Service Corrosion Experiments

Results of the in-service corrosion experiments are shown in Fig. 12. The corrosion weight losses after 10,000 miles operation closely paralleled those obtained in the glassware corrosion experiments at 200 F. In most cases a slightly higher corrosion weight loss was obtained for the in-service tests, but this could be expected because of the more severe operating conditions of the automobile coolant systems. Temperatures ranged from 180 F to as high as 230 F during operation. Excellent corrosion resistance was shown by the 89Zn-7Al-4Cu solder for the bulk

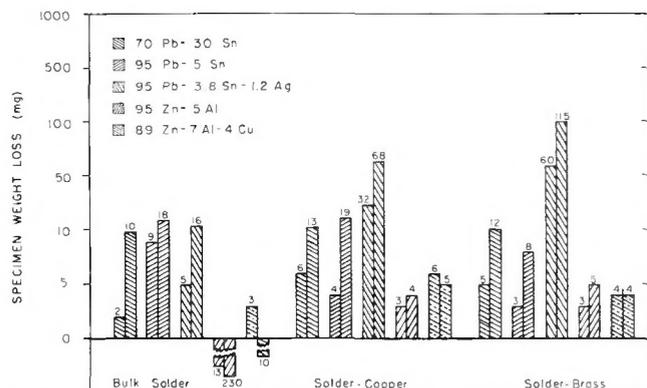


Fig. 10 — Glassware corrosion tests — weight loss vs. solder composition and temperature — coolant C (left side of each bar shows 165 F weight change; 200 F on the right)

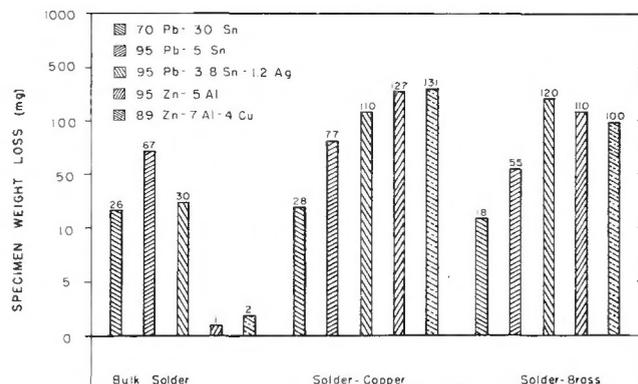


Fig. 11 — Glassware corrosion tests — weight loss vs. solder composition — coolant D at 200 F

specimen and also when applied as a coating on the copper and brass coupons.

The other zinc base solder exhibited good corrosion resistance when coated on the coupons, but corrosion of the bulk solder specimen occurred in the form of cracks and small blisters as it did in the glassware corrosion tests. The high lead solder showed good corrosion resistance in the bulk form, but corrosion did occur in the solder portion of the coated copper and brass substrates. The excellent correlation between the glassware corrosion experiments and the in-service tests serves to enhance the results obtained from the glassware tests.

Summary

In corrosive water the lead base solders exhibited their usual superior corrosion resistance, especially as-coated on copper and brass. The zinc base solders were not very good in corrosive water. Corrosion occurring for both types of solders was always more pronounced on the bulk specimens, and at the higher temperatures.

For solution A the zinc solders, except for the bulk 95Zn-5Al solder at 200 F, showed very little corrosion. The lead base solders having 95 percent lead exhibited moderate corrosion in the bulk form, but corroded very badly when coated on copper and brass. The 70Pb-30Sn solder had excellent corrosion resistance in this solution.

All the lead base solders exhibited acceptable corrosion resistance in solution B, whether in bulk form or as-coated on copper and brass. Copper and brass substrates coated with zinc solders also exhibited excellent corrosion resistance; however, some corrosion of the bulk zinc solders was noted.

Only slightly more corrosion of the 70Pb-30Sn solder occurred in coolant solution C than with the other two solutions. The high lead solders yielded a corrosion resistance at a level between solutions A and C. Corrosion resistance of the zinc solders was excellent in this coolant solution with the exception of bulk 95Zn-5Al at 200 F.

The corrosion resistance of the bulk zinc base solders in coolant solution D, the antirust solution, was excellent. All the remaining bulk solders and solder coated copper and brass coupons corroded badly, and in some cases worse than in corrosive water.

