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A Study of the Physical Properties of Low Tin Solders

Cornelius P. Dwyer

A STUDY OF THE PHYSICAL PROPERTIES
OF LOW TIN SOLDERS

A Thesis

Submitted to

the Department of Metallurgy

Montana School of Mines

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science in Metallurgical Engineering

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INTRODUCTION

Economics

In 1947, out of the 100,000 long tons of tin consumed in the United States, 25,000 tons went into solder. Tin plate took 39,000 tons while babbit, bronze and collapsible tubes accounted for approximately 17,000 tons. Solder ranked second to tin plate and required more than the next three major uses combined.

The major uses for solder were in dip soldering automobile radiators and in soldering cans. The ordinary can for food, the sanitary can, has solder only in the side seams. The ends are pressed on over a rubber sealing gasket. The floated end can for evaporated milk, on the contrary, has both ends soldered, and is filled through a hole in the top which is then sealed with a drop of solder.

Early in 1943 the War Production Board issued a General Preference Order designed to cut tin consumption in 1943 to about one half the 1941 consumption, a large portion of the saving to be effected by limiting the tin content of general-purpose solders to twenty percent tin and restricting the use of solder containing tin.[8]

[8] References are at the end of the paper.

The workability, or ease of application, of low tin solders and the strength of joints obtainable with them were then of current interest. Now, however, with the cessation of the war the conservation of tin is of lesser importance. The problem becomes a matter of financial economics rather than conservation.

Basic Considerations

The maximum liquidus temperature of a solder is determined by the particular application involved and the temperature that can be obtained by the source of heat.

If a soldering iron is used, it must not only melt the solder but also heat the components being soldered to the soldering temperature. High temperatures may cause excessive oxidation of the solder and may also warp and buckle the component parts being joined. This is very important in connection with fine radio equipment.

When a torch or furnace is used to heat the parts of a soldered joint, high temperature may bring about an undesirable change in the physical properties of the components, either by a change in metallurgical structure or by excessive penetration of the solder.

The solidification range is of utmost importance in governing the workability of a solder. If the range is too great, the segregation of intermetallic compounds causes sluggishness before complete solidification occurs. Excessive thickness of the intermetallic compound layers causes a decrease of joint strength. Furthermore, it may be difficult to hold the components rigid during the solidification of the solder. Conversely, if the temperature range is too narrow, the solder will solidify before sufficient spreading and penetration has taken place. Therefore, the solidification range of a general purpose solder must necessarily be a compromise between the two extremes.

The wetting quality of a solder, or its ability to spread on the base metal, is a property, which in conjunction with the liquidus temperature largely determines the ease of the soldering operation. The mechanism of wetting is essentially one of surface tension, which in turn is dependent upon the difference between the cohesive forces within the solder itself and the adhesive forces between the solder and the base metal. In order to have good wetting properties, the adhesive forces must greatly exceed the cohesive forces.

The forces involved in capillarity are comparable to those which occur in the wetting of a flat surface, except that in the former adhesion is acting against gravity. In addition, the distance between the components being soldered plays an important role, as capillary action varies inversely with the distance. Experimental work by other investigators has shown that the soundest soldered joints are obtained with clearances ranging from 0.003 to 0.005 inch. This indicates the importance of the wetting and capillary qualities of the solder, since these two properties are responsible for penetration into such small openings.

The tensile strength of solder itself bears little relation to the strength of a soldered joint. The important factors are the thickness of the solder layer and the nature of the bond between the solder and the components. Dirt, oxides, flux and excess intermetallic compounds all tend to break the continuity of the solder bond and lessen the shear strength of a joint. The initial composition of the solder and the base metal, the temperature and duration of application, the lapse of time before testing, as well as the thickness of the solder layer, have a marked effect on the ultimate strength of a soldered joint. Since these factors also govern the formation of new phases (solid solutions or compounds) by the process of diffusion, it is evident that the effects of diffusion cannot be disregarded when considering all factors that determine the strength of a soldered joint. However, owing to the time involved, direct measurements on the actual effects of diffusion products on joint shear or tear strength were not made in this investigation. A number of investigators have treated the problem quite thoroughly.[1,3,4.]

The appearance of a solder as to whether it is bright or dull may not indicate a serious change of physical properties. However, poor appearance may have a rather important effect on the mechanic who is accustomed to working with the high tin solders, because too much emphases might be placed on the correlation between brightness and solderability. A comparison of the appearance of the solder as cast, and after a period of storing, offers a fairly good criterion on which to predict the amount of oxidation to be expected during storage.

Properties of Solders

Many factors regarding the properties of solders can be determined from an examination of the equilibrium diagram shown on the following page.[7] The eutectic mixture contains 61.9% Sn, and 38.1% Pb. It freezes at 183.3°C. while pure lead freezes at 327°C. and pure tin freezes at 232°C. Except for the eutectic alloy, solidification occurs over a range of temperature. Through this range of temperature these alloys can be readily worked since they are in a semi-liquid condition.

