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MSM
HISTORICAL
COLLECTION

THE TRANSFORMATION OF THE ALUMINUM-ZINC
EUTECTOID ALLOY AT SUBCRITICAL
TEMPERATURES

BY
THOMAS JOSEPH BURKE

A
THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

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MSM
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COLLECTION



Approved by -

Daniel S. Eppelsheimer

Daniel S. Eppelsheimer
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INTRODUCTION

Interest in the mechanism of the austenite eutectoid transformation in iron-carbon alloys, especially as produced by the isothermal sub-critical techniques introduced by Davenport and Bain⁽¹⁾, has resulted in the application of

(1) Davenport, E. S., and Bain, E. C., Trans. AIME, Vol. 90, p. 117, 1930.

similar heat treatment studies to the eutectoid transformations in other alloy systems. The study of the eutectoid transformation is of both fundamental and industrial interest because past experience has shown that these studies yielded much information concerning the nature and mechanism of the changes in eutectoid alloys during the decomposition of the phase stable at high temperatures and has also contributed much toward the development of new properties to be attained by heat treatment methods never before attempted.

The desire of the author to know more about the exact nature of eutectoid transformations, in general, and to study, in particular, the transformation in a system which had heretofore been only partially investigated has led to choice of this research topic. Therefore, the object of this investigation is to attempt to determine the rate of transformation of the aluminum - zinc eutectoid alloy

(79.0 % zinc) at several subcritical temperatures.

A number of more or less reliable methods have been used for the study of the rate of transformation of austenite at subcritical temperatures. The author began this research with the intention of utilizing the technique of Davenport and Bain in which the progress of transformation is followed by metallographic examination. However, the method was discarded as impractical because of the nature of the transformation.

In this particular eutectoid alloy, the decomposition of the solid solution which is stable at high temperatures is manifested by the evolution of heat. The author has attempted to establish the onset and completion of transformation by measurement of this heat evolution against time and, from this data, to construct a Time-Temperature-Transformation curve for the alloy.

TABLE I
BINARY ALLOY SYSTEMS CONTAINING EUTECTOIDS

<u>Number</u>	<u>System</u>	<u>Temperature °C</u>	<u>Wt. Percent Comp</u>
1.	Al-Ag	610	8.0 Al
2.	Ag-Cd	443	48.5 Cd
3.	Ag-Zn	240	36.0 Zn
4.	Al-Au	424	96.9 Au
5.	Al-Cu	537	88.2 Cu
6.	Al-Fe	1080	57.5 Fe
7.	Al-Mn	750	72.5 Mn
8.	Al-Zn	270	79.0 Zn
9.	As-Fe	800	53.0 Fe
10.	Au-Cd	370	49.2 Cd
11.	Au-Cr	1022	14.0 Cr
12.	Au-Fe	840	95.0 Fe
13.	Au-Mn	570	83.0 Mn
14.	Au-Ni		90.0 Ni
15.	Au-Zn	a. 404 b. 250 c. 150 d. 150 e. 150 f. 416	14.0 Zn 7.0 " 14.0 " 46.0 " 55.0 " 62.0 "
16.	B-Ni		
17.	Be-Cu	576	6.0 Be
18.	C-Co	1300	2.4 C
19.	Fe-C	721	0.86 C
20.	C-Ni	1315	2.2 C
21.	Cd-Li	80	14.5 Li

22.	Cd-Sn	128	95.0	Sn
23.	Co-Cr	1271	4.9	Cr
24.	Co-Mo	1340	71.0	Mo
25.	Co-S	788	28.0	S
26.	Cu-Fe	833	96.0	Fe
27.	Cu-Ga	620	25.7	Ga
28.	Cu-In	574	32.0	In
29.	Cu-Sb	420	42.0	Sb
30.	Cu-Si	710	9.0	Si
31.	Cu-Sn	a. 520 b. 570	26.8 35.0	Sn Sn
32.	Cu-Zn	555	74.0	Zn
33.	Fe-Mn	a. 740 b. 1028	63.0 72.0	Mn Mn
34.	Fe-Mo	1180	63.0	Mo
35.	Fe-N	591	2.35	N
36.	Fe-O	a. 1370 b. 570	23.0 23.5	O O
37.	Fe-Zn?	623	25.0	Zn
38.	Li-Zn	a. 161 b. 168 c. 65	62.0 73.0 85.0	Zn " "
39.	Mn-Sb	677	6.5	Sb
40.	Ni-S	a. 535 b. 400	25.5 26.0	S S
41.	Ni-Zn	640	58.0	Zn
42.	Pb-Tl	140	94.0	Tl
43.	Pl-Sb	530	40.5	Sb
44.	S-Se	75	35.0	Se
45.	Sn-Tl?	144	85.0	Tl

TABLE II
BINARY ALLOY SYSTEMS CHOSEN FOR PRELIMINARY
INVESTIGATION

System	Eutectoid Composition (Weight Percent)	Eutectoid Temperature (Degrees Centigrade)
Ag-Al	8.0 Al	610
Ag-Cd	48.5 Cd	430
Ag-Zn	36.0 Zn	240
Al-Mn	72.5 Mn	750
Al-Zn	79.0 Zn	275
Be-Cu	6.0 Be	576
Cd-Sn	95.0 Sn	128
Su-Sb	42.0 Sb	420
Cu-Sn	26.8 Sn	520

PRELIMINARY INVESTIGATION

No comprehensive isothermal study of eutectoid transformation has been accomplished on binary alloy systems other than the iron-carbon and the copper-aluminum. At the outset of this investigation, a survey was made of all known binary alloy equilibrium diagrams which contained the eutectoid field. M. Hansen's ⁽²⁾ collection of binary

(2) Hansen, M., Der Aufbau der Zweistofflegierungen, Springer, 1936.

equilibrium diagrams was assumed to be authoritative on this subject. The survey showed forty-five such binary systems. (See Table I.) Of the forty-five systems, nine were chosen for preliminary investigation. These are listed in Table II. The general plan was to choose for an intensive study of the eutectoid transformation at sub-critical temperatures, the alloy best suited to available laboratory facilities.

The system silver-aluminum was disregarded because it was demonstrated by Hume-Rothery ⁽³⁾ that the beta phase

(3) Hume-Rothery, W., J. Inst. Metals, Vol. 66, p. 209, 1940

does not undergo eutectoid transformation as previously reported, but that on cooling it changes into a single hexagonal close packed phase.

The silver-zinc alloy was discarded because the equilibrium diagram had been re-investigated since the work published by Hansen⁽⁴⁾. It was found that an alloy

(4) Hansen, *op. cit.*, p. 6

of eutectoid composition transformed into a single phase below the eutectoid temperature.

The systems aluminum-manganese, beryllium-copper, copper-antimony, copper-tin, silver-aluminum and cadmium-tin were later discarded for various reasons on advice of Eppelsheimer⁽⁵⁾ and the aluminum-zinc eutectoid alloy

(5) Eppelsheimer, D. S., Oral Discussion of Thesis Subject, Feb. 9, 1950.

was chosen for extensive investigation by the author.

REVIEW OF LITERATURETHE EUTECTOID TRANSFORMATION

Davenport and Bain⁽⁴⁾ opened a new field for investi-

(6) Davenport and Bain, op. cit., p. 1

gation of eutectoid transformations when they established a Time-Temperature-Transformation diagram for the iron-carbon eutectoid alloy in 1930. Using the interrupted quenching method and metallographic examination to evaluate the amount of transformation which had taken place after a given length of time at a given temperature, their procedure was as follows: Many samples of the alloy to be investigated were heat-treated in a batch until the material was completely austenitic. Then the batch was quenched to some temperature below the eutectoid temperature, and transformation was allowed to proceed isothermally. In order to evaluate the amount of transformation in a given length of time individual samples from the batch were again quenched at intervals, from this temperature to the temperature of ice-brine. It is known that austenite, if cooled in excess of some particular critical cooling rate, will not all be retained but will transform to martensite plus some small amount of retained austenite; and also that, if austenite is allowed to cool at a rate less than the critical cooling

rate, the austenite will transform to pearlite, or to bainite. Davenport and Bain evaluated the amount of austenite transformed at high temperatures into pearlite or bainite on a percentage basis of the field observed metallographically. From this evaluation they established their Time-Temperature-Transformation curve.

Smith and Lindlief⁽⁷⁾, in their prize winning paper,

(7) Smith, C. S. and Lindlief, W. E., Trans. AIME, Vol. 133, p. 204, 1933.

utilized essentially the same method of study for the decomposition of the beta copper-aluminum eutectoid alloy and also refined their measurements and conclusions by means of electrical resistivity measurements on the alloy during isothermal transformation. They found that the mechanism of the decomposition of the alloy was much the same as for the iron-carbon alloys, that a pearlitic structure was evident and that rapidly quenched alloys yielded an acicular product very similar to the martensite of steels. They established a Time-Temperature-Transformation curve for this alloy, as did Davenport and Bain for the steel.

In 1934, Wasserman⁽⁸⁾ attempted to compile some of the

(8) Wasserman, G., Transformation in Eutectoid Alloys, Zeitschrift fur Metallkunde, Vol. 26, p. 256, 1934.

various properties manifested by alloys eutectoid in nature. He used the iron-carbon and copper-aluminum eutectoid decompositions as examples and compared crystal structures, formation of stable and unstable phases, similarities of microstructures, etc. in an attempt to make certain predictions concerning alloy systems not yet investigated.

Since the original work of Davenport and Bain in 1930, an extensive number of investigations have been done on the isothermal transformation of steels. Subsequent to the study by Smith and Lindlief⁽⁹⁾, only one extension of their

(9) Smith and Lindlief, op. cit., p. 9

work has appeared, that of Mack⁽¹⁰⁾ in 1947; yet only one

(10) Mack, D. J., "The Isothermal Transformation of a Eutectoid Aluminum Bronze", AIME T.P. 2242, Sept. 1947.

comprehensive study of isothermally transformed eutectoids analagous to steel has appeared, that of Hibbard, Eichelman and Saunders⁽¹¹⁾ on the kappa eutectoid transformation in

(11) Hibbard, W. R., Eichelman, G. H. and Saunders, W. P. "The Kappa Eutectoid Transformation in the Copper-Silicon System", AIME T.P. No. 2441, Sept. 1948.

the copper-silicon system. It was found in this research that the eutectoid transformation at subcritical tempera-

tures was extremely sluggish and that the microstructures, in general, bore no resemblance to the usual eutectoid type structures.

Although the work cited above is the only research done with the object of establishing transformation rate curves, many valuable contributions have been made toward a better understanding of the structures developed in such systems. Important papers have been published by Kurdjumow, Gridnew and their co-workers (12-24), and Obinata (25,26), Greninger (27,28) and others (29,30,31).

(12) Ageew, H. W. and Kurdjumow, Metallurg, Vol. 7, pp. 3-21, 1932.

(13) Kurdjumow, G. and Stelletszkaya, T., Metallwirtschaft, Vol. 13, p. 304, 1934.

(14) Gridnew, V. and Kurdjumow, G., Metallwirtschaft, Vol. 15, (10), pp. 229-31, (11), pp. 256-9, 1936.

(15) Gawranek, V., Kaminsky, E. and Kurdjumow, G., Metallwirtschaft, Vol. 15, (16), pp. 370-1, 1936.

(16) Gridnew, V. and Kurdjumow, G., Metallwirtschaft, Vol. 15, (19), p. 437, 1936.

(17) Gridnew, V. and Kurdjow, G., Zhur. Tehnich. Fiziki, Vol. 6 (5), pp. 775-80, 1936.

(18) Kurdjumow, G., Izvestia Akademii Nauk, USSR, (Chim), Vol. 2, pp. 271-84, 1936.

(19) Gridnew, V. and Kurdjumow, G., Zhur. Tehnich. Fiziki, Vol. 7, (22) 2090-2102, 1937.

(20) Gridnew, V., Metallurg., Vol. 4, pp. 62-7, 1938.

(21) Kurdjumow, G., Mirezkiy, V. and Stelletzkaya, T., Zhur. Tehnich. Fiziki, Vol. 8 (22/23), pp. 1959-72, 1938.

(22) Kurdjumow, G. and Mirezkiy, V., Zhur. Tehnich. Fiziki, Vol. 8 (20), pp. 1777-80, 1938.

(23) Gruzin, P. L. and Kurdjumow, G., Zhur. Tehnich. Fiziki, Vol. 10, pp. 1680-84, 1940.

(24) Kurdjumow, G. and Mirezkiy, V., Zhur. Tehnich. Fiziki, Vol. 10, pp. 1685-90, 1940.

(25) Obinata, I., J. Min. Inst. Japan, Vol. 50 (592), pp. 649-62, 1934.

(26) Obinata, I. and Hoyaski, M., Tetsu to Hogane, (J. Inst. St. Japan), Vol. 23 (11), pp. 1092-99, 1937.

(27) Greninger, A. B. and Mooraidan, V. G., Trans. AIME Vol. 128, pp. 337-55, 1938.

(28) Greninger, A. B., Trans. AIME, Vol. 133, pp. 204-27, 1939

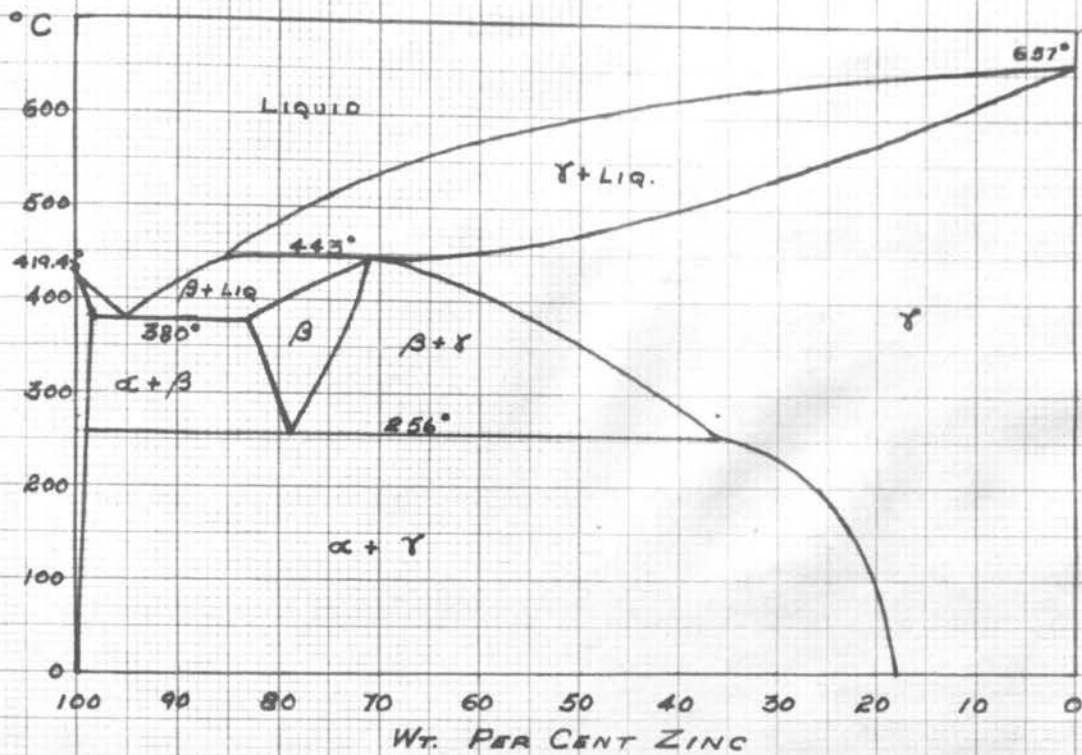
(29) Dehlinger, U., Metallwirtschaft, Vol. 1e, pp. 204-6, 1934

(30) Ballay, M., Compt. Rend., Vol. 17, pp. 1304-11, 1939.

