

# Substitute solders

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**S**OMEWHAT in excess of one-fifth of the tin consumed in the United States goes into the manufacture of solders; no one type of application, with the single exception of tin plate, uses more than one-third this amount. With the growing possibility of curtailment in tin supplies to the United States, it is appropriate that an effort be made to find satisfactory substitutes in an application such as this which is vital both to peace-time industry and to the manufacture of war materials.

## In the first world war

During the first World War much work was done in Europe and some in the United States in an attempt to reduce the percentage of tin in solders. No generally applicable tin-free solder was developed but tin-poor solders were developed to the point where the German Government felt justified in prohibiting the use of more than 15 per cent Sn in any solder; this represented a saving of about two-thirds of the tin normally allotted to this use. Because of their inferior quality, few of the substitute solders survived through the peace years; there has been little recent advance in this field and much of what was known previously has been forgotten.

Before entering upon an extensive search for new substitute solders, it will be advantageous, therefore, to examine carefully what was done in this field during the former emergency, in order that new studies may be begun where work was discontinued in 1919. It is the purpose of the present paper to present a tabulation of the principal solder combinations that have been proposed together with a comparison of the properties of these solders made upon a uniform basis. This should serve the purpose of providing a list of tested compositions from which substitutes for immediate use may be drawn and should forestall needless duplication of research effort in any further quest for better substitutes.

The literature has been searched to obtain a list of 75 alloys which are representative of virtually all of the types of compositions that have been proposed as soft solders excepting those intended only for the

joining of aluminum. Since the claims made for special properties in these alloys are necessarily based upon a wide variety of tests, it has been found advisable to re-examine this entire group with a series of standardized tests. The results of this work are recorded in the Table.

The tin-lead alloys are remarkable in the latitude of their usefulness. They may be employed for the joining of a majority of the common metals, ranging all the way from the relatively high-melting metals of the copper group down to low-melting metals such as tin, lead, zinc, and their alloys. Moreover, the tin-lead alloys can be handled by relatively simple techniques; they are not subject to rapid oxidation when molten or to severe corrosion in use; and they produce the strongest joints of all of the known low-melting alloys. Although these solders have been in use continuously for thousands of years, no generally useful competitive alloys have appeared. It is too much to expect, therefore, that any one alloy will be found suitable for all of the applications to which tin solders are normally put. At best, it may be hoped that a number of tin-poor or tin-free alloys may be found which will collectively cover the main range of usefulness of the tin-rich solders.

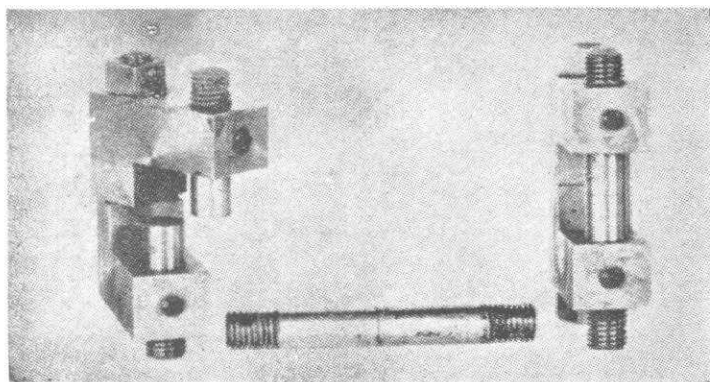
## Possible substitutes classified

The search for substitute solders may well be divided into several classifications, such as materials suitable for joining.

1. Copper and its alloys.
2. Galvanized iron.
3. Tin plate.
4. Lead and pewter.
5. Aluminium and its alloys.

Of these classes copper and its alloys present by far the most difficult soldering problem, partly because of the limited number of alloys that will properly wet copper, and partly because of the exacting requirements involved in the fabrication of copper and brass articles. Zinc and tin-coated materials and the white metals present a much less difficult soldering problem, because most of these can be joined either with lead-rich or zinc-rich alloys; and there are a great many of these available. Little soldering of aluminum

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1 Jig for producing tensile and torsion test joints. At left, jig open for tinning; at right, closed to complete joint; at centre finished test bar

is practised; tin-free alloys are currently in use for this purpose. The tests here reported have been confined, therefore, to the most pressing problem—the joining of copper; it is assumed that solders suitable for joining copper will also be suitable for joining the majority of the copper alloys, but some exceptions will be found.