Practically all commercial solders fall within the range of 16 to 61.9 percent tin. Therefore, the solidified

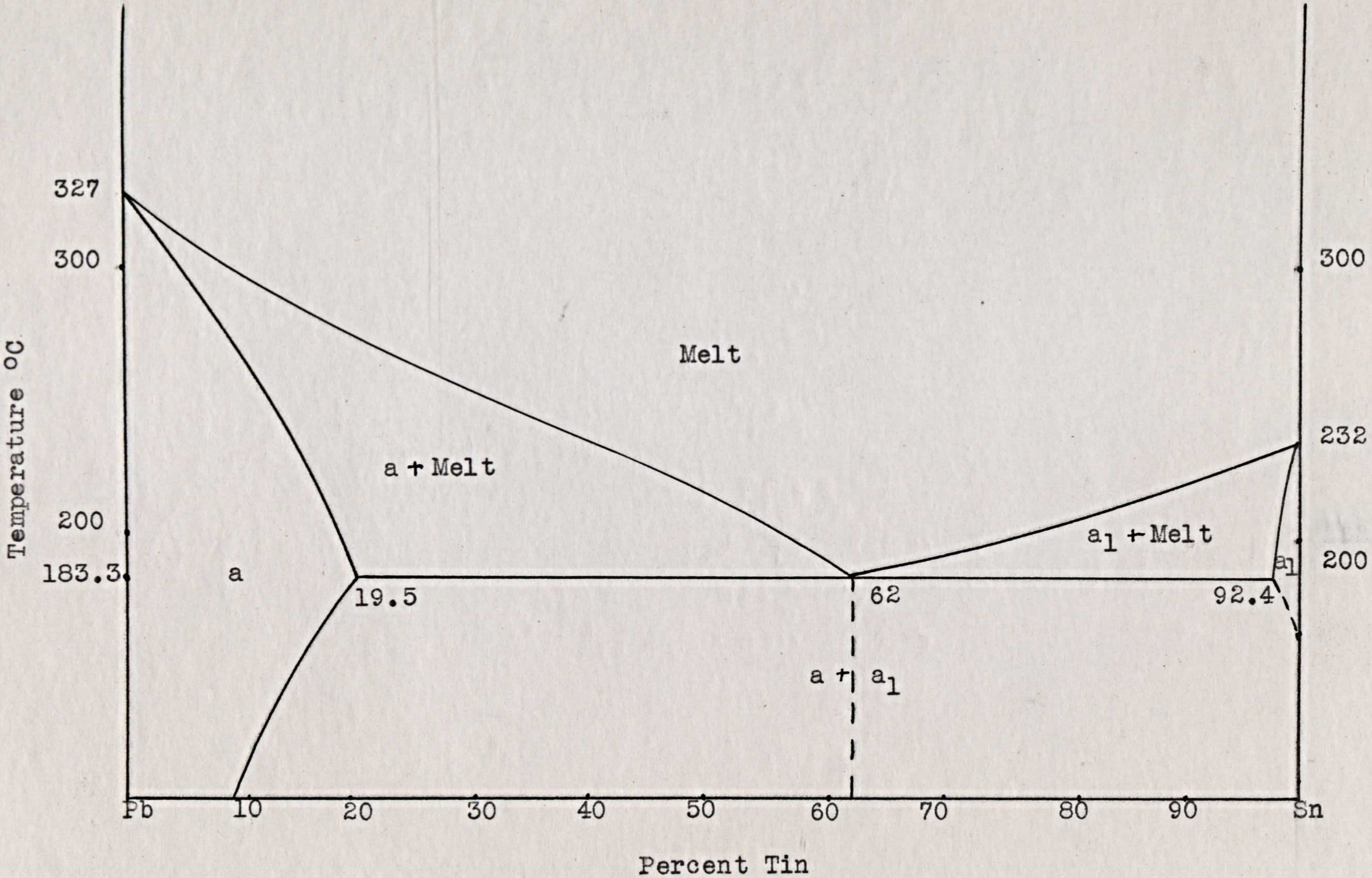


FIGURE 1

LEAD - TIN EQUILIBRIUM DIAGRAM

solders consist of crystals of alpha surrounded by eutectic. As the tin content increases within this range, the relative proportion of eutectic to alpha is also increased. Upon approaching the eutectic composition, the freezing range becomes correspondingly smaller. As is seen from the diagram, the solubility of tin in lead is about nine percent at $100^{\circ}C.$, but lead is only very slightly soluble in tin.

<u>Fluxes</u> [6]

It was ascertained in early investigations that the standard fluxing agents, as used by the soldering trade, were not suitable for utilization with the higher-melting substitute solders. The higher temperatures required caused this difficulty. The flux would either vaporize or carbonize before the solder reached its flow point, thereby losing all the benefits of a fluxing medium. The chief purposes of a flux are : (1) to protect the metal against oxidation, (2) to remove dirt and oxides from the metal, (3) to increase the wettability of the metal by the solder and thereby increase the flowing characteristics of the solder, and (4) to make better and stronger soldering possible. It has been a recognized fact in the soldering trade that tin is an excellent wetting agent for other metals. It is obvious that solder cannot join two pieces of metal unless it wets those pieces. Pre-tinning for soldering, and especially for joining bearing backs and lining metals, has long been considered a good technique. It has also been realized that the lower the tin content of a solder the more important the pre-tinning and fluxing becomes. A solder low in tin makes it essential that the surfaces to be soldered be carefully prepared. This may also be stated in another way, that is, the more carefully the surfaces to be soldered are prepared, the lower the tin content may become.

Statement of Problem

The primary purpose of this investigation was to modify the flow and wetting properties of some solders which have been previously modified in other respects, but which still do not meet the requirements for flow and wetting power.

The secondary purpose was to carry out the aforementioned experimentations without seriously affecting other properties such as tensile strength, solidus and liquidus temperatures.

EXPERIMENTATION

Proceedure

Five solders of the following composition were made up in three-hundred gram portions.

TABLE I [5]

PERCENTAGE COMPOSITION OF BASE SOLDERS

Alloy Number	Tin	Lead	Antimony	Silver
1-1	15%	85%	-	-
2-1	-	99%	-	1%
3-1	20%	79.25%	-	.75%
4-1	20%	77.25%	1.5%	1.25%
5-(60-40)	40%	60%	-	-

The 60-40 solder was used throughout all tests as a reference solder. The other four solders were divided into three parts and each part was weighed. To a sample of each of the four solders, 0.075 gram of copper **was** added. To another portion of the four base-solders, 0.50 gram of antimony was added. This produced thirteen solders of different compositions, eight of which were the solders that were tested as modifications of the base solders. The percentage composition of these eight new solders is listed in Table II.