(31) Smith, C. S., Trans. AIME, Vol. 137, p. 313, 1940.

FIG. 1

ZINC-ALUMINUM EQUILIBRIUM DIAGRAM (HANSON AND GAYLER-PIERCE)



ZINC-ALUMINUM EQUILIBRIUM DIAGRAM (G. V. RAYNOR)

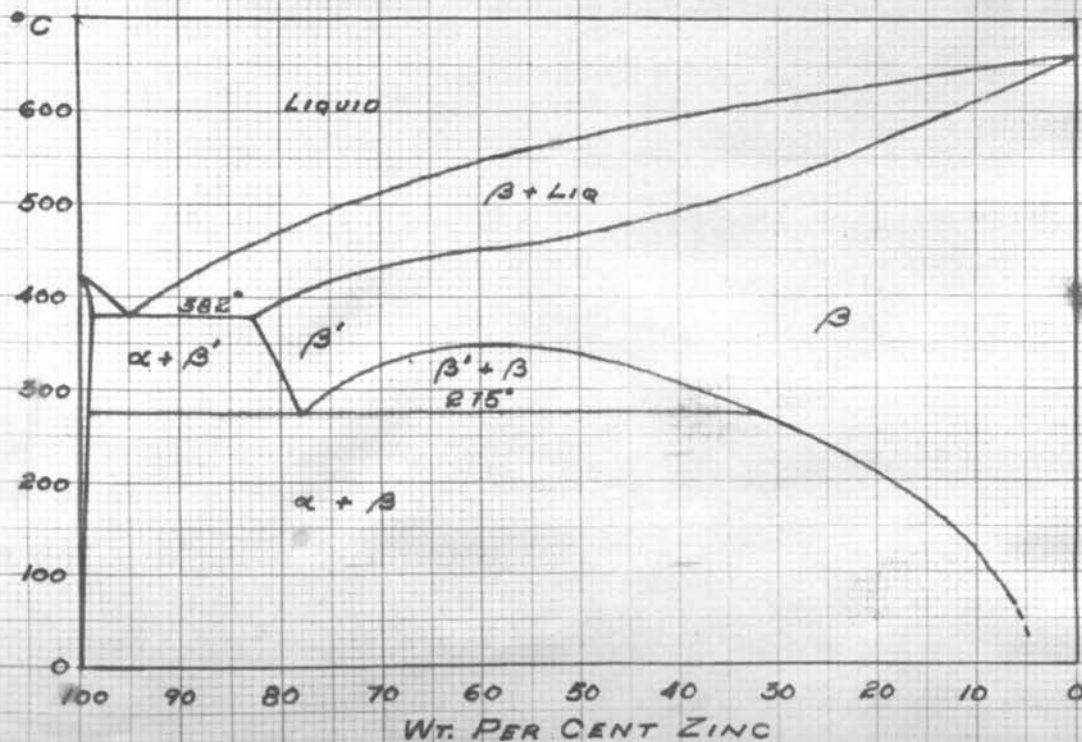


FIG 2

THE SYSTEM ALUMINUM-ZINC

In the years past, the aluminum-zinc alloys have been the subject of many investigations. This has been due not only to their commercial importance but also to their alloying behavior, which has rendered them of great scientific interest. This has been especially true with regard to the beta phase.

The equilibrium diagram as published by Hanson and Gayler was generally accepted as correct⁽³²⁾. (See Figure 1.)

(32) Hanson, D. and Gayler, M. L. V., J. Inst. Metals, Vol. 27, p. 267, 1922.

Later, it was further investigated by Schmid and Wasserman⁽³³⁾, who improved the previous thermal analysis results

(33) Schmid, E. and Wasserman, G., Ztch. fur Metallkunde, Vol. 26, p. 145, 1934.

by x-ray measurements of lattice parameters of heat treated and quenched specimens. Fink and Willey⁽³⁴⁾ also studied

(34) Fink, W. L. and Willey, L. A., Trans. AIME, Vol 122, p. 244, 1936.

the solubility limits between fifty and eighty weight per cent zinc and between three hundred and four hundred and fifty degrees centigrade, using isothermal electrical resistivity methods, and as a result, proposed the changes in

the equilibrium diagram which are now an integral part of
 the diagram as accepted by Raynor^(35,36) and other inves-
 tigators^(37,38).

(35) Raynor, G. V., Inst. Metals (London), Annotated Equilibrium Diagram Series, No. 1, undated, presented in 1943.

(36) Raynor, G. V., and Wakeman, Phil. Mag., Vol. 49, p. 404, 1949.

(37) Gayler, M. L. V. and Sutherland, E. G., J. Inst. Metals, Vol. 63, p. 123, 1938.

(38) Owen, E. A. and Pickup, L., Phil. Mag., Vol 20, p. 761, 1935.

The main alternations in the equilibrium diagram since 1932 have resulted from evidence that a peritectic reaction does not exist between fifty and eighty weight per cent zinc, and also the establishment of a two phase region which exists between thirty-one and six-tenths and seventy-eight weight percent zinc. (See Figure 2.)

The first investigators to report on the beta eutectoid were Rosenhain and Archbutt⁽³⁹⁾, whose determination of the

(39) Rosenhain, W. and Archbutt, S. L., Proc. Roy. Soc., Vol. 22, p. 315, 1912.

eutectoid temperature of two hundred and fifty-six degrees centigrade had been most generally accepted. Tanabe⁽⁴⁰⁾ and

(40) Tanabe, T., J. Inst. Metals, Vol. 32, p. 415, 1924.

(41) Ishihara had also determined this temperature, which

(41) Ishihara, T., J. Inst. Metals, Vol. 33, p. 73, 1925.

they reported as two hundred seventy and two hundred eighty degrees centigrade, respectively.

(42) Hanson and Gayler were the first to observe the

(42) Hanson and Gayler, op. cit. p. 14

peculiar nature of the beta constituent. They noted the great similarity of the decomposed beta to the pearlitic structure of plain carbon steels, and found that the decomposition time at room temperature was approximately ten minutes. They also reported that the beta decomposition was an exothermic reaction and that a hardness increase with subsequent softening of the alloy resulted after complete transformation. It was concluded that the beta phase was not an intermetallic compound, as hitherto had been supposed by Rosenhain and Archbutt⁽⁴³⁾, but rather a solid solution

(43) Rosenhain and Archbutt, op. cit., p. 15

the structure of which was essentially different from that

of the neighboring solid solutions, that is, the alpha and gamma solid solutions.

Edmunds⁽⁴⁴⁾ found that the beta phase was crystallog-

(44) Edmunds, G., Masters Thesis, Yale University, May 1929.

raphically identical with gamma and therefore not similar to the usual type of intermetallic compound. The two phases, by virtue of difference in composition, differ only in lattice parameter.

Owen and Iball⁽⁴⁵⁾ demonstrated by means of x-ray

(45) Owen, E. A. and Iball, J., Phil Mag., Vol. 17, p. 433, 1934.

powder patterns the dual phase structure in the beta plus gamma region. This, as mentioned before, was later studied by Fink and Willey⁽⁴⁶⁾, who also found that the solubility

(46) Fink and Willey, op. cit., p. 14

increases from 5.5 percent at 125 degrees centigrade to 31.6 weight per cent zinc at 275 degrees centigrade, then suddenly increases to 77.7 per cent and slowly increases to 81.4 per cent at 350 degrees centigrade. A solubility gap in the aluminum solid solution extends from 31.6 to 77.7 weight per cent zinc just above 275 degrees centigrade. At higher

temperatures, the solubility gap narrows and finally disappears at 353 degrees centigrade, and 60 per cent zinc.

Investigations by Meyer⁽⁴⁷⁾ and Bugakow⁽⁴⁸⁾ have

(47) Meyer, H., Ztch. fur Physik, Vol. 76, p. 268, 1932., and Ztch. fur Physik, Vol. 78, p. 854, 1932.

(48) Bugakow, W., Physik Ztch. Sowjetunion, Vol. 3, p. 632, 1933.

also been reported concerning the velocity and mechanism of the beta transformation using hardness, electrical conductivity, and density measurements.

Kennedy⁽⁴⁹⁾ published the results of a study of the beta

(49) Kennedy, R. G., Metals and Alloys, Vol. 5, p. 106, 1934.

constituent and its decomposition, purporting to correlate the density change accompanying the beta decomposition with the shrinkage in freshly-cast, zinc-alloy castings. Fuller and Wilcox⁽⁵⁰⁾ extended this work and found that the beta

(50) Fuller, M. L. and Wilcox, R. L., Trans. AIME Vol. 117, p. 338, 1935.

decomposition had little or nothing to do with the dimensional changes in aluminum-zinc die castings.

Gebhardt⁽⁵¹⁾ investigated the influence of additions

(51) Gebhardt, E., Ztch. Metallkunde, Vol. 33, (8/9), pp. 328-332, 1941.

of other elements on the rate of beta decomposition. He found that the rate of decomposition is retarded strongly by a small amount of copper, but the rate for any given copper content depends on the aluminum content. He reported also that, of the elements tested for their effect on the rate of decomposition of beta in the 21 per cent aluminum-zinc alloy, only tin, copper, indium, cadmium, lithium and magnesium showed any appreciable retarding effect.

From the above review of the literature on the subject, it can be seen that many investigations have dealt with studies concerning the nature of the transformation of the beta aluminum-zinc phase. It will be noted that these studies have embodied density changes, dimensional changes, electrical resistivity and conductivity changes, etc., many of which were on an isothermal basis. However, to the knowledge of the author, no comprehensive isothermal study has been accomplished in which the exothermic reaction of the beta decomposition was exploited as a method of measurement of the rate of transformation at many subcritical temperatures with a view toward construction of a Time-Temperature-Transformation curve for the alloy.

In order to avoid confusion regarding phase designations in the body of this thesis, the author will utilize

the phase nomenclature accepted at the present time. (See Figure 2.) That is, the eutectoid reaction will be referred to as:



instead of the older accepted convention:



PREPARATION OF ALLOY

High-purity zinc (99.99 per cent Zn) from the American Zinc Company and aluminum (99.975 per cent Al) from the Aluminum Company of America were utilized in the preparation of the eutectoid alloy.

The melting was performed in a Lindberg Pot-Type furnace. Temperature control was obtained by means of a chromel-alumel thermocouple in conjunction with a calibrated Lindberg Type-291 Controller unit. The thermocouple was calibrated against the melting points of pure zinc, antimony and cadmium. The complete furnace arrangement is shown in Figure 6.

A five-hundred gram alloy melt was prepared as follows:

$$500 \times 0.79 = 395 \text{ gm. zinc}$$

$$500 - 395 = 105 \text{ gm. aluminum}$$

The aluminum was melted in a clean, new graphite crucible at seven-hundred degrees centigrade. Pieces of zinc, cut to $\frac{1}{2}$ inch long by $\frac{3}{8}$ inch diameter, were added to the molten aluminum a few pieces at a time. After each zinc addition of about four-hundred grams, the melt was stirred with a carbon rod of the type used for spectrograph electrodes. Oxidation of the melt was minimized by keeping the temperatures of the furnace as low as possible consistent with the complete fusion of the alloy. It was not found practicable to protect the surface of the alloy by a flux, or other covering, without risking contamination from substances liable to be reduced by the molten aluminum.

After all the zinc had been seeded into the melt, it was stirred vigorously, then allowed to stand about two minutes, then chill-cast into steel molds measuring six inches long by 0.620 inches in diameter. Approximately one-half inch was cropped off each of the ingots. No visible evidence of oxidation was noted during the alloying.

The ingots, as cast, were cold swaged to thirty-five per cent reduction of area, then subjected to an homogenization heat-treatment at three-hundred and twenty-five degrees centigrade for thirty-five hours.

After heat-treatment, a representative five-gram sample was taken from the ingot bars for chemical analysis. (See Appendix A for method of chemical analysis.) The results of the analysis were as follows:

Zn	82.262%
Al	17.738%

The alloy, as prepared above, was then used as a "master" alloy. The composition had to be changed from 82.262 per cent zinc to 79.0 per cent zinc, the desired eutectoid composition. To accomplish this change, 227.62 grams of the master alloy were taken for re-alloying. Melt calculations were as follows:

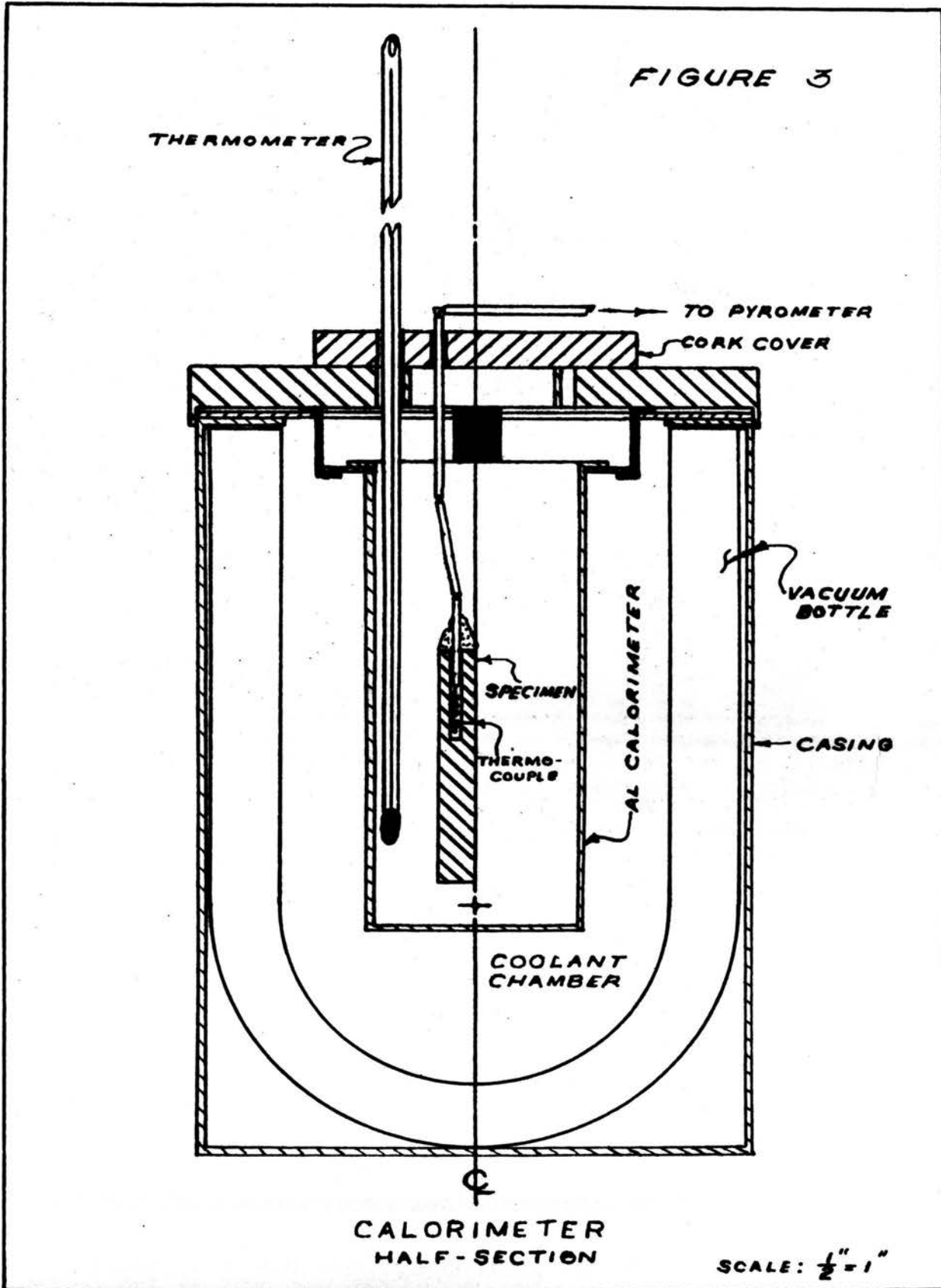
1. 227.62 gm. master alloy contained $(227.62 \times 0.18) = 40.9$ gm. Al.
2. Let X = weight of Al which must be added to yield alloy containing 21.0 per cent Al.