For corrosion tests made in antifreeze coolant solutions the degree of corrosion of the steel, cast iron, and cast aluminum specimens was dependent on test coolant composition only. In the corrosive water-rust in-

Table 2 — Coolant Solution pH

Coolant solution	pH before testing	pH after testing 336 hr ^(a)	
		165 F	200 F
A	7.8	7.7	7.6
B	10.4	9.6	9.0
C	9.1	8.5	8.2
D	9.0	—	8.3

(a) Average of three or more tests.

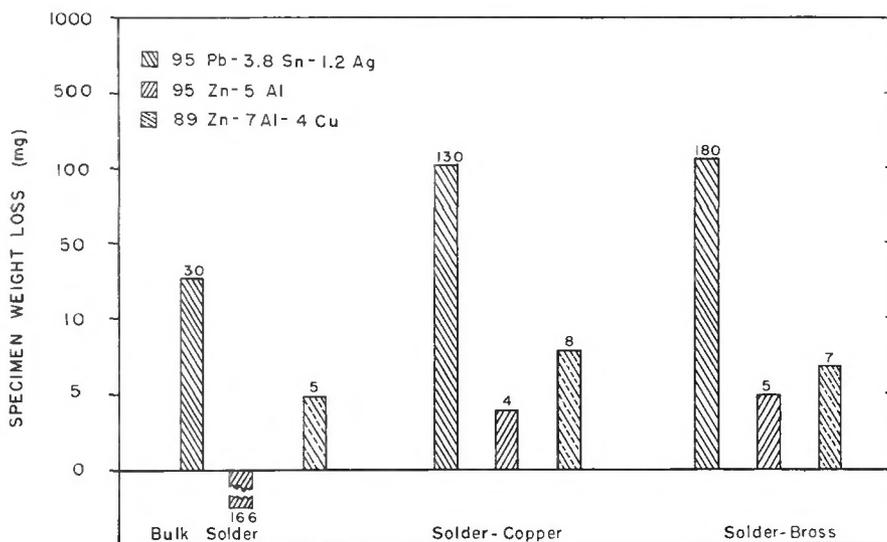


Fig. 12 — In-service corrosion tests — weight loss vs. solder composition — coolant A

hibitor solutions the amount of corrosion seemed to be related to the solder that was part of the specimen bundle. In antifreeze solutions, steel, cast iron, and cast aluminum specimens exhibited good corrosion resistance. In corrosive water the steel, cast iron, and cast aluminum were corroded badly when associated with lead base solders, but with the zinc solders, only the aluminum corroded. In the rust inhibitor solutions the cast iron and cast aluminum corroded when associated with the lead solders, but for the zinc solders only the aluminum was affected.

It is interesting to note that in solutions containing only rust inhibitor and corrosive water the aluminum specimens corroded excessively, exhibiting pits up to several millimeters deep. The labels on the rust inhibitors used stated that they were especially suited for aluminum. How these materials would react when combined with a regular antifreeze in the solution was not investigated. However, a regular antifreeze in solution with corrosive water seemed to provide sufficient protection for aluminum without further help.

These tests were undertaken to evaluate the possibilities of the new,

high temperature soldering system for automobile radiators. The results imply these conclusions — that the zinc base soldering system is compatible with regular automotive cooling systems, and that an antifreeze solution to prevent corrosion with this system is already available and could be improved if needed.

References

1. Beal, R. E., *Welding Journal*, v. 51, No. 6, 1972, Research Suppl., pp. 295-s-303s.
2. Schwaneke, A. E., Falke, W. L. and Crosser, O. K., *Welding Journal*, v. 51, No. 7, 1972, Research Suppl., pp. 361s-368s.
3. Hannigan, H. J., "Coolant Performance at High Temperature," SAE Paper 680497 presented May 1968.
4. Rowe, L. C., *Corrosion*, v. 13, No. 11, 1957.
5. *Annual Book of ASTM Standards, Part 22*, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp. 214-221.
6. *Annual Book of ASTM Standards, Part 22*, American Society for Testing and Materials, Philadelphia, Pa., 1971, pp. 402-413.