#### Choice of a flux

It has been necessary to eliminate another variable, namely, the choice of flux. A flux composed of zinc chloride, with or without ammonium chloride additions, has been found to be generally useful in handling all soft solders. In certain industrial applications it is impractical to use this type of flux because of its chemical reactivity; rosin is commonly used as a substitute. Since the zinc chloride-ammonium chloride flux is most widely useful, however, it has been selected as a standard in making the present group of tests. The composition employed was 65 per cent  $ZnCl_2$  and 35 per cent  $NH_4Cl$  dissolved in water.

#### Experimental procedure

The alloys were all made from pure metals melted together in clay-graphite crucibles in a gas furnace. Charcoal was employed as a cover. One pound of each alloy was prepared in a single heat. Since significant deviations from the nominal compositions are not to be expected among alloys of this class, no chemical analyses have been made. There was evidence of loss by oxidation only among the alloys containing cadmium and zinc; it is believed that these losses were not significant. After thorough stirring the molten metal was cast as conveniently shaped bars in a horizontal iron mold.

The following physical tests were made:

1. Tensile strength of a soldered joint between copper bars.

2. Shear strength of a soldered joint between copper bars.
3. Capillary rise of solder between parallel copper bars.
4. The spread of a drop of solder on a horizontal copper surface under flux.
5. The rate of corrosion of the solder itself in a standard salt spray test.

The purpose of the tensile and shear tests is self-evident. Strengths of the solders themselves are often reported in the literature, but it is felt that the strength of a soldered joint, which may bear little relation to the strength of the solder itself, will be of greater practical significance in the present case. The capillary rise of solders is a property of increasing importance with the growing use of soldering techniques that depend upon capillary flow to fill the joint. An indication of the "wetting" ability of the solder is given by the "spread of a drop" test. Corrosion resistance is a property that cannot be satisfactorily determined without reference to the specific environmental conditions in which the material is to be used, but those alloys of marked inferiority will generally be identified by a standard salt spray test.

In order to standardize the soldering procedure, all joints were made at a temperature  $60^\circ C$  above the liquidus temperature of the solder. Capillary rise and "spread of a drop" tests were also made at this temperature. For the most part, the melting temperatures (liquidus and solidus) of the alloys were obtained from the literature. Where such data were not available, they were determined directly with the solder used in the tests. Liquidus temperatures were determined in the usual way, by means of cooling curves. Solidus temperatures, when they could not be read accurately from the cooling curves, were determined by the Hanson technique, that is, by measuring the temperature at which a loaded bar of the solder suddenly ruptures upon slow heating. Some idea of the maximum useful temperature range of the solder can be obtained from the solidus temperature.

#### Tensile strength

The tensile strength of a soldered joint is very critically dependent upon the thickness of the solder layer. To a less marked extent the time of heating will also influence the strength of the joint. In general, there is an optimum thickness of joint somewhere in the neighbourhood of 0.005 in., where the best tensile strengths are reached; beyond this thickness, the strength drops off rapidly. Lower tensile strengths found in joints thinner than about 0.003 in. are quite possibly the result of difficulties involved in producing perfect joints. Increased times of heating increase the thickness of the inter-metallic compound layers in the solder and frequently result in a decrease in the tensile strength. Thus the best conditions for testing seem to be: a joint thickness of 0.005 in. made with the shortest possible time at the soldering temperature.

Test bars made by joining two copper rods each  $\frac{3}{4}$

in. in diameter and machined flat on the abutting ends were produced in a special jig which held the ends of the bars exactly the pre-determined distance apart. In soldering the assembly was heated in a thermostatically controlled, pit-type, electric furnace until a temperature of 60°C above the melting point of the solder was attained. Flux was then applied to the ends of the test bars and solder immediately flowed on. During this operation the two parts of the test bars were hinged apart, in order to provide easy access and to insure perfect tinning. As soon as the solder had been applied the ends of the bars were brought together in a wiping motion designed to push out all air bubbles, oxide and remnants of flux. Perfectly clean joints were consistently obtained in this way. This method was found to be far superior to the more usual technique of allowing the solder to rise between fixed surfaces. Immediately after soldering, the jig assembly was removed from the furnace and was allowed to cool until the solder was frozen, whereupon cold water was applied to reduce the temperature as quickly as possible.

A minimum of 5 joints of each alloy, made in this way, were loaded to rupture in a tensile machine. The average ultimate strengths so measured are reported in the Table. Some deviation in the strengths from bar to bar is inevitable in tests of this sort; for the most part, the deviation was not greater than  $\pm 10$  per cent of the reported ultimate strength, usually much less. It is noteworthy that the alloys showing the greatest tensile strengths generally break *through* the solder, whereas those showing relatively low tensile strength frequently break *between* the solder and the copper.