3. Total weight of alloy x per cent Al = Total Al
4. Per cent Al = 21% = $(40.9 + X) / (227.62 + X)$
5. X = 8.61 gm. Al to be added to bring composition to 79.0 per cent Zn.

The melting and casting procedures were executed as described for the preparation of the "master" alloy. After casting, the ingots were cropped to remove the pipes and then cold swaged to thirty-five per cent reduction of area. Metallographic samples were taken from the ingots and the microstructures of the alloy examined. (See Figures 25 and 26.) The swaged bars were given an homogenization heat-treatment at three-hundred and fifty degrees centigrade for ninety-three hours, and then, a representative five-gram sample was taken for chemical analysis. The chemical composition of this second alloy was as follows:

Zn	78.26%
Al	21.74%

This alloy was used for all subsequent studies referred to in this investigation.



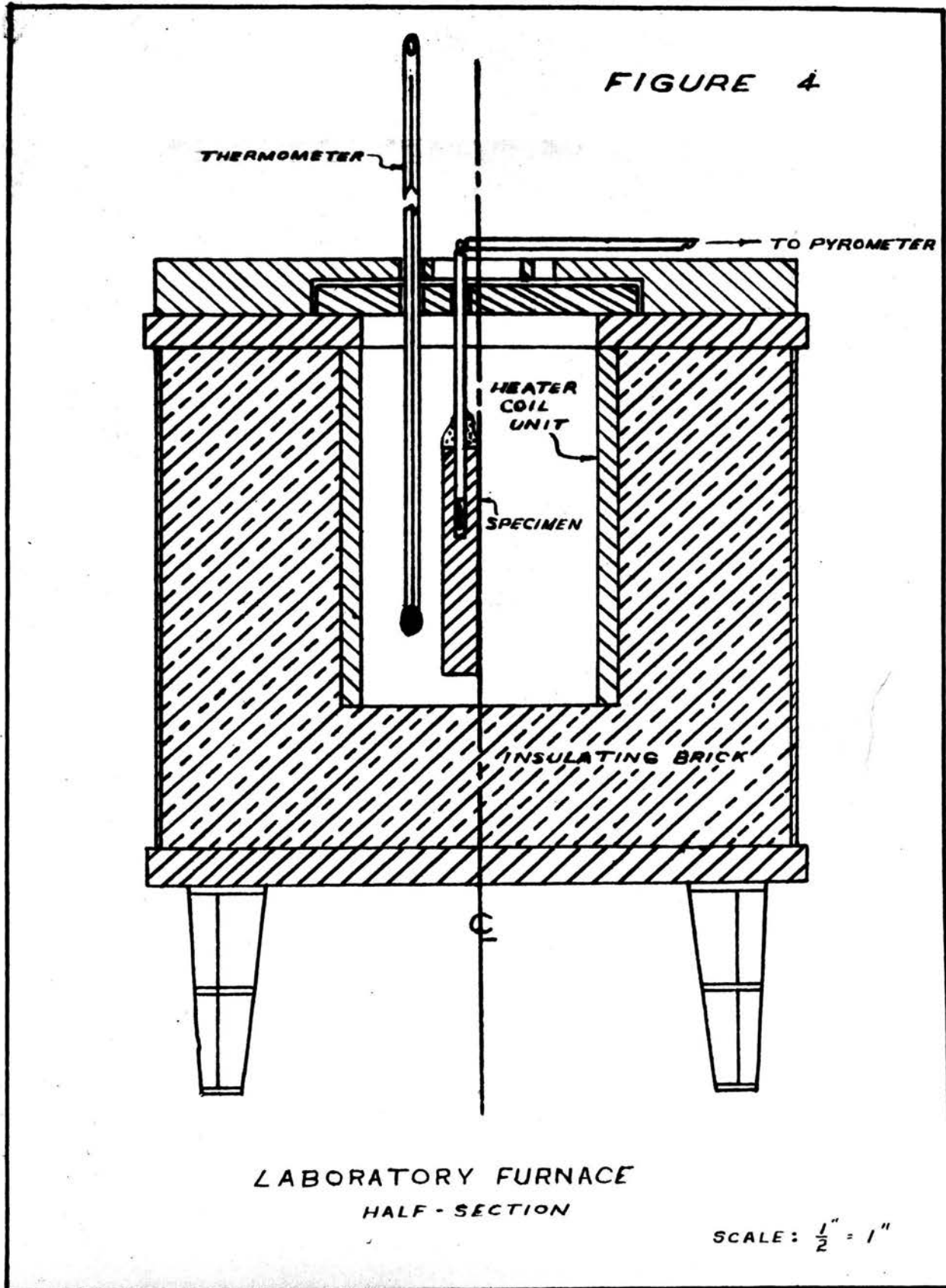




Figure 5

Furnace Arrangement for Thermal
Analysis between 50°C and 250°C

- A - Hoskins Thermoelectric Pyrometer - Type HA
- B - Mercury Thermometer
- C - Chromel-Alumel Thermocouple From Specimen
- D - General Electric A.C. Ammeter
- E - Variable Resistor
- F - Cenco Carbon-Pile Variable Resistor
- G - Superior Electric Company Powerstat - Type 1256

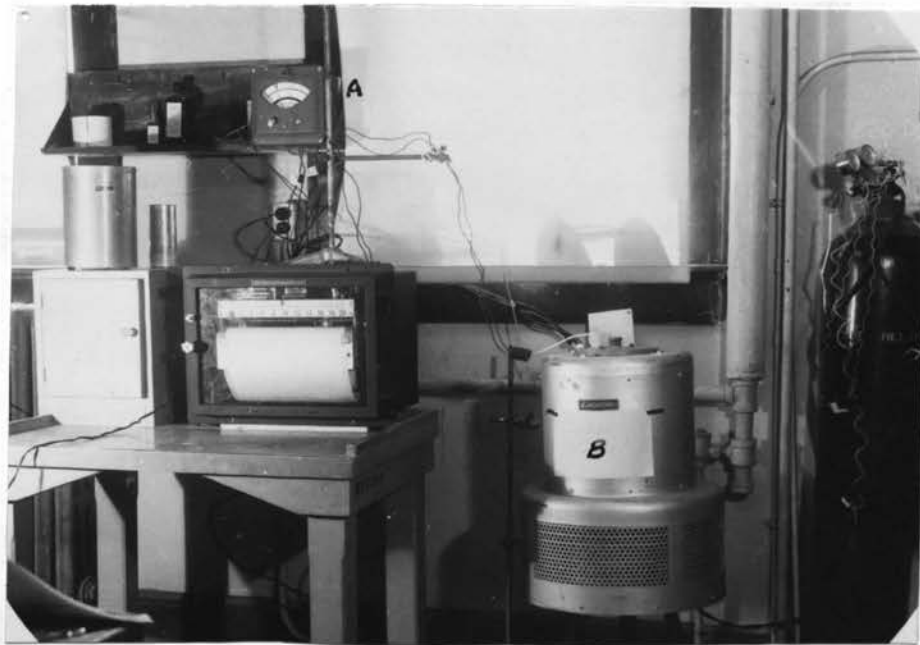


Figure 6

Melting And Heat-Treatment Furnace Arrangement

**A - Lindberg Pot-Type Electric Resistance
Furnace**

B - Lindberg Controller Unit - Type 291

INVESTIGATION OF THE RATE OF TRANSFORMATION AT
SUBCRITICAL TEMPERATURES

THERMAL ANALYSIS

It was known that the decomposition of beta-prime was manifested by a spontaneous rise in temperature. Therefore, by establishing a time-temperature relationship for each specimen during the course of transformation, the onset and completion of the transformation could be determined. The beginning of the reaction was taken as the time at which the temperature first began to rise, and the completion was taken as the time at which the temperature began to drop off.

At the outset of the investigation, it was thought that the transformation at the various temperature intervals, between zero degrees centigrade and the eutectoid temperature, could be followed by temperature measurements while the specimen was held in a liquid bath maintained at the temperature desired for the test. However, it was found that this method of study was not feasible due to the rapidity with which heat was conducted away from the specimen by the medium.

Finally, it was found that, if the specimen was held in an air filled container of sufficient volume (a furnace muffle or a calorimeter), that the air acted as an insulator and did not allow rapid conduction of the heat of reaction away from the specimen. Under these conditions, the temperature rise caused by the heat of decomposition could be mea-

sured and there would be little change in the temperature of the air in the container.

After suitable cold swaging and heat-treatment to insure uniformity of chemical composition throughout the alloy, the alloy bars were cut into four specimens which measured two and one-half inches in length by one-half inch in diameter. A hole, three-sixteenths inches in diameter, was drilled to a depth of three-fourths of an inch along the longitudinal axis of each specimen. A chromel-alumel thermocouple was inserted into the hole of each specimen and sealed in place with Sauereisen Asbestos cement. Copper lead-wires were welded to the thermocouples. All thermocouples had previously been calibrated with a Hoskins Type-HA Thermoelectric Pyrometer, against the melting points of pure zinc, antimony and cadmium. This combination was subsequently used to measure all temperature changes in the specimens during later test runs.

Three of the four specimens prepared were used for each test run at a given temperature, except in cases where results were extremely erratic. In this event, the experiment was re-run and the additional results were noted and plotted on time-temperature graphs. (See Figures 7 to 23. Also Table III.)

In general, the test procedure was as follows: All specimens were subjected to an annealing heat-treatment at three-hundred and forty to three-hundred and sixty degrees

centigrade for twelve to eighteen hours prior to each test. Lead-wires from the specimen to be tested were connected to the Hoskins pyrometer and the specimen was quenched from the heat-treating furnace into a liquid medium, either water or Crisco, held at the temperature desired for the test. Zero time was taken as the instant the specimen touched the quenching medium. In all cases, the specimen was held in the quench for fifteen seconds to assure complete cooling to temperature of the bath. After this time had elapsed, the specimen was immediately transferred to the air-filled container maintained at the same temperature as that of the quenching medium. Temperature readings were then recorded at fifteen-second intervals until completion of the decomposition. The maximum rise in temperature of the air in the furnace and calorimeter was observed to be five degrees centigrade.

The procedure of attaching the thermocouple leads to the pyrometer prior to quenching proved to be a very satisfactory time-saving device. The author could easily make all necessary manipulations of the apparatus and begin recording time-temperature measurements well within thirty seconds of zero time.

Transformation studies were made at zero, twenty-eight, fifty, one-hundred, one-hundred and fifty, two-hundred, two-hundred and thirty-five, and two-hundred and fifty degrees centigrade.

The apparatus utilized for study of the transformation at zero and twenty-eight degrees centigrade is shown in Figure 3. At zero degrees centigrade, temperatures were maintained by packing the thermos jacket with chipped ice. Specimens were quenched into ice-water from the heat-treating furnace.

The transformation study at twenty-eight degrees (room temperature) centigrade presented no difficulties. Water was used as the quenching medium.

The apparatus utilized for study of transformation at elevated temperatures, between fifty and two-hundred and fifty degrees centigrade, is shown in Figures 4 and 5.

The choice of a quenching medium for the transformation study at fifty and one-hundred degrees centigrade presented little difficulty. Water was easily heated to fifty degrees; and boiling water was reasonably close to one hundred degrees at the existing barometric pressure. However, the choice of a quenching medium for temperatures above one-hundred degrees presented quite a problem. Many different liquids were considered before a choice was made. It was found that Crisco, the commercial animal and vegetable fat shortening material, was the most suitable medium for this type of study. It was finally used as a quenching medium for all studies above one-hundred degrees, including the highest temperature employed, that of two-hundred fifty degrees.

Furnace temperatures were measured by means of a standard

mercury thermometer. The temperature of the furnace used for these studies was controlled by adjusting the current flow in the furnace resistors by means of a carbon-pile variable resistor and a powerstat variable voltage regulator all connected in series with the furnace. (See Figure 5.) Accuracy of temperature control was considered to be of the order of about plus or minus five degrees centigrade for all runs.

The time-temperature graphs for each individual test run are to be found in Figures 7 to 23, inclusive. A summary of the onset and completion of transformation data is tabulated in Table III. Experimental averages were taken from individual test data, and the mean beginning and end of transformation calculated for each temperature investigated. This information was then utilized for the construction of the Time-Temperature-Transformation diagram indicated in Figure 24.

METALLOGRAPHIC INVESTIGATION

An attempt has been made to record the structural changes which take place during the progress of the transformation of the beta-prime constituent. This attempt is by no means the first which has been made with this object in mind. However, the author was curious to know whether or not the transformation as reported by other investigators could be duplicated, and if so, if it were possible to record

the decomposition at intervals closer to zero time. The following is a detailed account of the techniques employed for the metallography and the results obtained.

In order to gain some information as to the structural appearance of the eutectoid alloy in the "as chill cast" condition, metallographic samples were taken from the cropped portion of the original ingots. (See Figures 25 and 26.)

Samples were also taken from each of the alloy bars which had been swaged in the "as chill cast" condition. Examination indicated no visible change in the microstructure except that the size of the dendritic matrix was smaller. This observation was to be expected since no intermediate heat-treatment was employed. In view of this, no photomicrographs were taken.

No further attempt was made at microscopic examination until after completion of the thermal study of the alloy.

Each of the three thermal study specimens was sectioned for metallographic samples and subjected to an annealing treatment at three-hundred and forty to three-hundred and sixty degrees centigrade for one-hundred and five hours. The furnace temperature was then reduced to two-hundred and ten degrees centigrade for a period of fifteen hours, after which the specimens were furnace cooled to room temperature. It was hoped that the above heat-treatment would yield a representative equilibrium structure of the alloy in the annealed condition. (See Figures 27 and 28.) The same

samples were later used for transformation studies.