TABLE II

PERCENTAGE COMPOSITION OF SOLDERS

Solder	Lead	Silver	Tin	Copper	Antimony
1-2	83.50	-	14.80	-	1.70
1-3	84.80	-	15.00	0.20	-
2-2	95.30	2.35	-	-	2.35
2-3	98.65	1.00	-	0.35	-
3-2	77.40	0.65	19.45	-	2.50
3-3	79.10	0.75	20.00	0.15	-
4-2	75.90	1.25	19.65	-	3.20
4-3	77.00	1.25	19.95	0.18	1.62

All solders were melted in fire-clay crucibles, using charcoal as a protective covering. Melting was accomplished by means of a Fisher burner.

From each melt, several samples were taken by means of a glass tube to which was attached a suction bulb. These samples were drawn into the glass tube and had the same cross-sectional area, 0.317 centimeters. The glass tubes were immediately dipped into cold water, which caused the glass to crack and allow the sample to be recovered.

TESTS

Hand Bend Tests

Samples of the same cross-sectional area, 0.317 centimeters, were used in these tests. A solder bar was considered to be very ductile if it could stand a 180 degree bend without cracking; ductile if able to withstand a 180 degree bend with slight cracking; slightly ductile if the specimen fractured between 90 degrees and 180 degrees; brittle if the fracture occured between 45 degrees and 90 degrees; and very brittle if the specimen fractured at an angle less than 45 degrees.

The results of these tests are listed in Table III below.

TABLE III

HANDBEND TESTS

Alloy Number	Degree of Bend	Bend Test
1-1	180	Very ductile
1-2	180	Very ductile
1-3	180	Very ductile
2-1	180	Very ductile
2-2	180	Very ductile
2-3	180	Very ductile
3-1	180	Ductile
3-2	60	Brittle
3-3	180	Ductile
4-1	120	Slightly ductile
4-2	100	Slightly ductile
4-3	135	Slightly ductile
Ref. (60-40)	180	Very ductile

Appearance Observations

The appearance of the top and bottom of the alloy bars was noted shortly after casting and also after a period of three months had elapsed.

The results of these observations are recorded in Table IV.

TABLE IV

APPEARANCE OBSERVATIONS

Alloy Number	Appearance After Casting	Appearance After 3 Months
1-1	Shiny silver	Dull silver
1-2	Shiny silver	Dull silver
1-3	Shiny silver	Dull silver
2-1	Leadish	Dull lead
2-2	Leadish	Dull lead
2-3	Leadish	Dull lead
3-1	Bright silvery	Unchanged
3-2	Silvery	Dull silver
3-3	Silvery	Dull silver
4-1	Silvery	Silvery gray
4-2	Shiny silver	Unchanged
4-3	Smooth, bright silver	Silvery gray
Ref. (60-40)	Shiny silver	Unchanged

Tinning Properties

Tinning properties were determined mainly by the readiness with which the solder adherred to a clean iron plate. A solder was said to have good tinning properties if it wet the iron readily. The soldering iron was filed and cleaned with eutectic zinc-ammonium flux before each solder was tested. The results of these tests are reported in Table V.

TABLE V

TINNING PROPERTIES

Alloy Number	Tinning Property
1-1	Fair
1-2	Fair
1-3	Fair
2-1	Fair
2-2	Fair
2-3	Fair
3-1	Good
3-2	Very good
3-3	Very good
4-1	Very good
4-2	Very good
4-3	Very good
Ref. (60-40)	Very good

Spread Test

The spread test was used as a measure of the wettability of a solder on base metal. Spreading tests were made on copper, brass, and iron. The purpose of the test was to determine the comparitive wettability of the various solders on the three base metals. Spread tests were made on plates of copper 1/16 inch thick, brass plates 1/16 inch thick, and iron plates 1/8 inch thick. The reason for this variance is that these were the only sizes available.

The volume of the drops used in the spread tests was 0.025 cubic centimeters. These volumes were calculated on the basis of the specific gravity of the metals involved and their percentage composition.

A Fisher burner was used to supply the heat. To assure a fairly accurate measurement of the temperature a thermocouple was attached to the plate being tested. All wetting tests were of 15 seconds duration and were carried on at a temperature about 60°C. above the liquidus temperature of the solder.

The eutectic flux containing 71 parts water, 19 parts zinc chloride and 10 parts ammonium chloride was used to clean the surface of the plates. In addition to the flux, a weak hydrochloric acid was necessary to clean the iron.

Results are shown in Table VI and Figure II.

TABLE VI

SPREAD TESTS
(0.025 cubic centimeter drops)

Alloy Number	Wetting (per square inch)		
	Copper	Brass	Iron
1-1	0.14	0.18	0.19
1-2	-	-	-
1-3	0.13	0.09	0.14
2-1	0.12	0.15	0.16
2-2	0.11	0.13	0.13
2-3	0.20	0.17	0.20
3-1	0.19	0.11	0.20
3-2	0.11	0.10	0.18
3-3	0.10	0.19	0.15
4-1	0.19	0.14	0.25
4-2	0.18	0.09	0.27
4-3	0.18	0.06	0.24
Ref. (60-40)	0.22	0.19	0.29

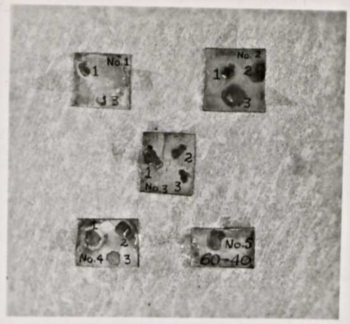


FIGURE II

SPREAD TEST ON BRASS

The effects of copper and antimony were detrimental on most of the solders as may be seen from Table VI. Solders of the number 1 series, that is 1-1, 1-2, and 1-3, were eliminated from further testing since the wettability of the base solder was not appreciably increased by the copper addition. Solders of the number 4 series were eliminated because neither addition had any effect on the base solder. Only solders of series 2 and 3 were subjected to further testing. Although the wettability was not increased, except for the 2-3 solder, it was intended to study the effects of the additions on the other properties.