#### Shear strength and capillary rise

Test bars similarly prepared were employed in the shear tests and were broken in a standard torsion testing machine. The results are again listed in the Table. It will be observed that there is little correlation between the tensile and shear strength among many of the alloys; presumably, a difference in the mechanism of failure is responsible for this divergence. This observation indicates the importance of choosing a solder for the particular service to which it is to be subjected.

For the capillary tests pairs of copper rods, each  $\frac{1}{4}$  in. in diameter, were clamped together with strands of cupro-nickel wire, 0.007 in. in diameter placed between them at the ends. The protruding ends of these wires were bound around the assembly to hold the rods tightly against the spacer strand. By using carefully straightened rods and limiting the length to 3 in., adequate precision was obtained in the control of the dimensions of the capillary space. The rod assembly was preheated to 60° above the melting point of the solder, which at the same time was brought to temperature in an electric furnace. Flux was applied to both the copper rods and the solder bath, and the assembly was immediately lowered a pre-determined distance into the solder. Fifteen seconds were allowed for the solder to rise in the capillary space, after which the assembly was removed from the furnace and cooled.

The maximum travel of the solder, readily detected by the traces of solder left between the bars, was measured with a ruler. The height of rise for each alloy is recorded in the Table.

#### Spread of a drop

As a qualitative test of the behaviour of the solder under working conditions, the extent of the spread of a bead of solder was observed. This was done by placing upon flat, level plates of copper, fluxed and held at a temperature 60°C above the melting point of the solder, samples of solder exactly 0.1 c.c. in volume. During a period of 15 sec. the solder was allowed to spread, whereupon the plates were removed from the furnace and were cooled as rapidly as possible with a blast of air on the underside. Some alloys spread very rapidly in this test, while others form a bead that spreads very little. Those that spread rapidly are seen to advance with a band of apparently solid alloy proceeding ahead of the main body of liquid. In such cases the area covered may be quite irregular. Two measurements have been recorded in the Table :

- (1) the area covered by the drop and
  - (2) the maximum thickness of solder on the plate.
- Large areas and small film thicknesses will generally correspond to an easily worked solder, that is, one that will wet copper readily.

#### Corrosion

While it might seem most useful to test the corrosion resistance of soldered joints rather than that of the solder itself, it did not appear advisable to attempt to standardize such a test within the short period of time available for the work. Instead, bars of the solder have been subjected to the action of a 3 per cent NaCl mist, in a standard salt-spray tank, for periods up to 6 mos. At the end of 3 mos., the bars were removed from the testing chamber, scrubbed and weighed. The percentage loss in weight for each alloy is listed in the Table. After examination the bars were returned to the testing tank for another 3 mos., when the examination was repeated. The samples, although not exactly uniform in size, were approximately  $2\frac{1}{2}$  sq. in. in surface area.

#### Surface appearance and ease of tinning

In addition to the physical tests, several qualitative observations of some interest to the user of solder have been recorded in the Table. The appearance of the cast surface of the solder observed on the original cast bars is described with a series of self-explanatory terms. While the surface appearance of solders is generally of more aesthetic than engineering importance, it does occasionally appear as a rather important factor in limiting the applicability of the solder; for example, those alloys that oxidize readily may be undesirable in the joining of electrical parts or for use in automatic soldering machines.

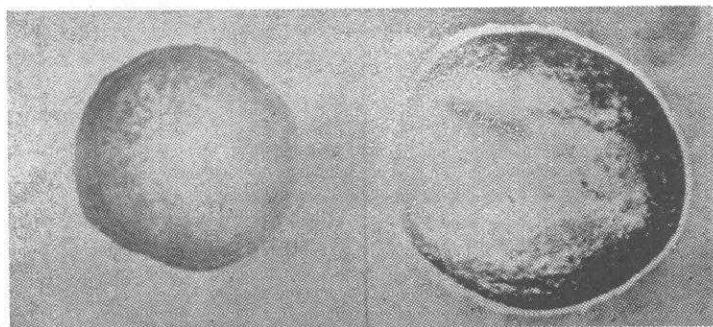
Table of Comparison of the Properties of Soft Solders