Considerable difficulty was encountered in the preparation of suitable specimen surfaces for metallographic examination. Because of the softness of the alloy a rather deep layer of disturbed metal was formed at the specimen surface during polishing. Consequently, the following polishing technique was developed, and the procedure was followed for preparation of all samples examined:

1. Careful hand grinding on #0 through #0000 emery papers lubricated with a solution of fifteen grams of paraffin in one liter of kerosene;

2. Hand grinding on the #0000 grit was followed by etching for about three minutes in three per cent Nital solution;

3. Followed by polishing on a canvas lap rotating at 250 rpm for a period of about one minute. Buehler Extra-Fine Emery in water suspension was used as the abrasive agent;

4. The samples were then washed in hot water, etched for about one minute in three per cent Nital and polished for about one minute on a Selvt lap, rotating at 250 rpm. Buehler Alumina Micropolish in water suspension was used as abrasive.

5. At this point the specimen was re-etched with three per cent Nital for about fifteen seconds, then hand-polished on a piece of silk cloth stretched over a plane glass back-

ing. Polishing was continued until no evidence of etching was apparent. The silk cloth was lubricated with the paraffin-kerosene solution and a very slight amount of Buehler Alumina Micropolish powdered into the silk cloth was used as the abrasive.

6. Final etching was accomplished as soon as the last evidence of surface etching had disappeared. All polishing was kept at a minimum to insure as little disturbed surface metal as possible. Final etching, by immersion, was of 30 seconds duration in three per cent Nital.

The metallographic samples employed to follow the course of transformation were heat-treated at three-hundred and forty to three-hundred and sixty degrees centigrade for a period of twelve to eighteen hours prior to quenching. These samples were prepared as indicated above, except that the final etch was omitted. After polishing, the samples were heat-treated, quenched, given a rapid repolish and etched at the time intervals indicated under the individual photomicrographs. (See Figures 29 to 36, inclusive.)

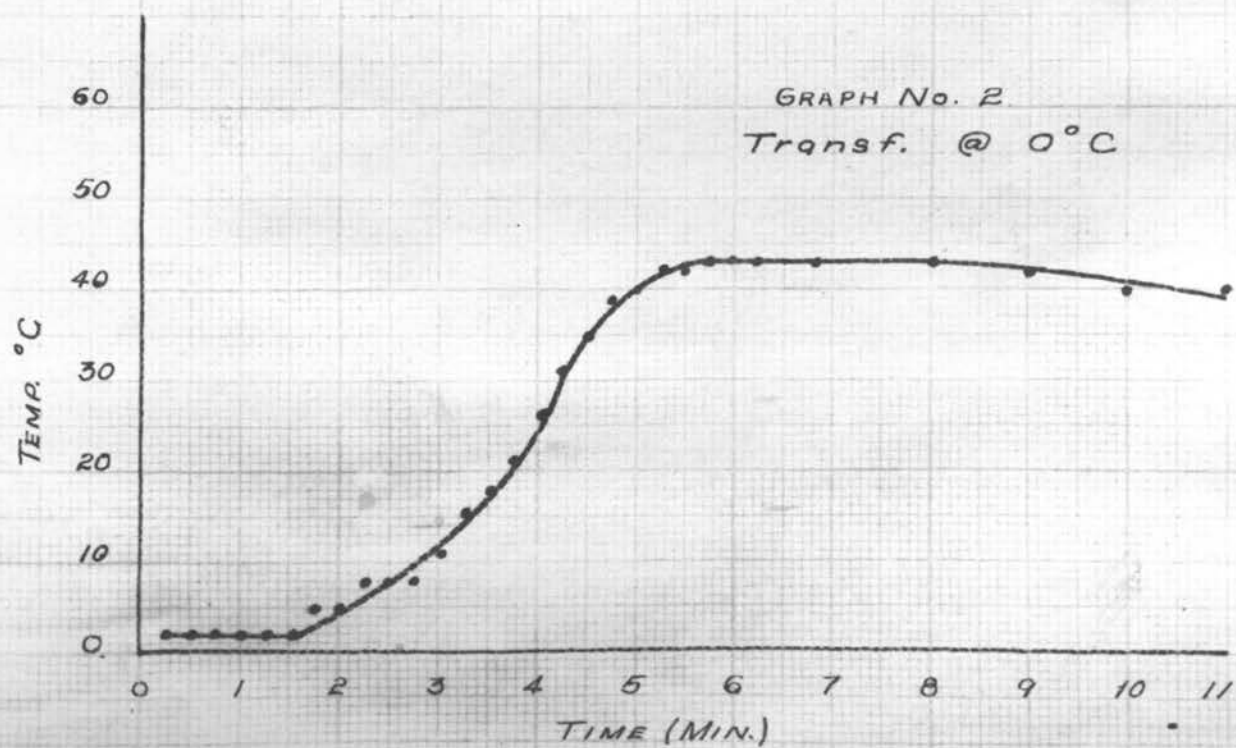
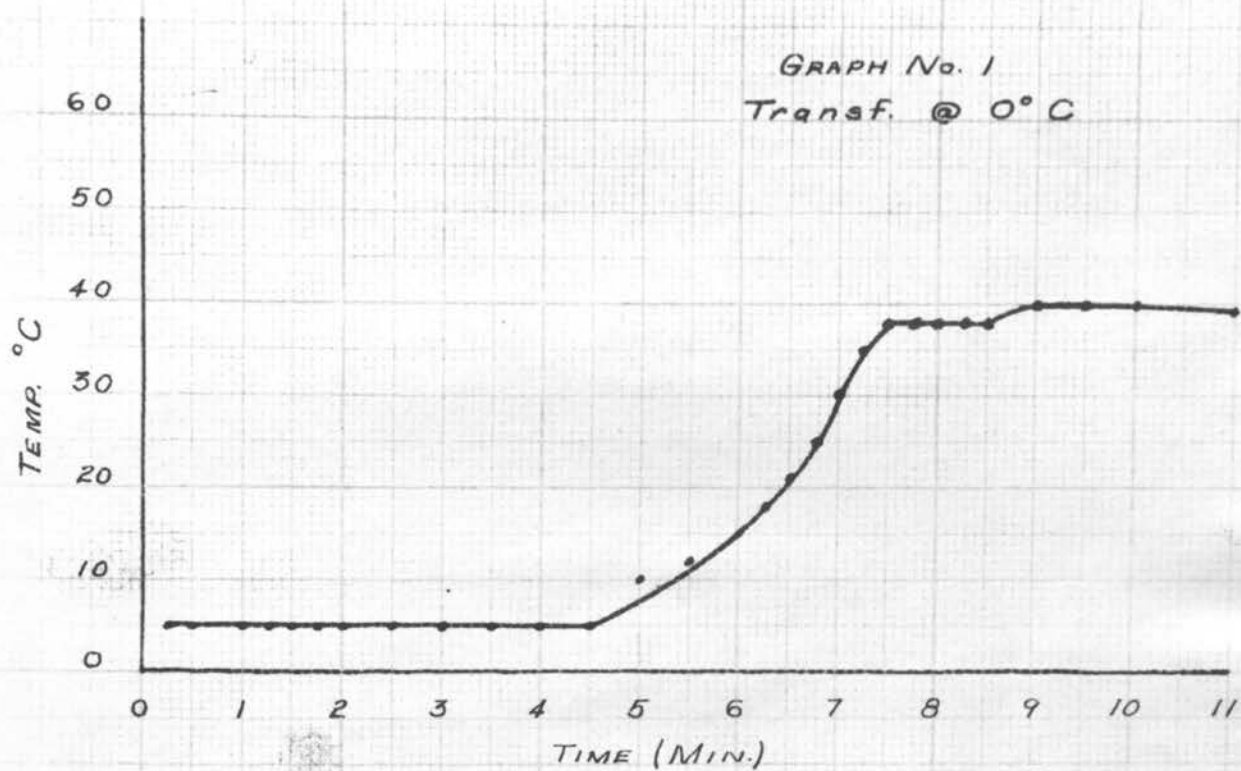
FIGURE 7

FIGURE 8

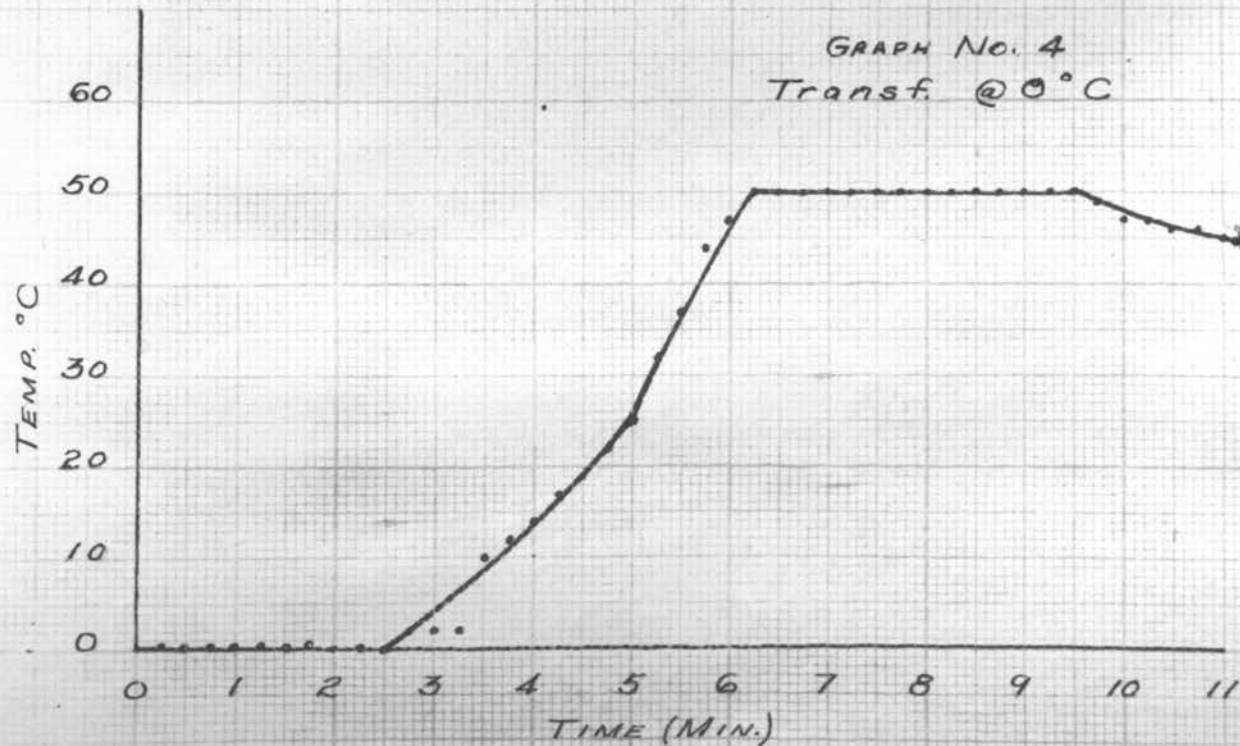
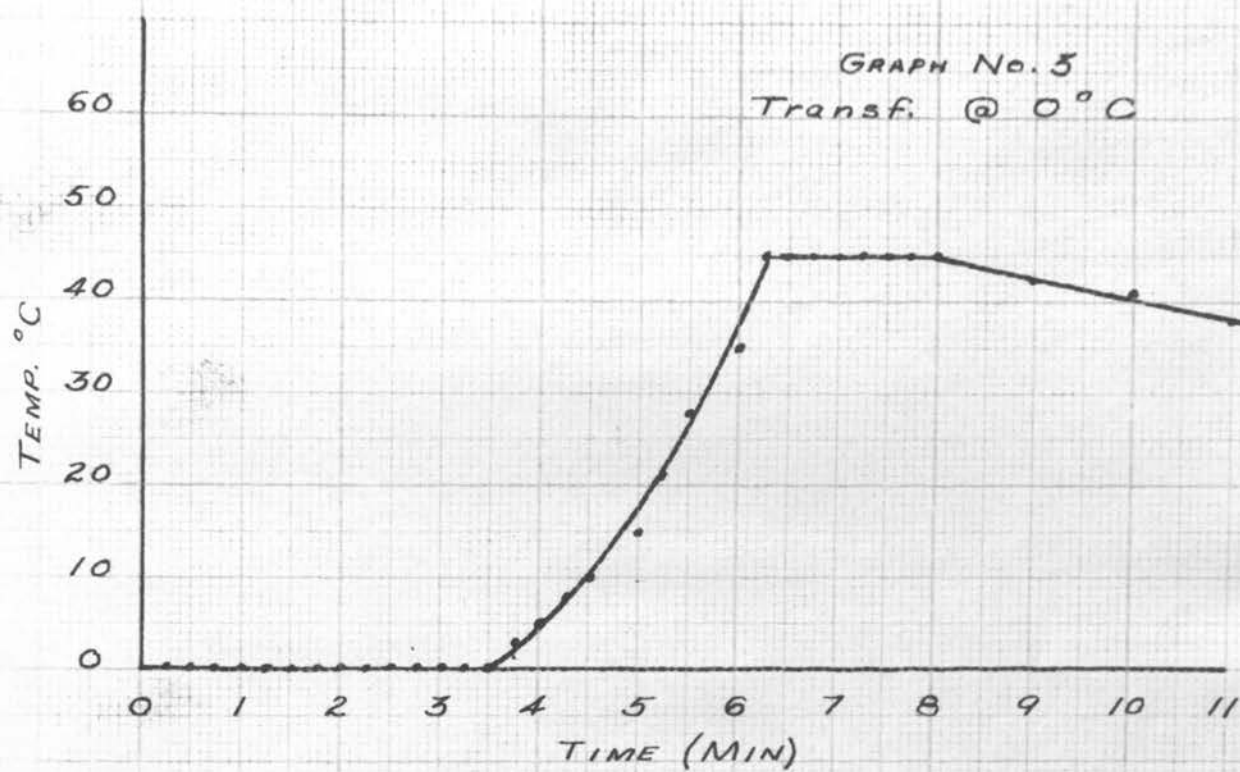