Thermal Arrests

Thermal arrests were determined on solders 2-2, 2-3, 3-2 and 3-3 by means of the apparatus shown in Figure III. For a basis of comparison the thermal arrest points of the 60-40 reference solder were also determined. The corresponding temperature points for the base solders, 2-1 and 3-1, were obtained from the literature.[5]

The thermal arrest points are tabulated in Table VII and the cooling curves for the various solders are shown in Figures 4,5,6,7 and 8. The data from which these curves were plotted are tabulated in Table VIII.

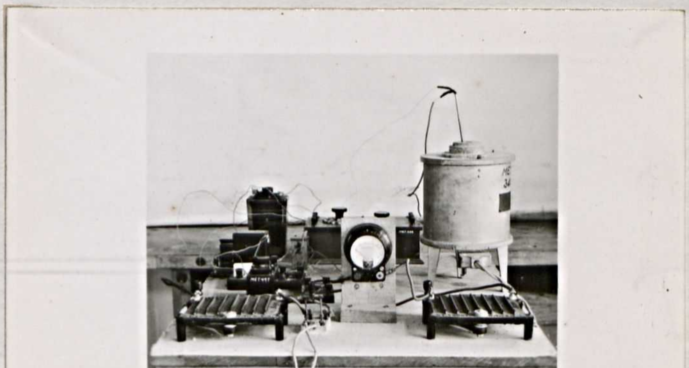


FIGURE III

APPARATUS USED FOR COOLING CURVES

Samples of 100 grams were melted in a controlled electric furnace, the sample being covered with charcoal to prevent oxidation. A thirty guage iron-constantan thermocouple was inserted into the melt and millivolt readings were taken every 15 seconds.

TABLE VII

SOLIDIFICATION

Solder	Liquidus	Solidus	Range
60-40	450°F	350°F	100°F
2-1	604°F	576°F	28°F
2-2	590°F	495°F	95°F
2-3	615°F	525°F	90°F
3-1	523°F	371°F	152°F
3-2	530°F	400°F	130°F
3-3	575°F	410°F	165°F

Upon examination of Table VII the following conclusions may be drawn:

1. (Solder 2-2)-- The addition of Antimony to the base solder depresses the liquidus temperature, depresses the solidus temperature and increases the solidification range.

2. (Solder 2-3)-- The addition of Copper to the base solder 2-1 raises the liquidus temperature, depresses the solidus temperature and increases the solidification range.

3. (Solder 3-2)-- The addition of Antimony to the

base solder 3-1, raises the solidus temperature, raises the liquidus temperature slightly and decreases the solidification range slightly.

4. (Solder 3-3)-- The addition of Copper to the base solder 3-1 raises the liquidus temperature, depresses the solidus temperature and increases the solidification range slightly.