Alloy No.	Composition in Weight Per Cent							Liquidus temperature, Deg. C.	Solidus temperature, Deg. C.	Soldering temperatures used in tests, Deg. C.	Tensile strength copper joint 0.005 in. thick in lbs. per sq. in.	Shear strength copper joint 0.005 in. thick in lbs. per sq. in.	Capillary rise in inches between 1/4 in. copper rods 0.007 in. apart	Spread of a drop of 0.1 c.c. in volume on copper. Expressed in sq. in., Covered
	Sn	Pb	Sb	Cd	Bi	Zn	Others							
1	100							231.9	231.9	292	22,706	6,880	1.25	0.35
2		100						327.35	327.35	387	0	0	0.56	0.26
3	25	75						266	183	326	13,500	5,795	0.62	0.81
4	15	85						285	225	345	13,300	5,640	0.50	1.17
5	5	95						313	291	373	10,700	6,380	0.44	0.34
6	63	37						183	183	243	29,000	8,000	1.19	0.97
7	50	50						216	183	276	23,900	7,580	0.94	1.5
8	45	55						225	183	285	28,800	8,060	1.12	2.79
9	40	60						238	183	298	14,100	8,280	0.94	1.76
10	37.5	62.5						239	183	299	23,700	8,460	1.06	1.69
11	33	67						252	183	312	17,100	6,450	1.00	1.61
12	49.25	50	0.75					208	185	268	16,300	8,760	1.00	1.49
13	43.5	55	1.5					220	188	280	17,550	7,720	1.00	1.77
14	38	60	2					228	188	288	20,100	7,714	0.56	1.24
15	35.5	62.5	2					231	188	291	15,100	6,600	0.94	0.93
16	31	67	2					235	188	295	15,300	7,260	0.94	0.99
17	37.5	60	2.5					234	186	284	17,350	8,250	1.00	2.03
18	4	90	6					276	239	336	8,500	6,640	0.06	0.19
19	66	27.5		6.5				172*	137*	242	17,240	9,940	1.12	1.00
20	65	13.5		21.5				160*	137*	220	13,000	10,020	0.81	0.88
21	50	25		25				160	145	220	14,600	9,520	0.75	1.18
22	50	32		18				145.5	145.5	205	14,900	9,600	0.69	1.14
23	32.5	39.5		19		2		165	136	225	18,600	9,950	1.06	0.93
24	23	68		9				235	145	295	16,600	7,900	0.75	1.24
25	15	75		10				245	145	305	13,710	4,760	0.56	1.09
26	10	80		10				253	145	313	13,660	6,440	0.62	0.91
27	10	85		5				260	145	320	11,720	4,770	0.62	0.73
28	10	88		2				275	145	335	16,780	5,150	0.75	0.65
29	9	65		26				225	145	285	14,630	6,980	0.69	0.86
30	5	85		10				257	145	317	11,870	4,770	0.81	0.74
31	3	75		22				237	145	297	12,910	6,050	0.81	0.94
32	2	86		12				262*	239*	322	13,880	6,100	0.44	0.69
33	50	25			25			130*	110*	190	9,140	6,140	0.62	0.71
34	45	27.5			27.5			94		154	10,760	4,880	0.38	0.66
35	22	28			50			100		160	11,150	7,360	0.38	0.61
36	20	40			40			113		173	12,700	6,530	0.75	0.60
37	19	31			50			94		154	5,790	6,510	0.69	0.41
38	13	27			50			70		130	12,120	6,580	0.38	0.32
39	37.5			12.5	50			66		126	9,000	7,040	0.44	0.30
40	33.3			16.7	50			66		126	10,930	9,440	0.62	0.42
41	25			25	50			66		126	8,520	8,250	0.50	0.47
42		53.8		15.4	30.8			80		140	9,820	5,840	0.31	0.22
43		42.7		7.1	50			88		148	11,940	5,540	0.18	0.13
44		42		15.7	42.3			89.5		150	10,300	5,600	0.18	0.17
45	30			50		20		277*	157*	337	12,370	8,920	1.00	0.36
46	15			20		65		346*	157*	406	11,300	10,480	2.00	0.84
47	5			65		30		294*	229*	354	15,850	9,870	1.25	0.75
48		91.5		8.5				276	249	336	13,150	6,980	0.62	0.25
49		90		10				274	249	334	13,940	7,100	0.56	0.32
50		80		20				259	249	319	13,400	8,140	0.69	0.60
51		70		30				260	249	320	14,000	6,510	0.50	0.36
52		90	10					266	247	326	3,490	3,140	0.06	0.14
53		87	13					247	247	307	2,365	5,770	0.06	0.11
54				82.6		17.4		264.4	264.4	324	13,340	11,250	0.88	0.53
55				50		50		326	264.4	386	12,600	10,410	1.69	...
56				40		60		335	264.4	395	6,680	12,050	1.94	1.03
57				25		75		364	264.4	424	9,130	8,580	1.56	0.66
58		90.8		7.8		1.4		267	237	327	16,400	7,410	0.62	0.35
59		87.5		7.5		5		368	235	428	10,920	5,820	0.94	0.41
60	6	86					8 Hg	282*	247*	342	13,450	5,770	0.62	0.32
61	3	93					4 Hg	384*	270*	364	11,160	5,330	0.31	0.36
62	50		25	25				311*	214*	371	5,110	9,030	0.94	...
63	50	25				25		336*	155*	396	15,960	10,030	1.31	0.39
64	37.3	62.7					.1 As	240	183	300	16,550	7,910	1.12	1.79
65	95		5					240	232	300	14,200	11,080	0.88	0.29
66	41.5	56.5	2				.02 P	220		280	10,300	10,000	1.00	0.79
67		79.7	2.6	17.7				239*		299	14,600	7,130	0.06	0.13
68		95				5		418	318	478	9,460	4,770	0.94	...
69		97					0.25 Cu; 2.5 Ag	350	300	410	11,500	4,770	0.75	0.41
70				95			5 Ag	390	337	450	9,510	10,650	0.75	1.91
71						98	2 Ni	550	419	500	9,450	.....	0.88	0.31
72		98					2 Ag	308	304	364	9,560	4,420	0.50	0.35
73		95					5 Ag	365	304	425	9,100	4,100	0.62	0.41
74		98					2 Ti	310	308	390	8,600	5,890	0.69	0.20
75	95						5 Ag	295	221	305	14,100	10,610	1.00	0.91