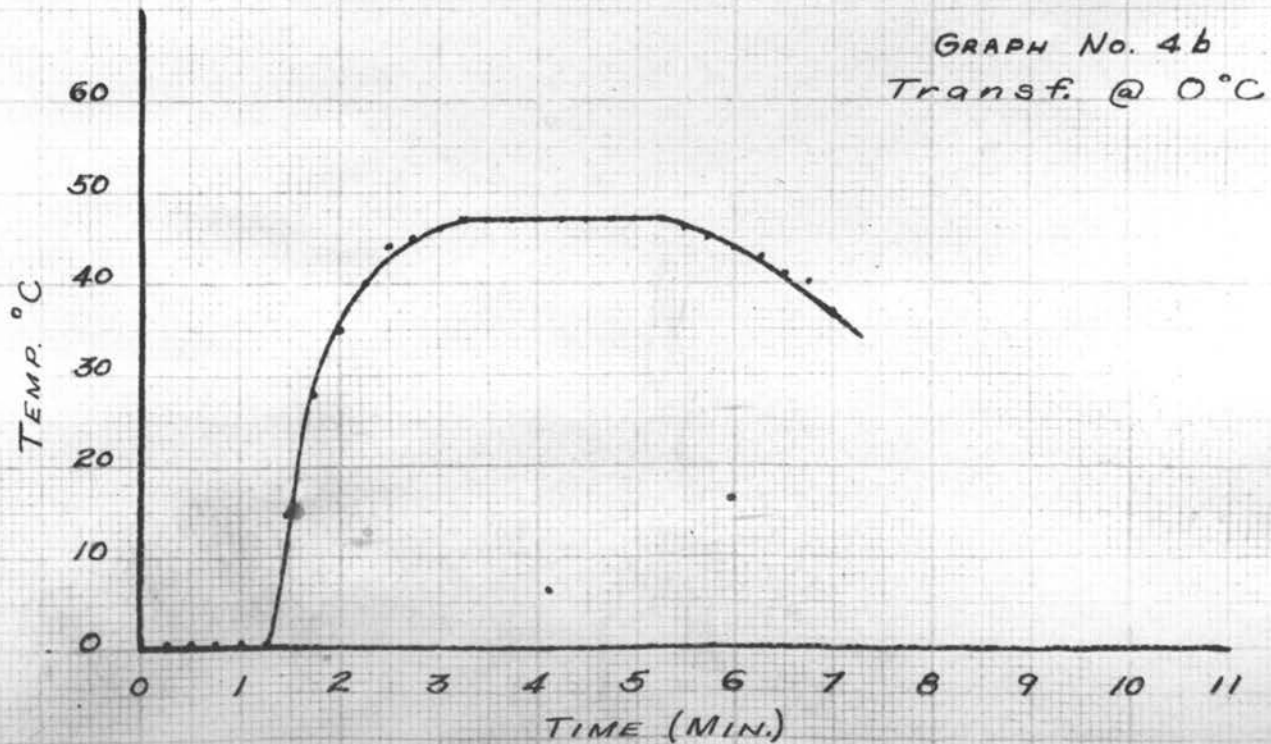
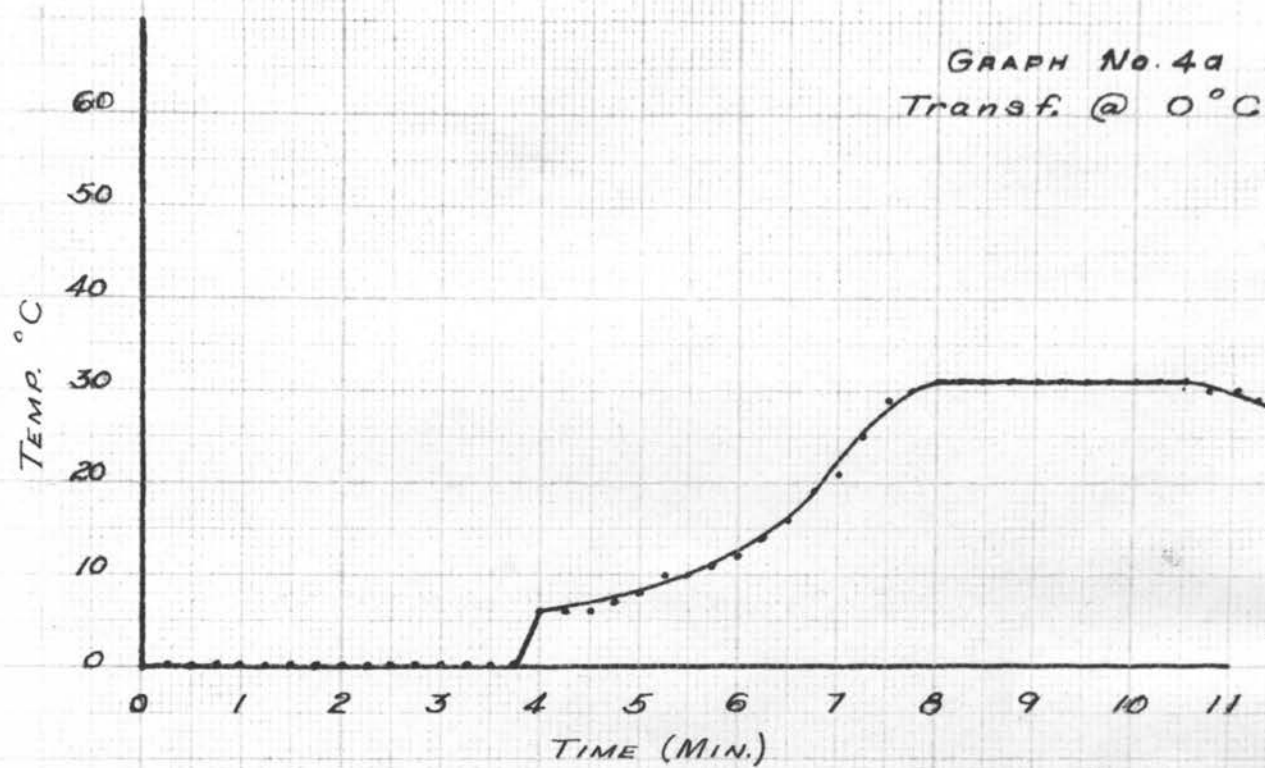
FIGURE 9

FIGURE 10

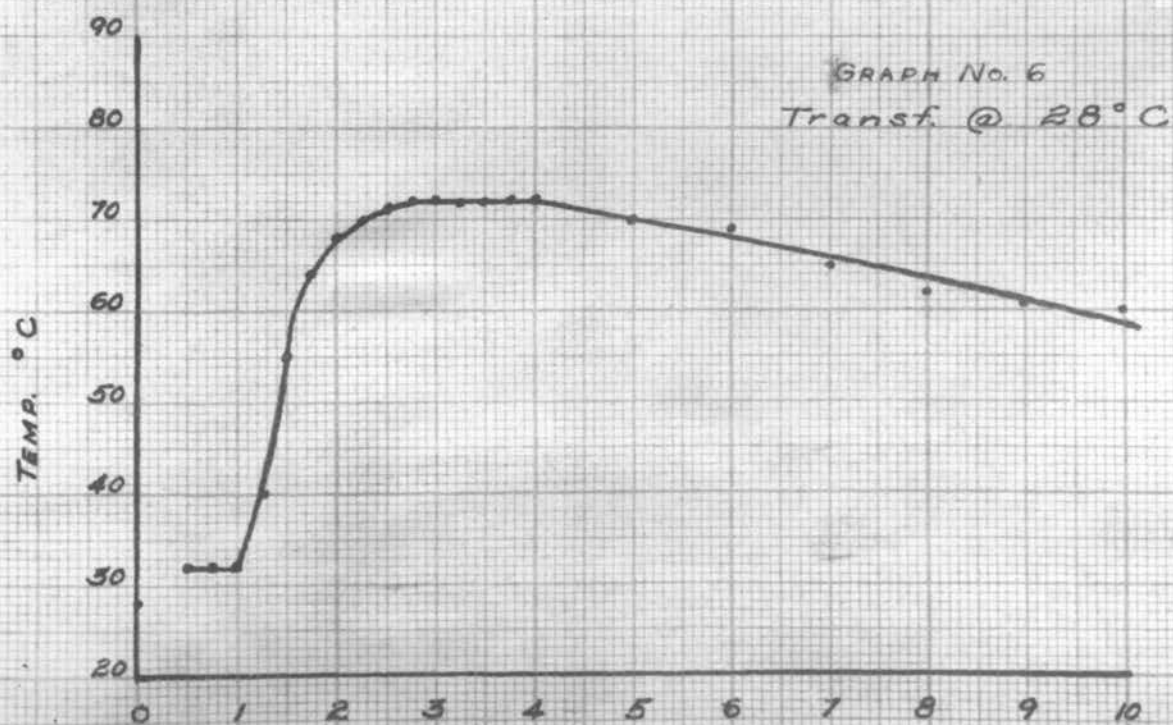


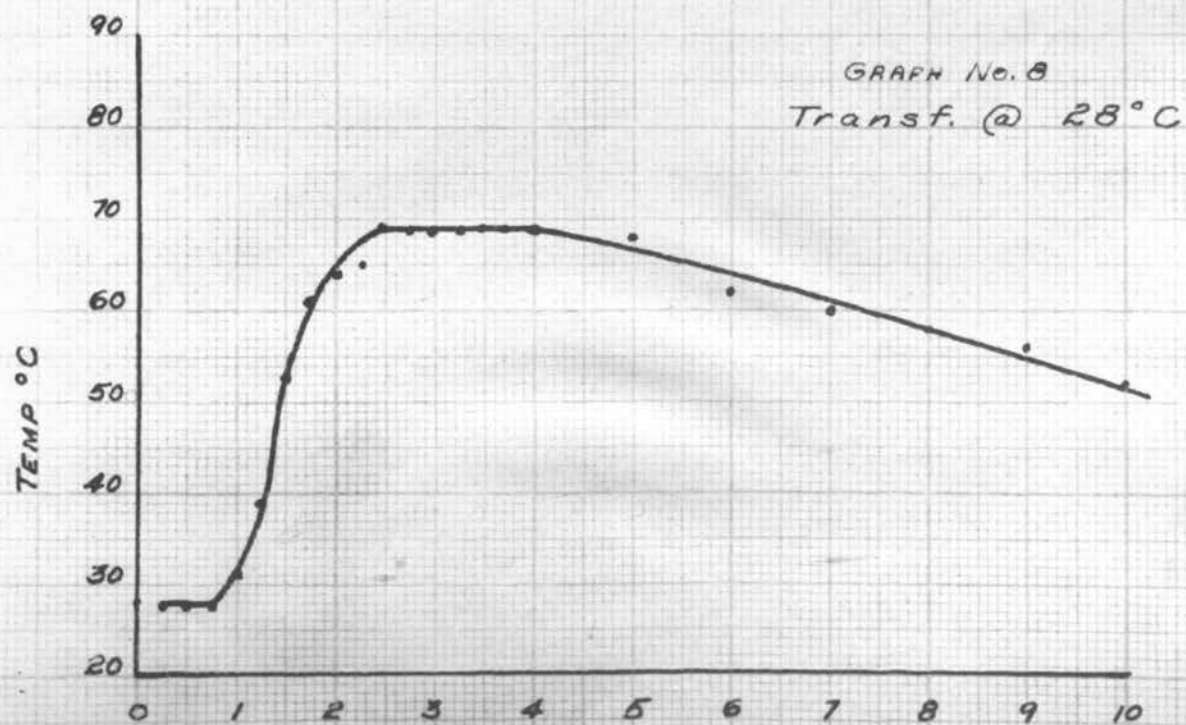
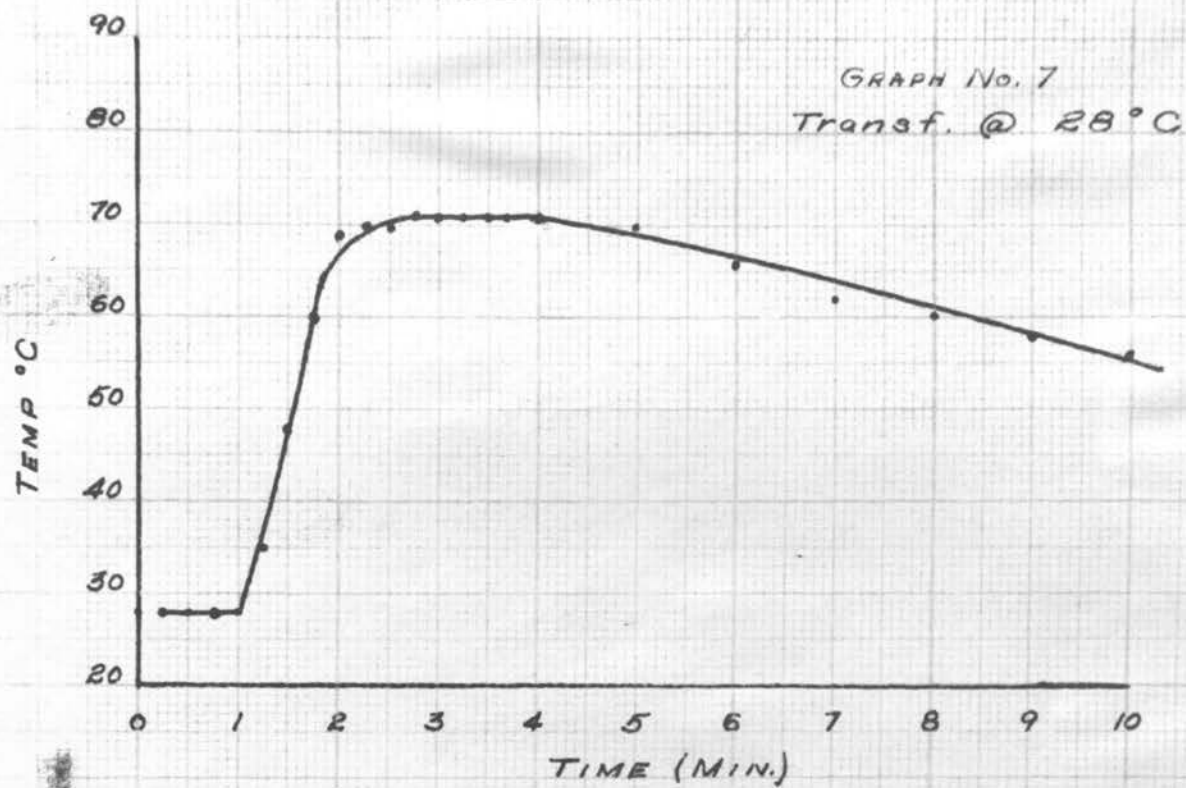
FIGURE 11