TABLE VIII

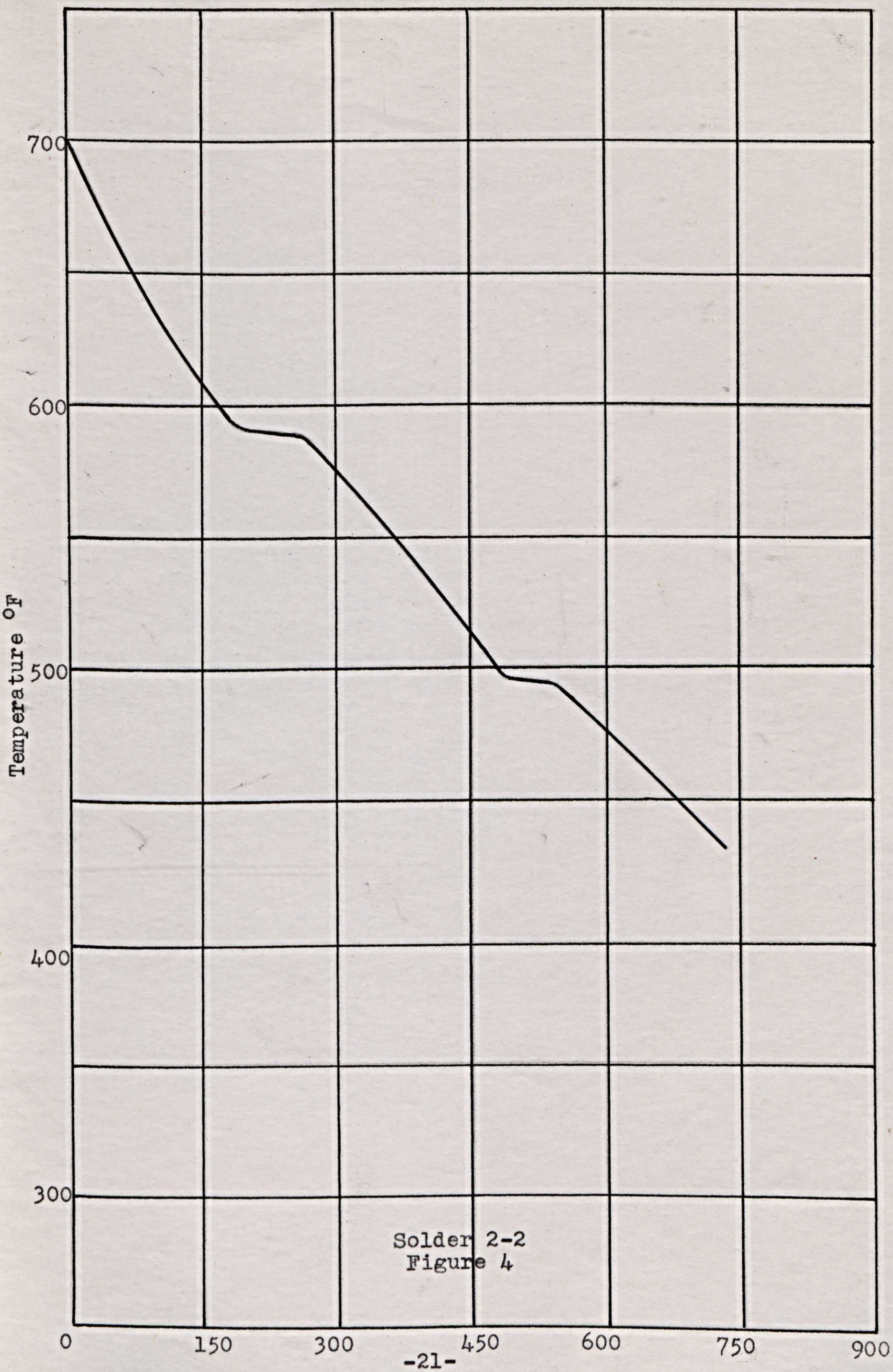
COOLING CURVE DATA

Time secs.	60-40 °F	2-2 °F	2-3 °F	3-2 °F	3-3 °F
0	500	700	700	700	700
15	494	690	690	693	689
30	490	680	682	685	678
45	485	671	673	678	668
60	481	660	665	670	659
75	476	652	658	661	650
90	470	643	650	653	640
105	463	632	643	646	631
120	458	625	656	640	623
135	453	619	650	632	615
150	451	610	644	625	607
165	450	602	637	618	600
180	450	595	630	610	591
195	449	592	622	601	583
210	449	590	616	592	578
225	440	590	616	588	576
240	441	589	615	580	575
255	437	588	615	576	574
270	433	585	615	574	574
285	428	580	614	562	570
300	424	574	610	555	565
315	420	568	601	543	558
330	417	561	592	539	550
345	414	556	583	536	545
360	410	550	572	533	540
375	406	542	565	532	532
390	403	534	554	532	521
405	400	527	543	530	515
420	396	520	534	529	506
435	391	515	529	523	500