\* Temperatures measured in this investigation.

Spread of a drop of 0.1 c.c. in volume on copper. Expressed in maximum thickness of film in inches

	Appearance of Cast Surface	"Tinning" qualities with reference to copper	Corrosion in 3% NaCl spray. Per cent loss after 98 days	Corrosion in 3% NaCl spray. Per cent loss in weight after 203 days	Recommended uses	References to Bibliography
0.0279	Bright, furrowed	Very good	0.220	0.442	Electrical equipment	17
0.0376	Dull	Very poor	0.120	0.247	None	21
0.0139	Frosty	Good	0.156	0.326	General low grade; filler	12
0.0102	Dull, very frosty, traces of a furrow	Fair	0.190	0.389	(General low grade; coating, jointing; high temp. uses)	22, 31, 41
0.0275	Bright, slight frostiness, slight furrow	Fair	0.097	0.260		12, 27
0.0164	Bright, slightly discolored	Good	0.325	0.708	Fine solder. General purpose	13, 15, 26, 36, 45
0.0060	Bright, traces of a furrow	Good	0.292	0.618	General purpose	9, 13, 15, 16, 26, 36, 45, 46
0.0055	Bright, slightly frosty in places	Good	0.288	0.678	Radiators, roofing	13, 15, 26
0.0070	Frosty, slightly discolored	Good	0.248	0.515	Wiping, radiators	13, 15, 46
0.0076	Very frosty	Good	0.260	0.525	Wiping, radiators	13, 14, 15
0.0119	Very frosty	Good	0.342	0.697	Wiping	13, 15, 26, 45
0.0096	Bright, slightly discolored	Good	0.455	0.765	General; tin plate	10, 13, 15
0.0075	Frosty, furrowed, slightly drossy	Good	0.429	0.930	General purpose	10, 13, 15
0.0093	Very frosty, slightly discolored	Good	0.457	0.709	Wiping	10, 13, 15
0.0155	Very frosty, slightly discolored	Good	0.292	0.756	Wiping	10, 13, 15
0.0135	Frosty, spotted, slightly drossy	Fair	0.314	0.629	Wiping	10, 13, 15
0.0055	Frosty and bright, spotted	Fair	0.272	0.688	Wiping	10, 12, 15
0.0534	Very frosty, furrowed	Poor	0.230	0.406	High temperature service	15, 41
0.0145	Dull, frosty, slightly furrowed	Fair	0.097	0.410	Wiping	19, 39
0.0162	White, frosty	Fair	0.162	0.950	Wiping	19, 39
0.0180	Bright, roughened trace of shallow furrow	Fair	0.153	1.175	General purpose	19, 46
0.0187	Bright, smooth	Good	0.040	0.594	Fusible safety devices	6, 39, 46
0.0170	Dull, frosty, spotted	Good	0.192	1.172	General purpose	9
0.0103	Dull, frosty, grainy	Good	0.017	0.443	Wiping	14, 39
0.0094	Slightly frosty	Fair	0.046	0.380	Coating and jointing	20, 39
0.0135	Dull, frosty	Fair	0.019	0.405	Gen.; elect.; cans; roofing	2, 5, 9, 19, 20, 25
0.0120	Dull, rough	Fair	0.214	0.494	General purpose	41
0.0200	Dull, frosty, furrowed	Fair	0.143	0.451	General purpose	41
0.0121	Bright, frosty, furrowed	Fair	0.150	0.684	General purpose	39
0.0141	Dull, frosty, trace of furrow	Fair	0.083	0.551	General purpose	19, 20
0.0114	Bright, rough furrow	Fair	0.236	0.743	General purpose	39
0.0197	Very dull and frosty, shallow furrow	Fair	0.250	0.787	General purpose	18
0.0170	Dull discolored, appears "etched"	Fair	0.151	0.289	Joining pewter	23, 26
0.0190	Bright, frosty, appears "etched"	Fair	0.223	0.473	Pewter, lead, tin, Britannia	23, 32
0.0290	Bright, slightly frosty, furrowed	Fair	0.216	0.340	Lead, tin, Britannia	23
0.0176	Very dull deep frost, trace of furrow	Fair	0.206	0.431	Lead, tin, Britannia	23, 32