FIGURE 12

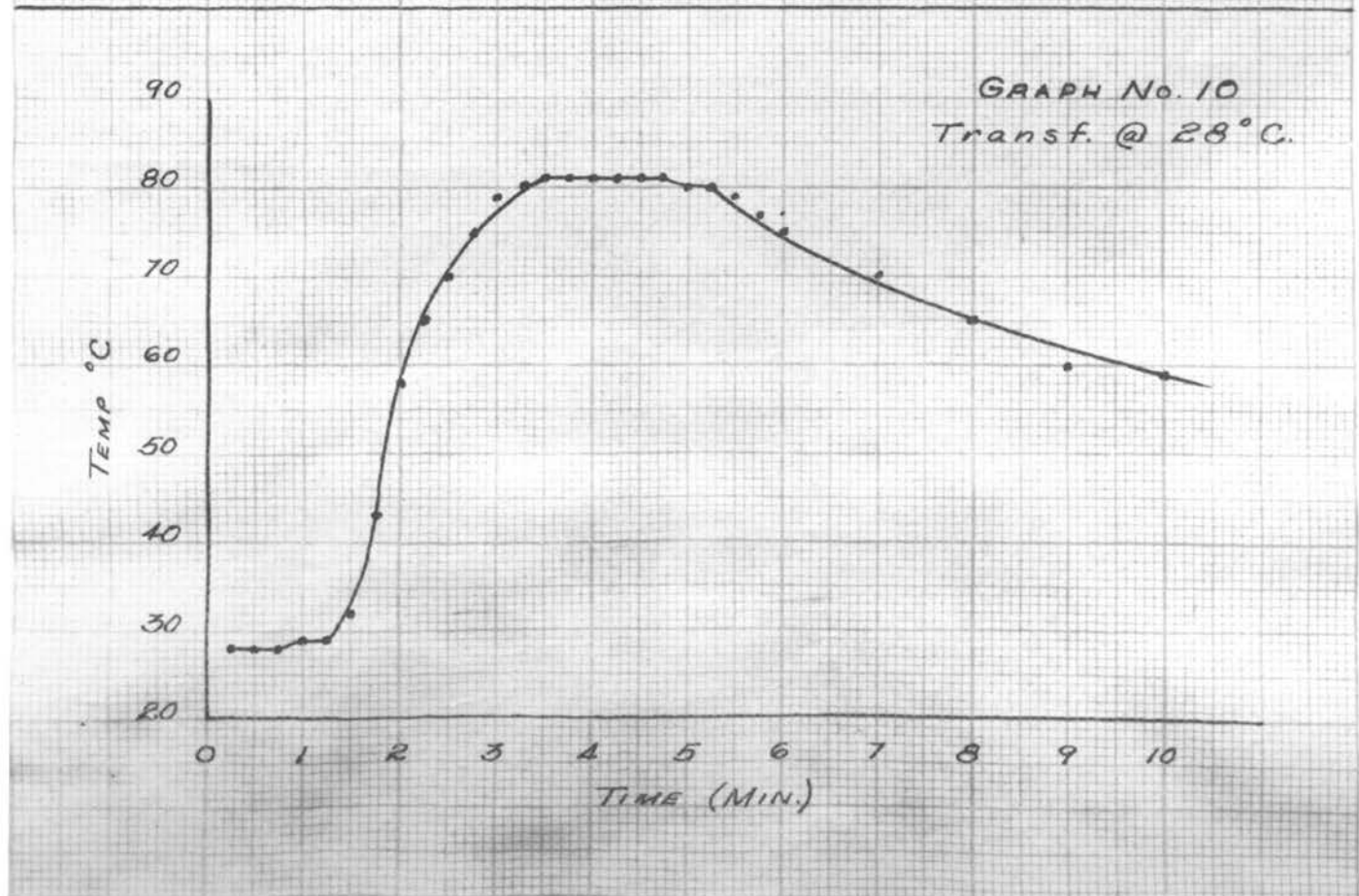


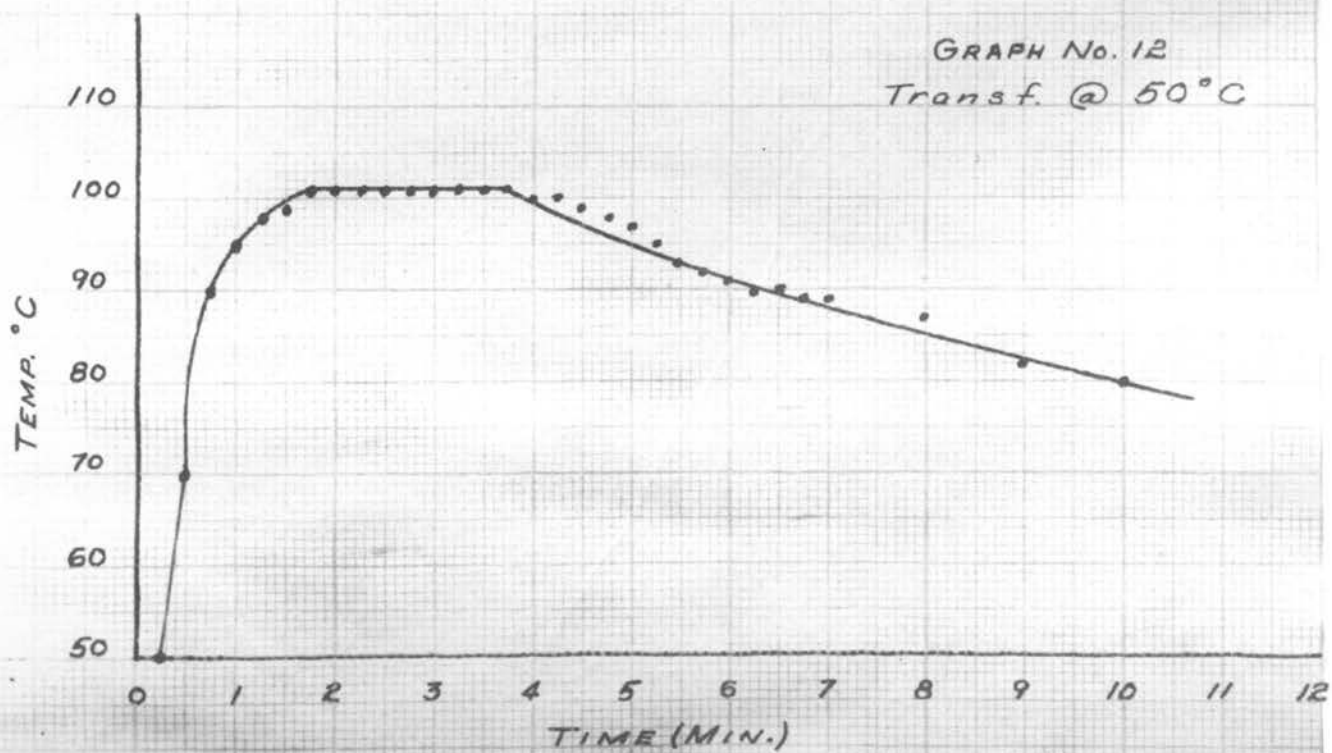
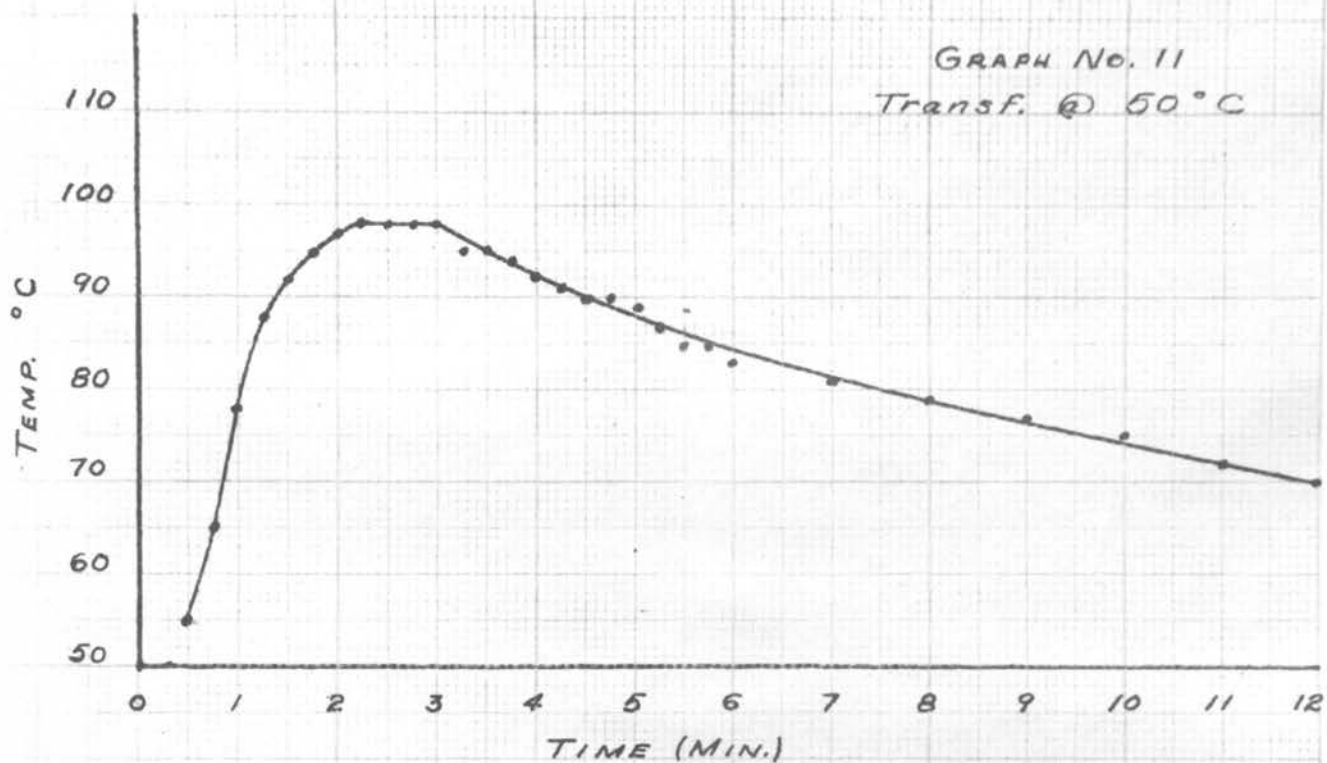
FIGURE 13

FIGURE 14

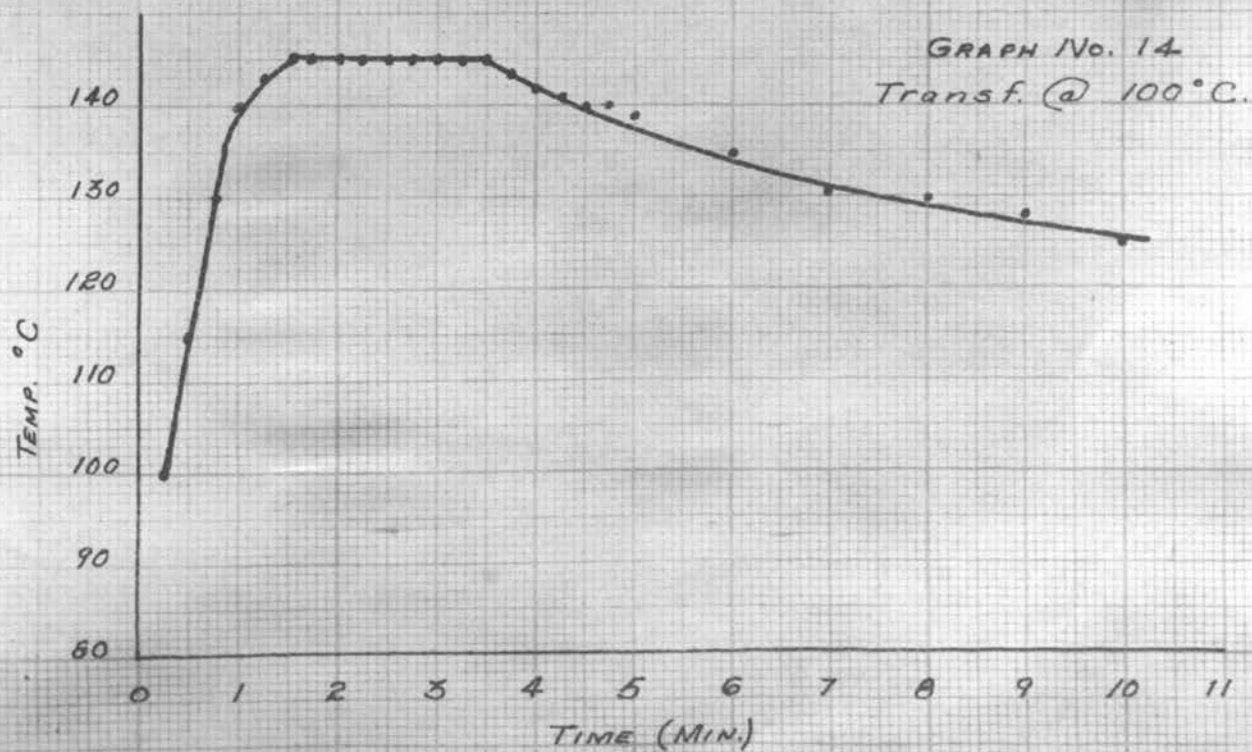
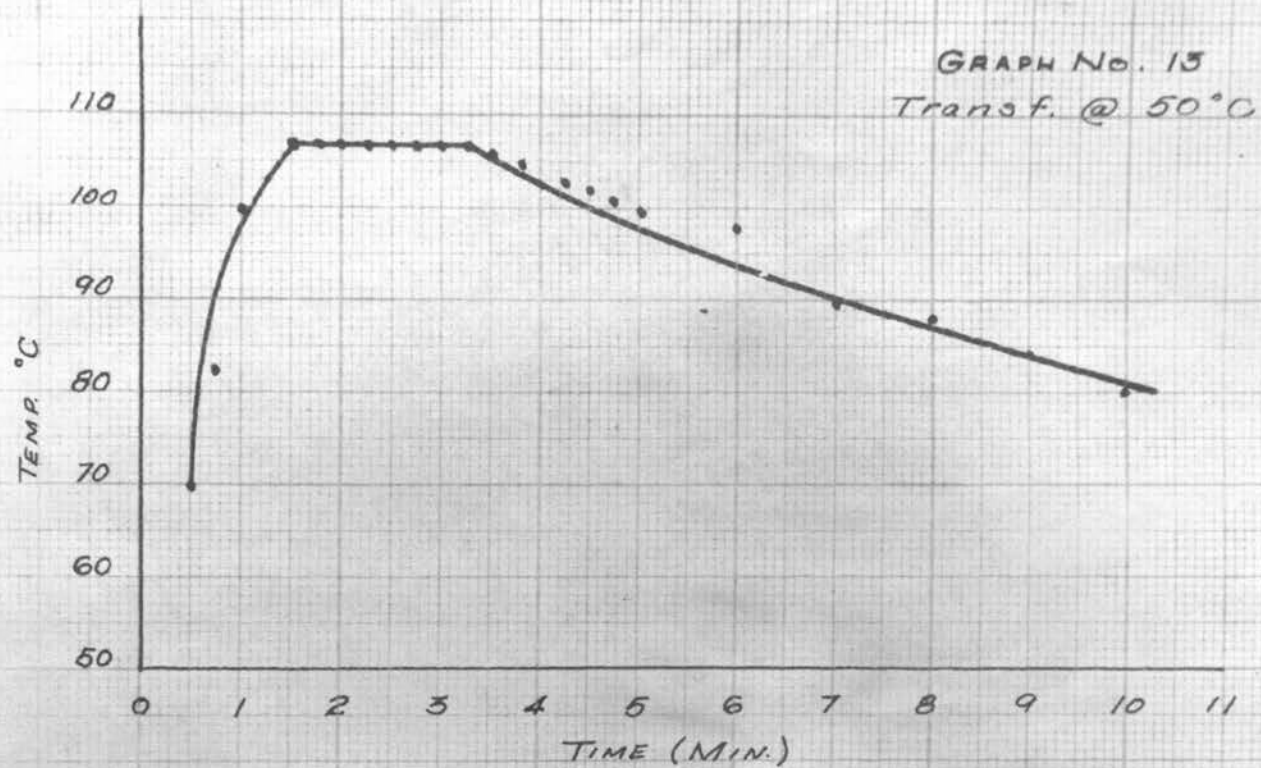