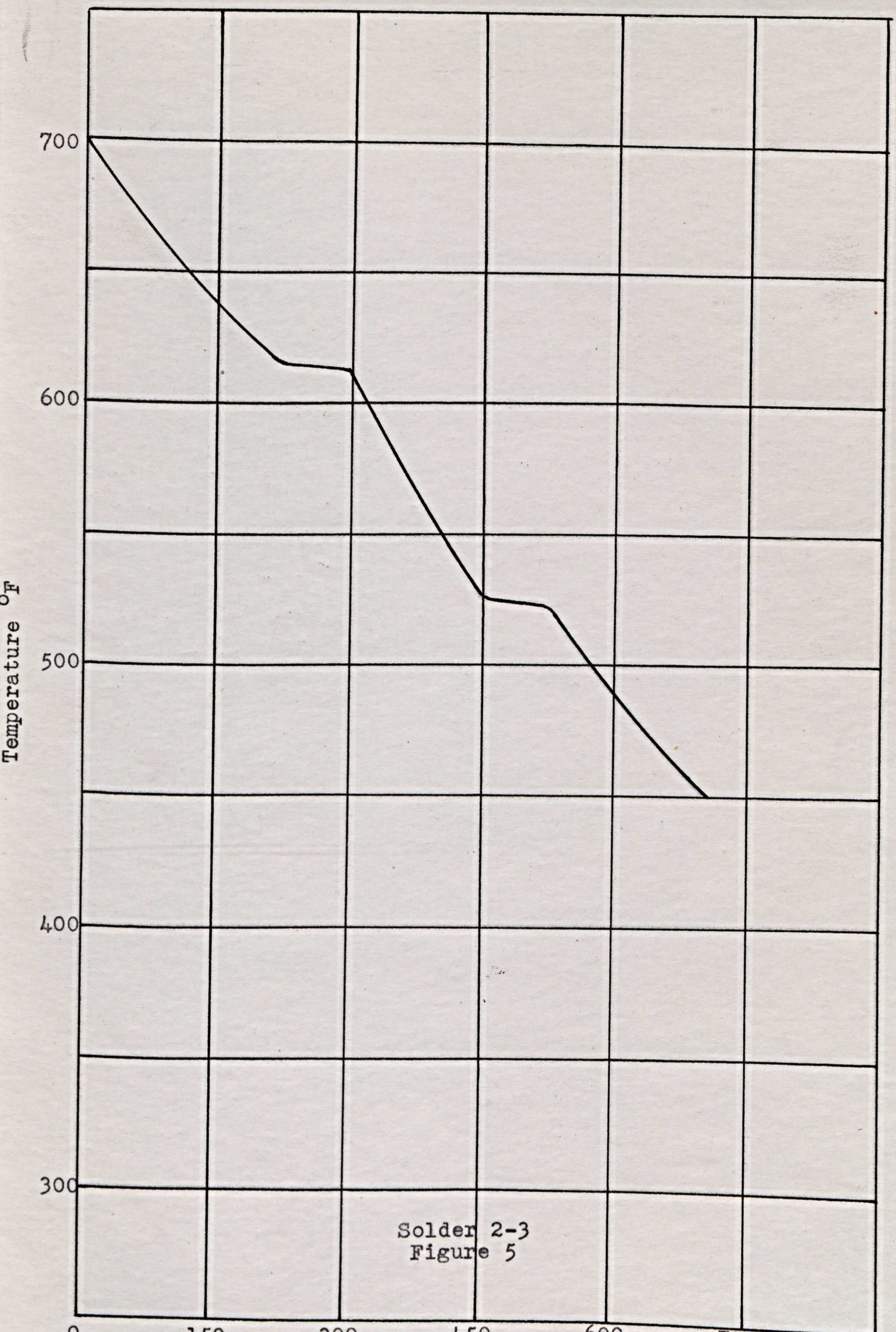
TABLE VIII

COOLING CURVE DATA

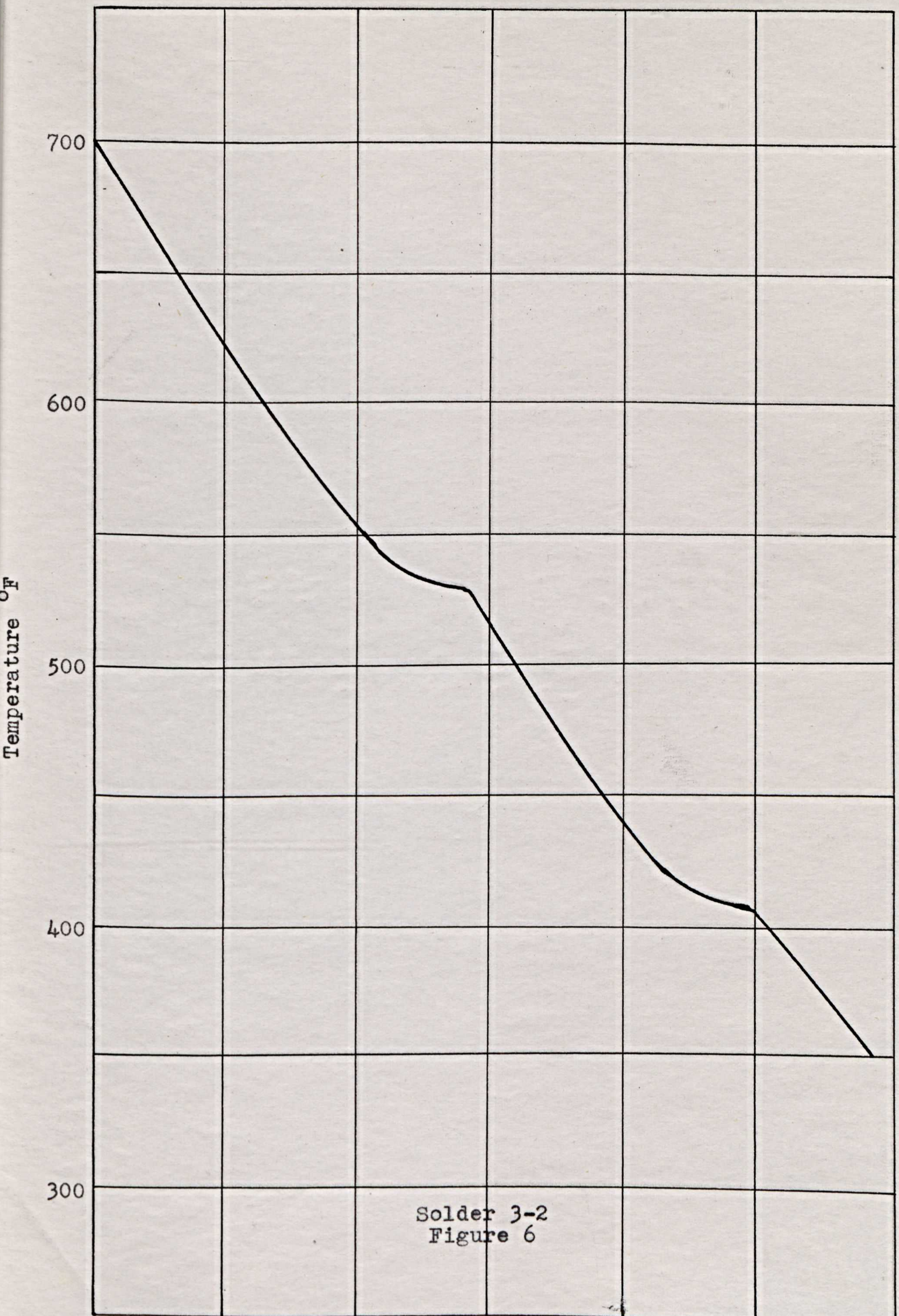
Time secs.	60-40 °F	2-2 °F	2-3 °F	3-2 °F	3-3 °F
450	387	509	527	518	493
465	382	503	526	510	485
480	378	497	525	501	479
495	375	497	524	492	472
510	372	495	524	485	465
525	368	494	522	477	458
540	363	494	516	470	450
555	360	490	510	462	441
570	356	484	501	454	432
585	353	480	493	448	425
600	351	476	486	440	419
615	351	470	480	431	415
630	350	465	475	425	412
645	349	461	470	420	410
660	349	456	464	415	409
675	348	450	458	413	409
690	346	445	450	410	407
705	343			409	402
720	340			409	395
735	336			408	390
750	332			404	385
765	328			400	380
780	323			395	374
795	319			389	369
810	314			382	362
825	309			375	356
340	303			370	350
855	397			363	
870	291			357	
885	285			350	