0.0250	Bright, slightly frosty, "etched," slight furrow	Fair	0.207	0.331	Britannia	12, 23
0.0315	Dull, frosty, slight furrow	Fair	0.334	1.048	Fusibility, glass-metal	12, 23, 44
0.0265	Dull, frosty, furrowed, appears "etched"	Fair	0.198	0.620	Fusible alloy	19
0.0230	Frosty, slight furrow, appears "etched"	Fair	0.342	1.371	Fusible alloy	19
0.0221	Frosty with bright facets	Fair	0.196	1.580	Fusible alloy	19
0.0459	Frosty with bright facets	Fair	0.405	1.347	Fusible alloy	19
0.0785	Dull deep frost	Fair	0.441	0.314	Fusible alloy	19
0.0520	Slightly frosty, showing facets	Fair	0.343	1.367	Fusible alloy	19
0.0095	Dull, frosty, showing facets	Fair to poor	1.685	3.999		19
0.0195	Dull white, frosty, appears "etched"	Fair to poor	2.190	4.810		29
0.0155	Frosty, acicular ridges	Fair to poor	1.130	3.740		19
0.0140	Dull brown oxide over all	Fair	.....	0.198	Carbon, Copper, Zinc, Iron	11, 19, 28
0.0350	Deep brown oxide over all	Fair	0.0215	0.509	Copper, zinc, iron	4, 17, 19, 25
0.0180	Bright, frosty, rough irregular surface	Fair	0.134	0.845		17, 19
0.0322	Dark blue-brown oxide over all	Fair	.....	0.340		19
0.0770	Bright, frosty	Very poor	0.128	0.368	Lead cable	38
0.0945	Bright, frosty	Very poor	0.244	0.425	Lead cable	38
0.0195	Bright, shiny	Poor	0.279	1.022	High temp.; galvanized	8, 12, 30, 33, 37
.....	Bright, frosty, rough	Poor	1.870	3.820	High temp. service	12
0.0155	White, frosty	Poor	2.230	4.470	Bronze; Al to Cu	19, 34
0.0201	Dull white, frosty	Poor	1.480	6.040	High temp. service	18
0.0279	Dull, frosty, spotted	Fair	0.0541	0.460	Copper, iron, tin, galv.	5, 19, 25, 46
0 1261	Bright, shiny, rough	Fair	0.519	1.028	Copper, iron, tin, galv.	3, 19, 46
0.0327	Bright, frosty	Fair	0.314	0.589	Galvanized, sheet iron	38
0.0275	Dull, appears "etched," coarse furrow	Fair	0.195	0.379	Galvanized, sheet iron	7, 38
.....	Bright, discolored, acicular ridges	Fair	0.106	0.476	Pewter, Britannia, Sb-lead	19
0.0370	Dull, frosty, coarse	Fair to poor	1.280	2.740	Aluminum	1
0.0065	White, frosty, spotted	Good	0.478	0.903	Wiping	40
0.0340	Bright, shiny, appears "etched," trace of furrow	Good	0.275	0.415	Electrical equipment	12, 17
0.0173	Bright, shiny, spotted	Good	.....	.....	General purpose	24
0.0680	Very dull frosty, rough	Fair	0.087	0.590		.....
.....	Bright, frosty, coarse	Poor	0.131	0.848	High temp. service	3
0.0361	Bright, spotted	Poor	0.138	0.513	Electrical equipment	42, 43
0.0400	Dull brown oxide over all	Fair	0.893	3.840	High temp. service	12
0.0440	Bright, frosty, rough, furrowed	Poor	2.240	10.210	Carbon; high temp.	3, 11
0.0280	Dull, rough, coarse furrow	Fair	.....	.....	Electrical; high temp.	17, 27, 43
0.0269	Dull, discolored, rough	Fair	0.098	0.379	Electrical; high temp.	17
0.0485	Bright, shiny, trace of furrow	Poor	.....	.....	Electrical; high temp.	27
0.0140	Bright, shiny	Good	.....	.....	Electrical; high temp.	17



2 'Spread of a drop' test showing manner in which the solder spreads with a margin of solid alloy growing ahead of the spreading molten mass. Tin-lead solder (50-50) on copper using a resin flux (left) and a zinc chloride-ammonium chloride flux (right). Mag. about 3X.