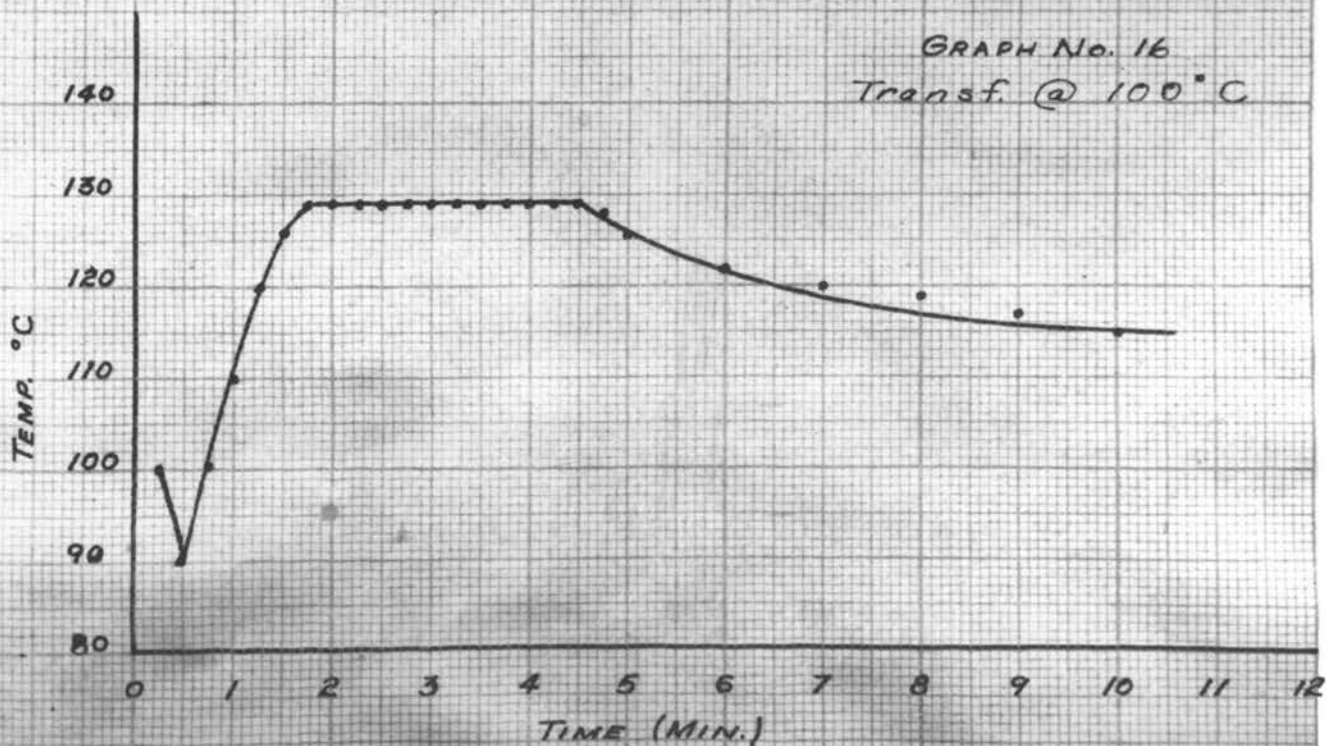
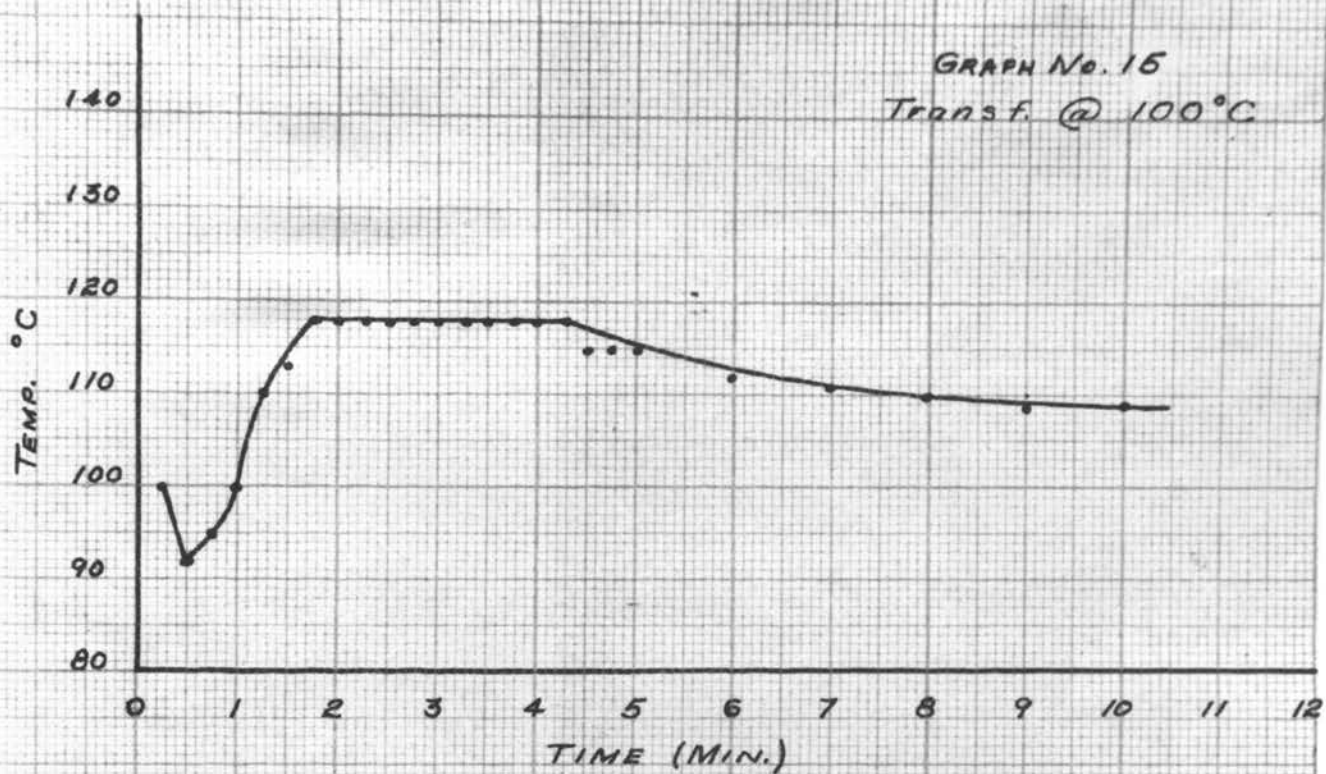
FIGURE 15

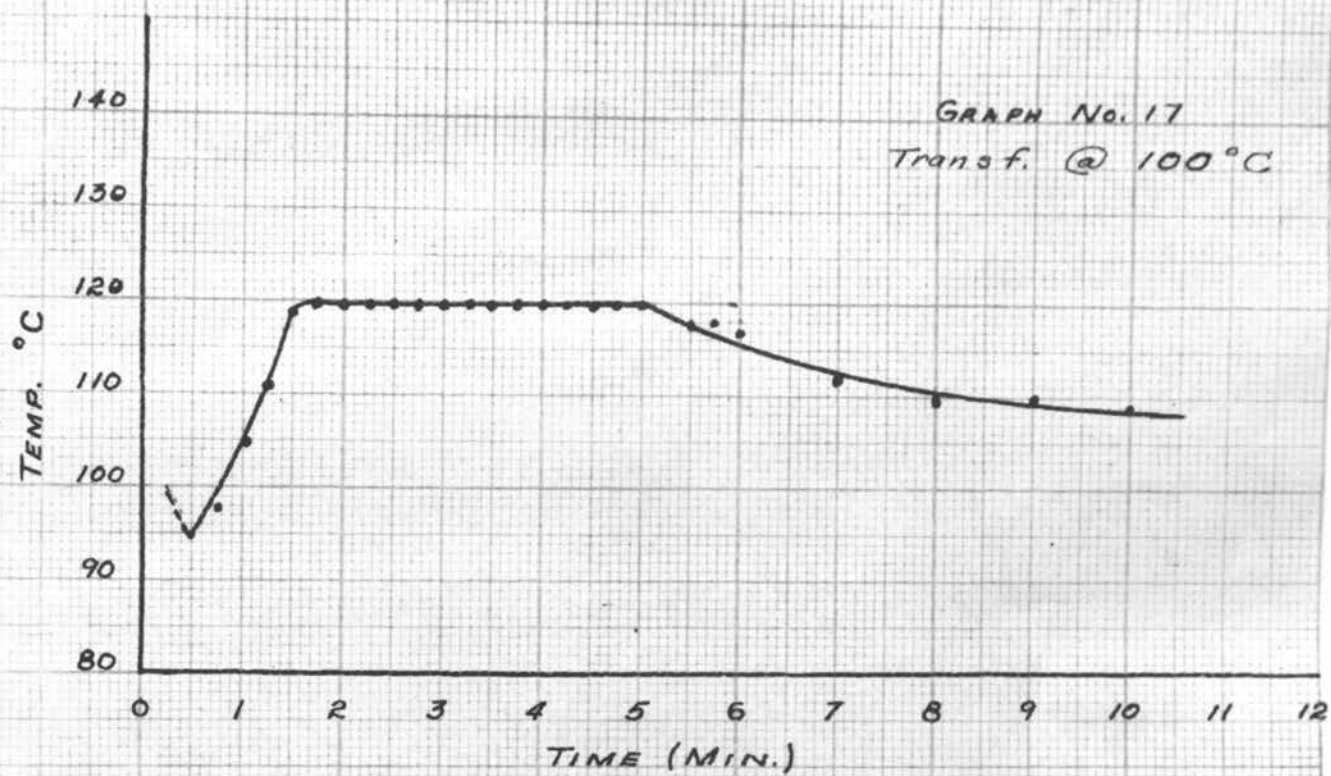
FIGURE 16

FIGURE 17

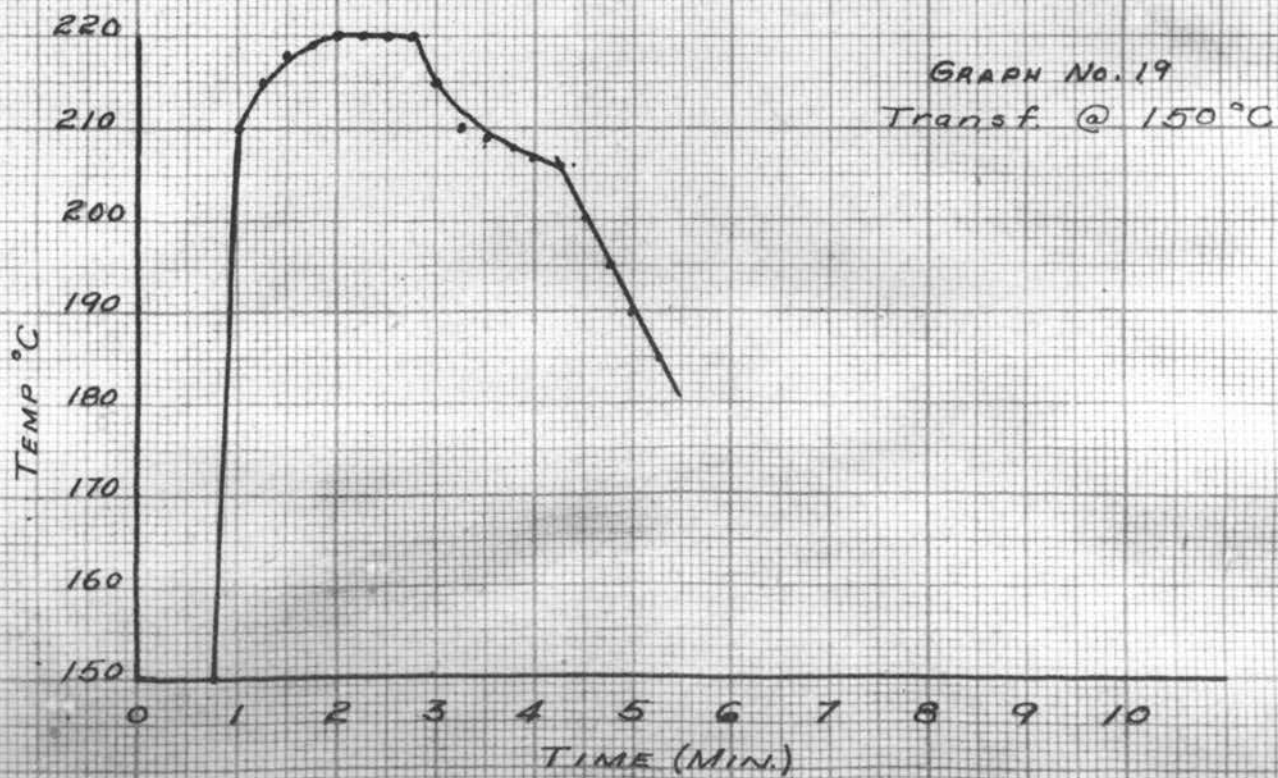
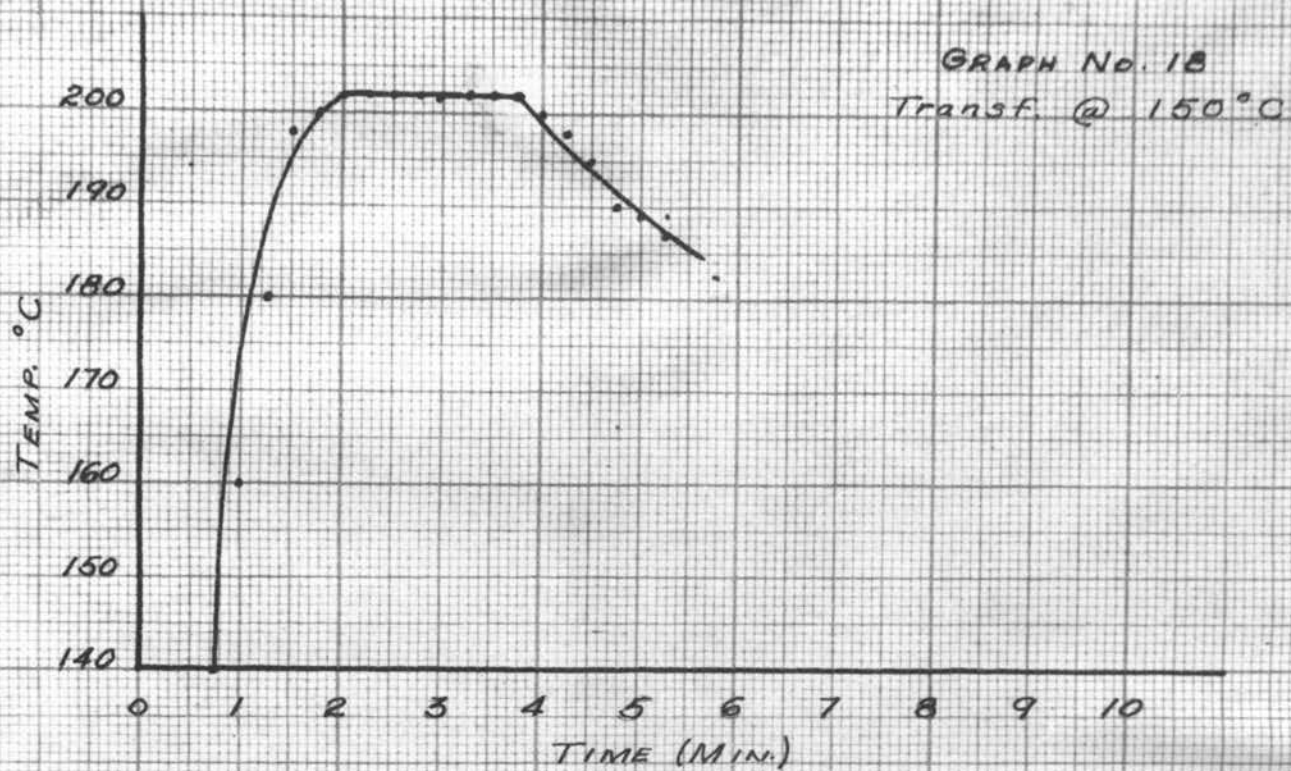