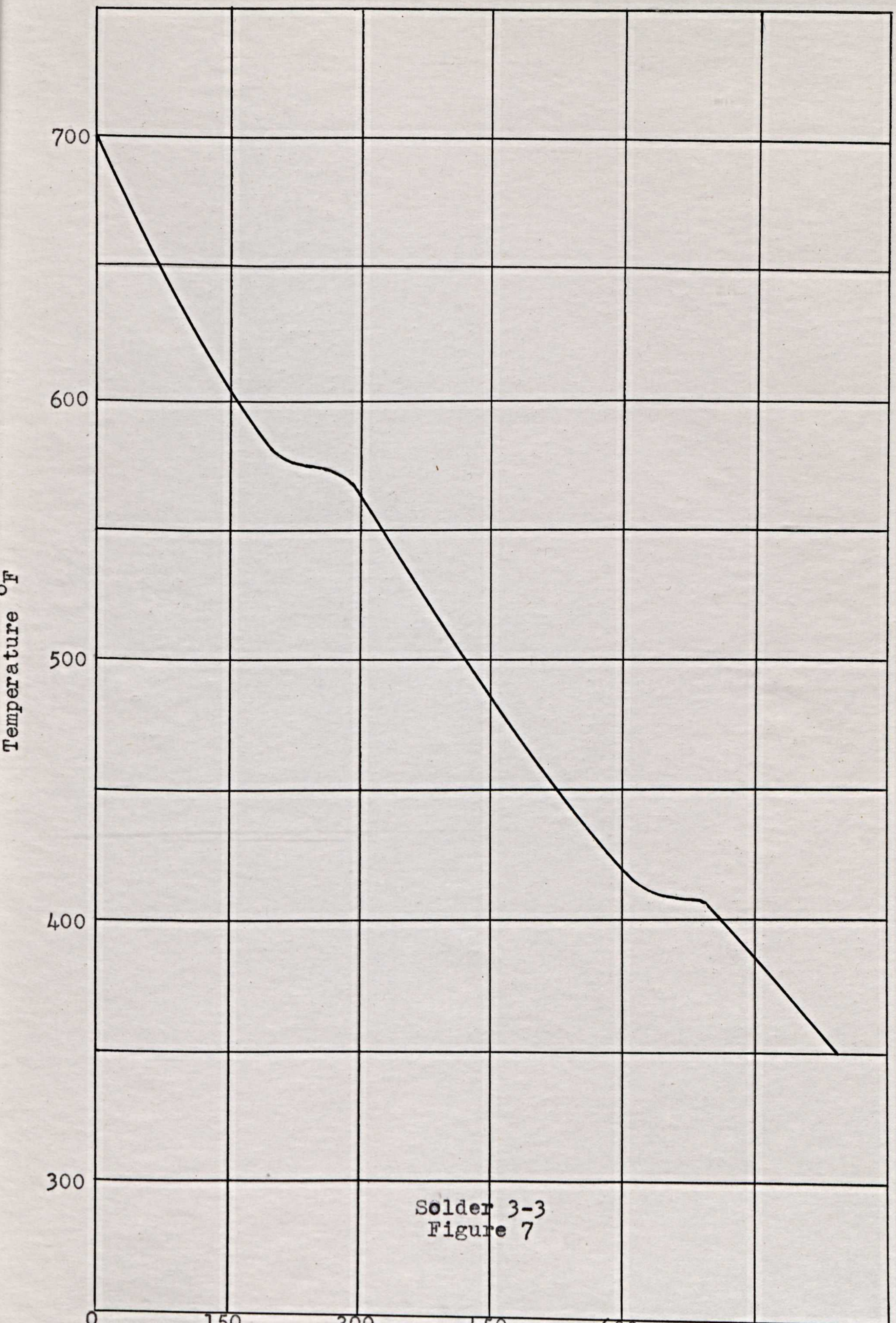
Solder 2-2
Figure 4



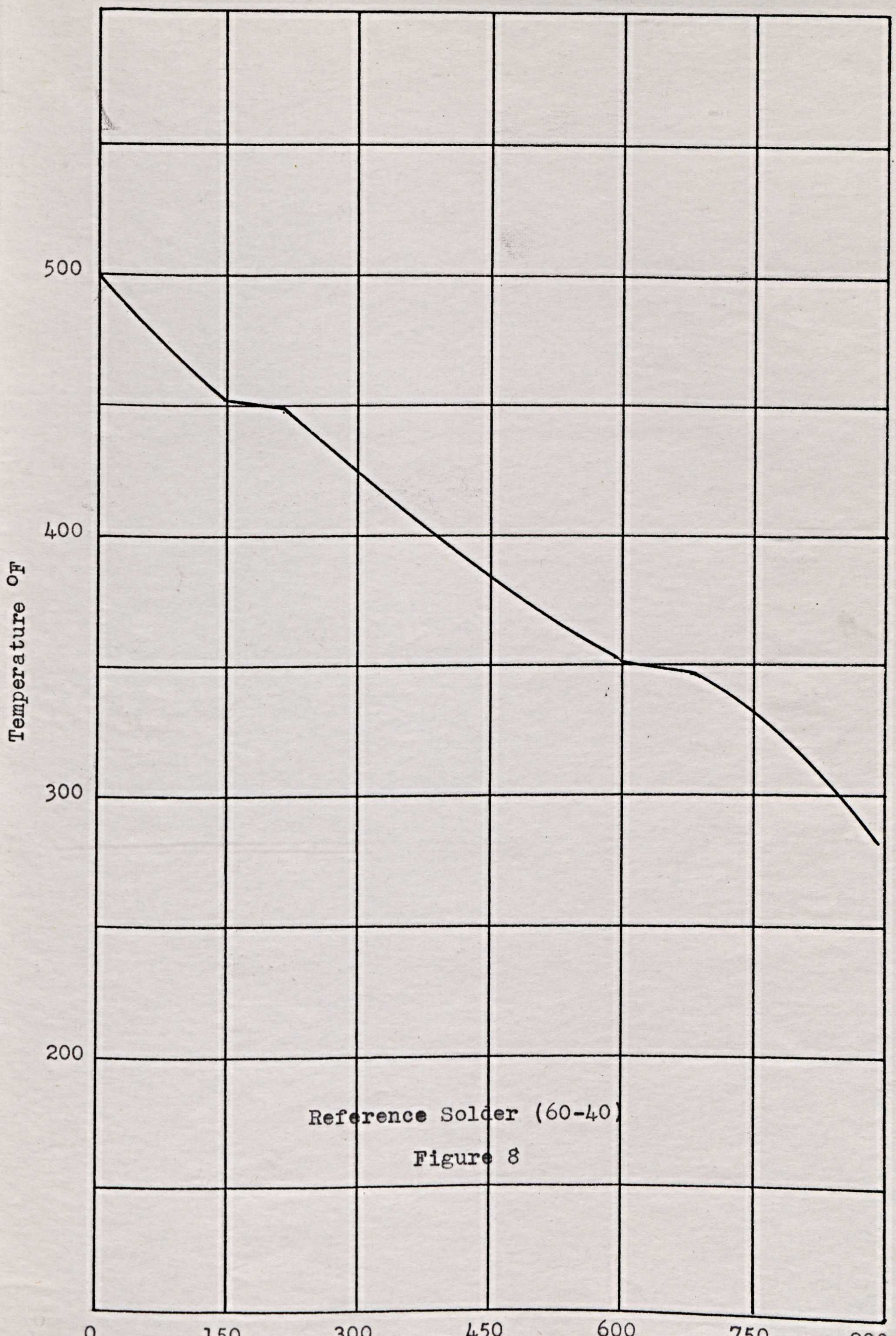
Solder 2-3
Figure 5



Solder 3-2
Figure 6



Solder 3-3
Figure 7



Reference Solder (60-40)

Figure 8

Tension Tests

Tensile strength tests were run on the solders after measurements of the area of lap and solder film thickness were made. A single lap joint was used in these tests and the constituents soldered consisted of two iron plates. Torch soldering was used. A single lap joint was used in this investigation for the following reasons: (1) the simple lap is representative of a large number of joints in use; (2) the sheet metal was readily available, whereas, materials for butt and sleeve joints were not; and (3) the facilities at hand made the use of simple lap joints relatively convenient.

The specimens were pulled apart in a 100,000 pound tensile testing machine on which the load was measured by a system of levers and counterpoises, Figure IX. The speed of the crosshead was 0.06 inches per minute for all tests. Wedge grips were used. The results of this test are indicated in Table IX.

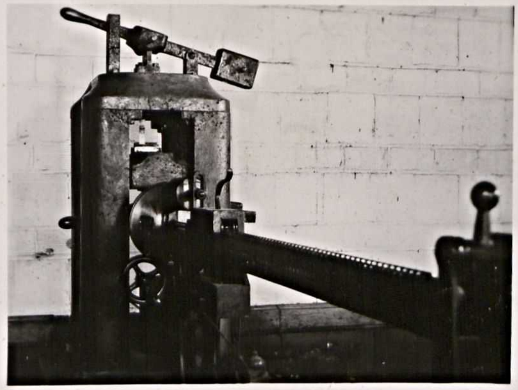


FIGURE IX

TENSILE MACHINE

TABLE IX

TENSILE TEST RESULTS
Area of lap - 2 square inches
Solder film thickness - 0.003 inches

Solder	Readings	Shear (psi)
Ref. (60-40)	6800	3400
2-1	4950	2475
2-2	5070	2535
2-3	6180	3090
3-1	5860	2930
3-2	6010	3005
3-3	6450	3225

Summation of Tests

The various tests just described are believed to be adequate for the purpose for which they were intended.

The test for capillary rise of solder in the joint has been eliminated from the above investigation, not because of its unimportance but because other investigators have found it not too troublesome. Previous investigators have used different types of quantitive tests to study the properties discussed in this paper, and it is realized that other properties are of equal, or greater importance, under certain conditions of temperature and stress.

CONCLUSIONS