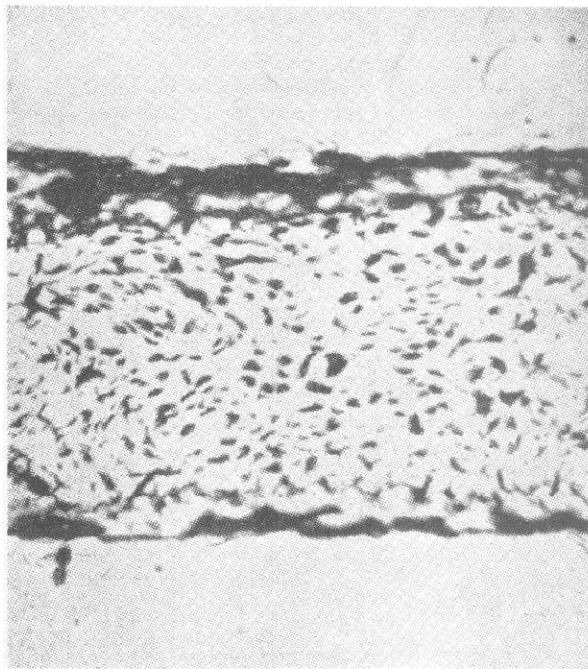
A more or less definite indication of the tinning qualities of the solder has been given by the spread of a drop test. Some indeterminate factors sometimes appear to come into play in influencing the general ease of handling a solder, however, and a series of comments on this point may be useful. Under the heading, 'Tinning Qualities', have been listed a technician's impressions of the working qualities of each alloy. Those marked 'poor' can be caused to wet the copper only by excessive rubbing, whereas those marked 'good' can be tinned by simply flowing the solder onto the copper.

## Uses

Although the present investigation has been purposely limited to the soldering of copper, it will be understood that many of the alloys tested are to be recommended for other purposes. In the Table under the heading, Recommended Uses, are listed the applications of each alloy claimed in the literature. The truth of these claims with respect to metals other than copper has not been examined in the present investigation. For the convenience of the reader, who may wish to obtain more specific information about any particular alloy, an abridged bibliography has been assembled, and a classified list of the references is given in the last column of the Table.

## Discussion

Among the alloys that have been tested is an extensive series of binary tin-lead compositions. This has been included in order to provide a basis for comparing the properties of substitute solders with the commonly used tin-rich compositions. In making the comparison it will be convenient to consider first those alloys in which the tin content is simply reduced and second those alloys from which tin has been entirely eliminated. Among the alloying elements that have been used as



3 Structure of a joint between copper rods soldered with a tin-lead solder. The centered band is a solder and the white outer bands copper. At the junction between the solder and copper, alloy layers can be seen. Etched with ammonia and hydrogen peroxide. 400X

partial substitutes for tin are antimony, cadmium, bismuth, zinc and mercury.

### Antimony

The lead-tin-antimony alloys have been extensively exploited, and it has been found through a long period of years that antimony cannot be substituted for tin beyond 7% of the tin content without damage to some of the useful qualities of solders.<sup>35</sup> Alloys containing large quantities of antimony have been marketed (not listed in the Table), but with unsatisfactory results. In no case can antimony be expected to substitute for a really substantial proportion of the tin used in soft solders. The alloys containing up to 7 per cent Sb, as is indicated in the Table, are entirely satisfactory for general use, and for some purposes are superior to the binary alloys because of greater strength at elevated temperatures and a slower creep rate.

### Cadmium

Cadmium can be substituted for tin in rather larger proportions than can antimony, partly because alloys higher in lead can be used when cadmium is present. This is done at some sacrifice of good working qualities and with a little loss in the strength of the joints formed. In the Table the alloys containing between 65 and 80

per cent Pb with 10 to 26 per cent Cd appear most promising. Within this range cadmium can be substituted directly for tin with no serious loss except in the tensile strength which is often unimportant. The lead-tin-cadmium alloys generally show a desirable rise in the capillary test and are well suited for soldering where a capillary action is employed. All are subject to rather severe oxidation when overheated; particularly is this true when the tin content is very low, i.e., below about 10 per cent. Cadmium oxide is poisonous and creates something of an industrial hazard. Moreover, there is a tendency for the oxide to become trapped in the joint with a resulting decrease in mechanical properties and an increase in porosity. Low temperatures are, therefore, to be recommended for handling these alloys. Where they can be used, a considerable saving of tin can be effected at slight inconvenience and some increase in cost. Special attention is directed to Alloys No. 29 and 31, which appear the most promising.