1. The effects of antimony additions to the base solders were for the most part detrimental. Antimony forms a compound with tin which causes brittleness. This compound is light and rises to the solder surface impairing the tinning and flowing characteristics of the solder. It is therefore recommended that the use of the base solders containing antimony additions be avoided.

2. With the exception of solder (2-3) it was found that the addition of copper produced no appreciable beneficial effects.

3. Copper increased the wetting power of the base solder (2-1) appreciably. This particular resultant solder is indicated in the text as (2-3).

4. It was found that the presence of copper in the base solder (2-1) raised the liquidus and solidus temperatures and increased the solidification range slightly.

5. The addition of copper to the base solder (2-1) impaired some of the physical properties, but not to an appreciable extent.

6. The qualities desired of a solder are dependent upon its particular application. Solder (2-3) is recommended for specific use where wetting power may be of more importance than liquidus temperature and solidification

range. However, in cases where this quality is not of major importance solder (2-1) is suggested.

7. Solder (2-3) may be used in bath operations and dipping pots, but is not recommended for hand operation.

RECOMMENDATIONS FOR FUTURE STUDY

1. Since solder (2-3) has no tin, further experimentation along the same lines as the previous tests should be made to determine more accurately all of its properties.

2. The four base solders should be tested, using the same previous tests, but additions of other elements should be made.

3. The eutectic zinc chloride, ammonium chloride and water flux is more satisfactory than the common zinc chloride and water flux, but it is still not quite satisfactory. A study of fluxes might be helpful in producing a new and better flux.

4. Since most solders are made from secondary metals, a study of the maximum amount of impurities in the four basic solders that will not seriously affect the properties is recommended.

5. A detailed study of the flowing and tinning qualities of solder (2-3) by addition of other elements is recommended.

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