#### *Bismuth*

Lead-tin-bismuth alloys, while more difficult to handle than the standard solders, are capable of producing acceptable joints (See the Table). Their principal disadvantage lies in their low melting points, which give rise to low strength above room temperature. Where this feature is not objectionable, bismuth may be used as a major constituent of soft solders. Lower lead contents must be used with bismuth so that the saving of tin is not directly proportional to the bismuth added. Several combinations containing both bismuth and cadmium have also been tested and these appear to give somewhat superior shear strengths, but use unduly large proportions of tin. The cost of bismuth is high, however, and considering with this the other disadvantages it is hardly to be expected that bismuth solders could be economically used except under extraordinary circumstances.

#### *Zinc*

The addition of zinc to lead-tin solders has generally proven unsuccessful. A great deal of dross forms during the working if the zinc content is at all high. Moreover, zinc interferes seriously with the wetting qualities of solder and markedly decreases the corrosion resistance; notice in particular Alloys Nos. 45, 46, 47, 54, 55, 56, 57, 63, and 71 in the Table. No substantial saving of tin is likely to be effected by the substitution of zinc.

#### *Mercury*

Mercury has been used only for obtaining solders with low melting points and is never added in major quantities. When it is present, distinctly larger lead contents may be used with excellent results, and in this way mercury solders can be regarded as tin solder substitutes. With a probable shortage of mercury during the war times, however, it seems unlikely that these alloys will be acceptable. Moreover, the handling of mercury alloys at soldering temperatures might prove detrimental to health.

While the alloys made without the use of any tin are distinctly less promising than those containing reduced quantities, there are several combinations that deserve special notice.

#### *Lead-cadmium solders*

Foremost among these are the alloys based upon lead and cadmium. They produce joints of acceptable strength and can be handled satisfactorily if precautions are taken against oxidation, that is, if the working temperatures are kept as low as possible and care is exercised in fluxing. Unfortunately all of these alloys melt at rather higher temperatures than do the tin-lead-cadmium alloys. Some special techniques by which oxidation is altogether avoided without the use of flux have been developed for handling the lead-cadmium alloys in special applications; for example, a leaf of solder may be subjected to heat and pressure between the surfaces to be joined. Under ordinary circumstances these solders characteristically form heavy brown oxide coatings. It seems altogether probable that they could be satisfactorily employed now in many places where tin-base solders are being used, but with some delay in establishing the most suitable working conditions.

#### *Cadmium-zinc solders*

The cadmium-zinc alloys exhibit many interesting properties; they make joints of acceptable strength and are not subject to the severe oxidation exhibited by the lead-cadmium series; Alloy No. 56 exhibited the highest shear strength of any composition tested, half again as large as the best tin-lead solder. Their chief disadvantage lies in the difficulty of tinning the joints. Possibly, by the use of special techniques this trouble could be overcome. The quantity of cadmium used is considerably higher than in the lead series with a consequently higher cost. For this reason these alloys are less to be recommended except where a high shear strength is of paramount importance.

#### *Lead-silver solders*

Lead-silver alloys have recently received considerable attention and are being successfully used in a number of applications. They give joints of moderately good strength but unattractive in appearance. The working temperatures are rather high; this is compensated for by the advantage of a somewhat higher strength at elevated temperatures. Except for the high cost, these alloys seem well suited for substitute solders, and the price differential is not prohibitive.

#### **Summary**

A table has been made of the alloys which have been proposed as soft solders and as substitutes for the standard tin-lead compositions. It has been pointed out that no one alloy can be expected to serve all of the purposes now served by the tin-base alloys,

and that a group of alloys covering the various needs must be employed. All of the alloys listed have been subjected to a series of standard tests for comparison, so that compositions possessing those particular characteristics of the tin-base alloys that may be desired can be readily selected. These tests have all been made with reference to copper as the metal being joined. It appears, on the whole, that the alloys containing reduced amounts of tin rather than tin-free solders will be found most acceptable for soldering copper. Among these the tin-lead-cadmium combinations appear most promising. Some compositions of outstanding merit have been pointed out. Of the alloys containing no tin, the lead-cadmium and lead-silver series are most attractive. Cadmium-zinc alloys and tin-lead-bismuth combinations should also find some domains of special usefulness.

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