FIGURE 18

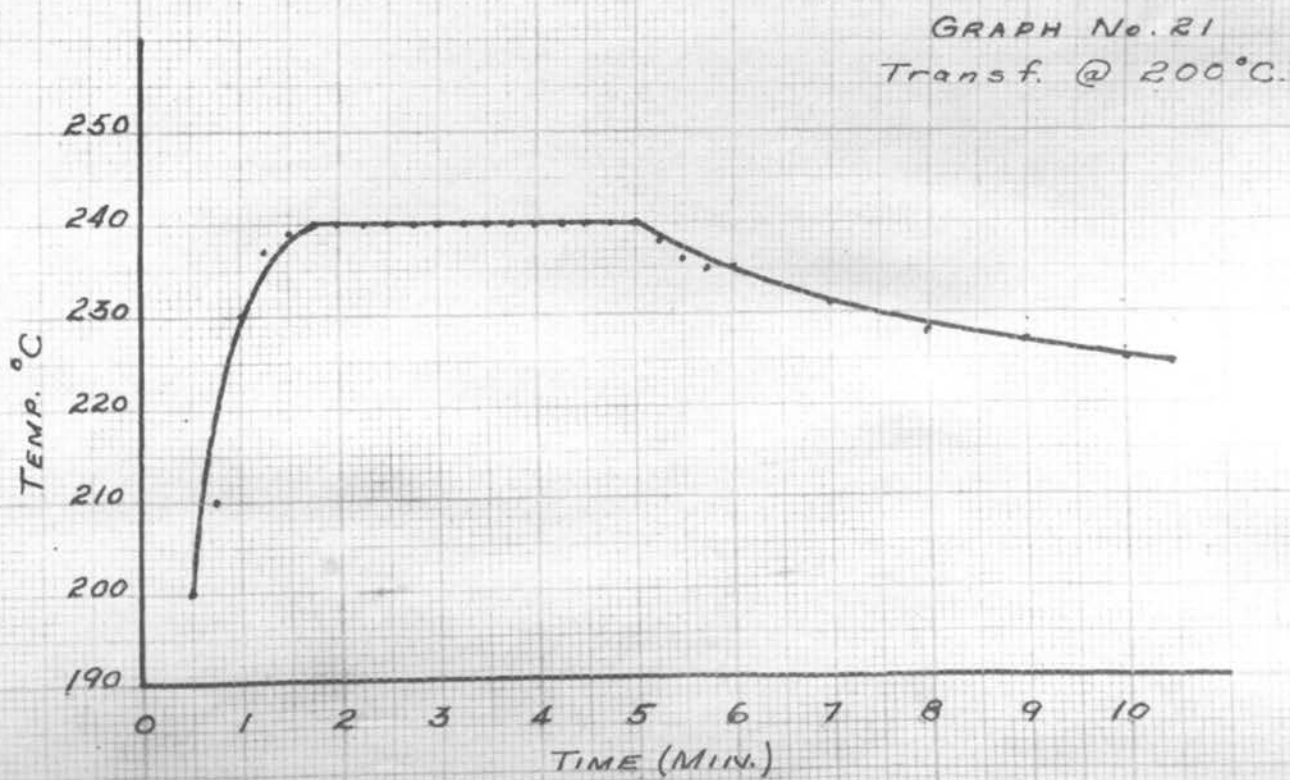
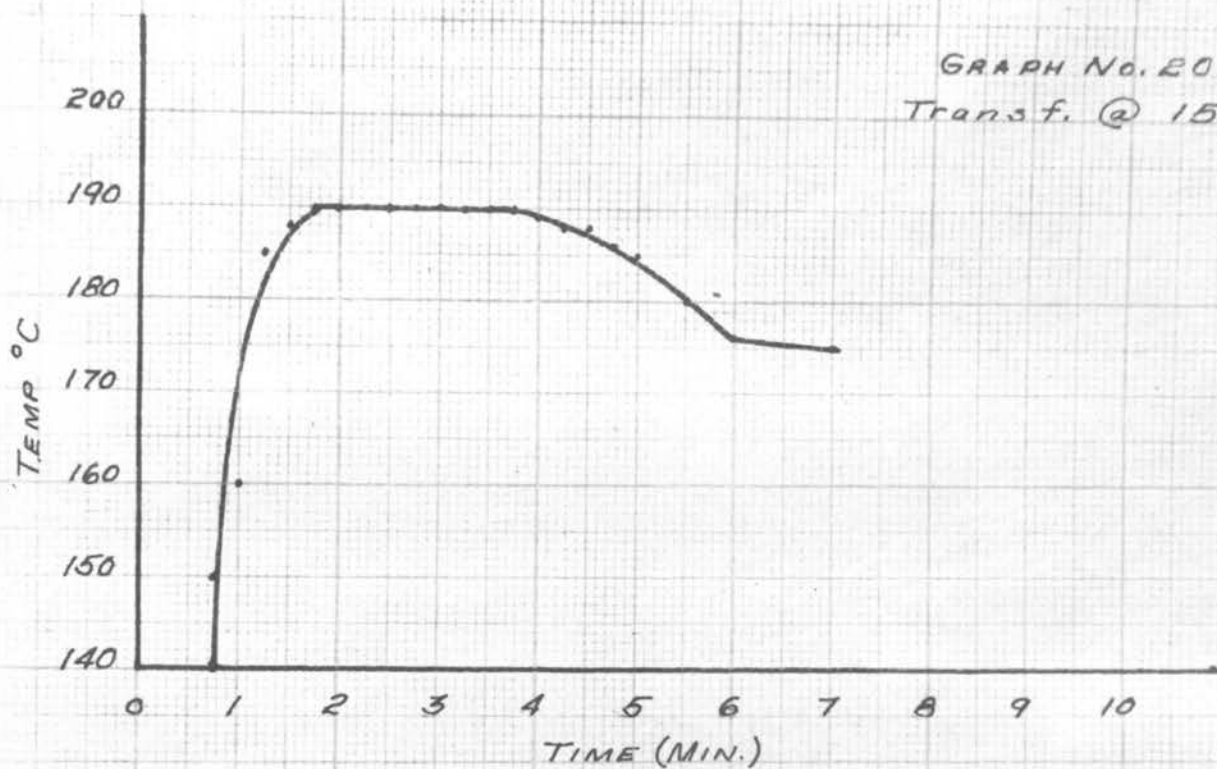


FIGURE 19



GRAPH No. 24
Transf. @ 235°C

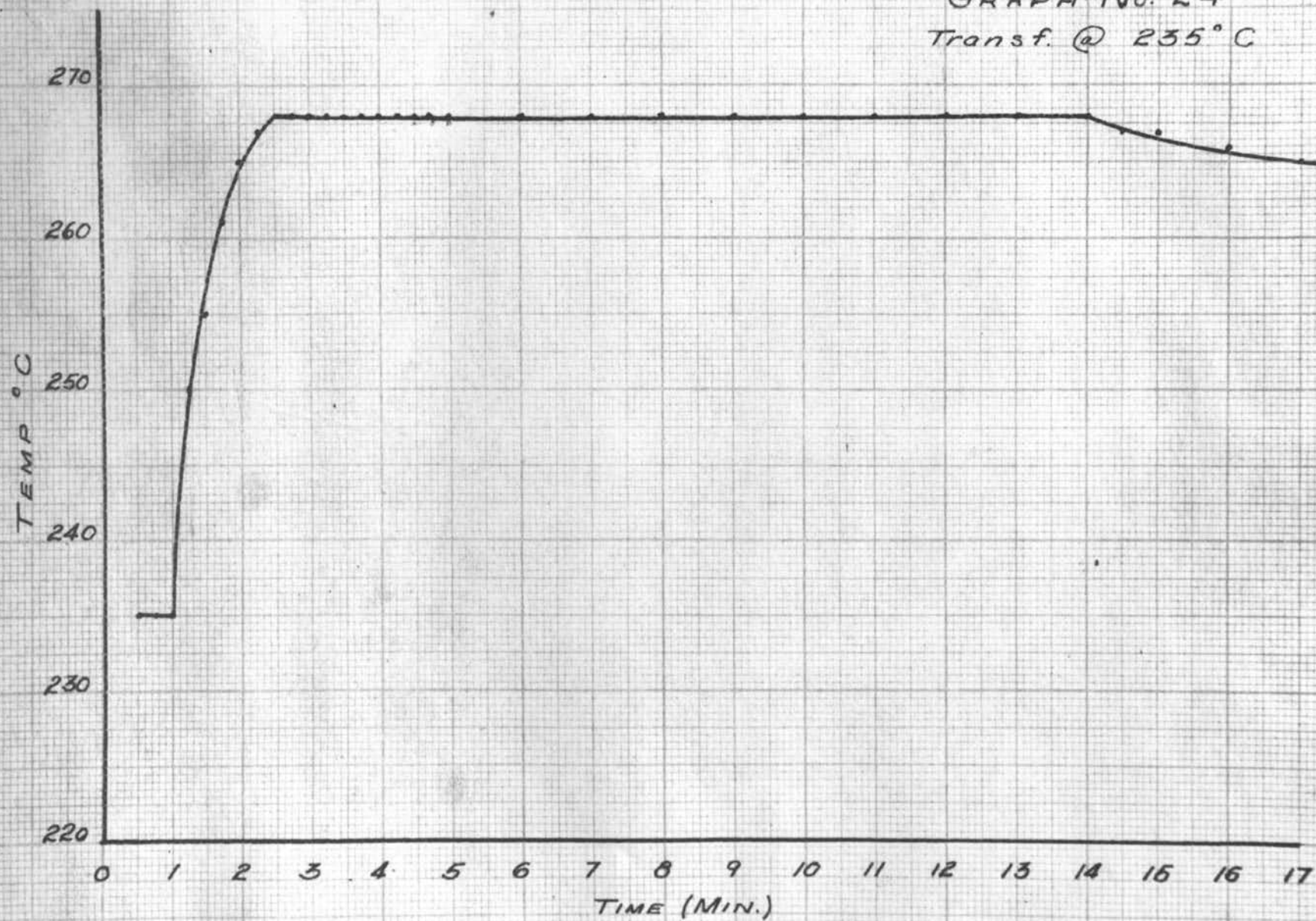


FIGURE 20

GRAPH No. 25
Transf. @ 235°C.



FIGURE 21

GRAPH No. 26
Transf. @ 235°C.

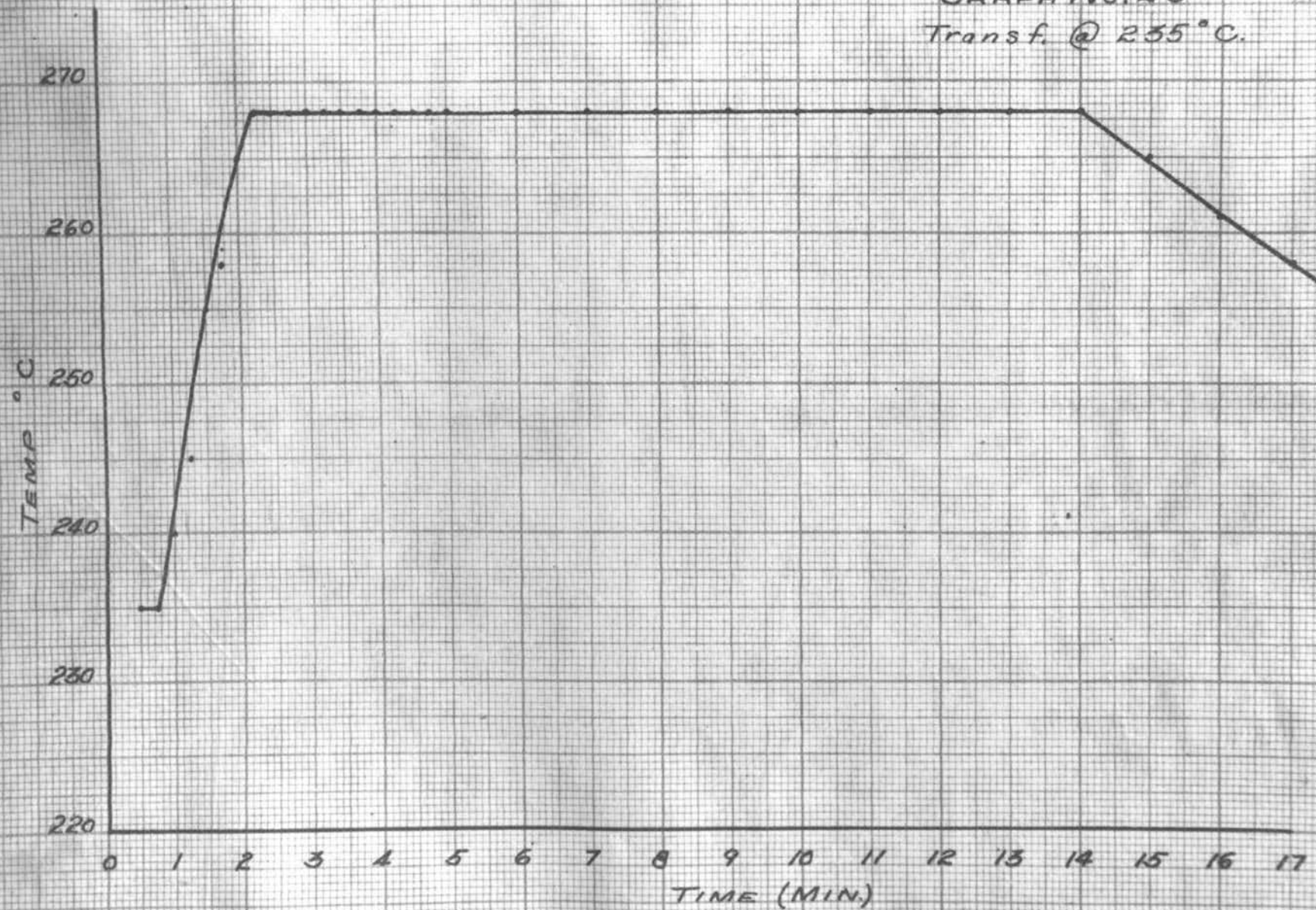


FIGURE 22

GRAPH No. 27
Transf. @ 250°C.

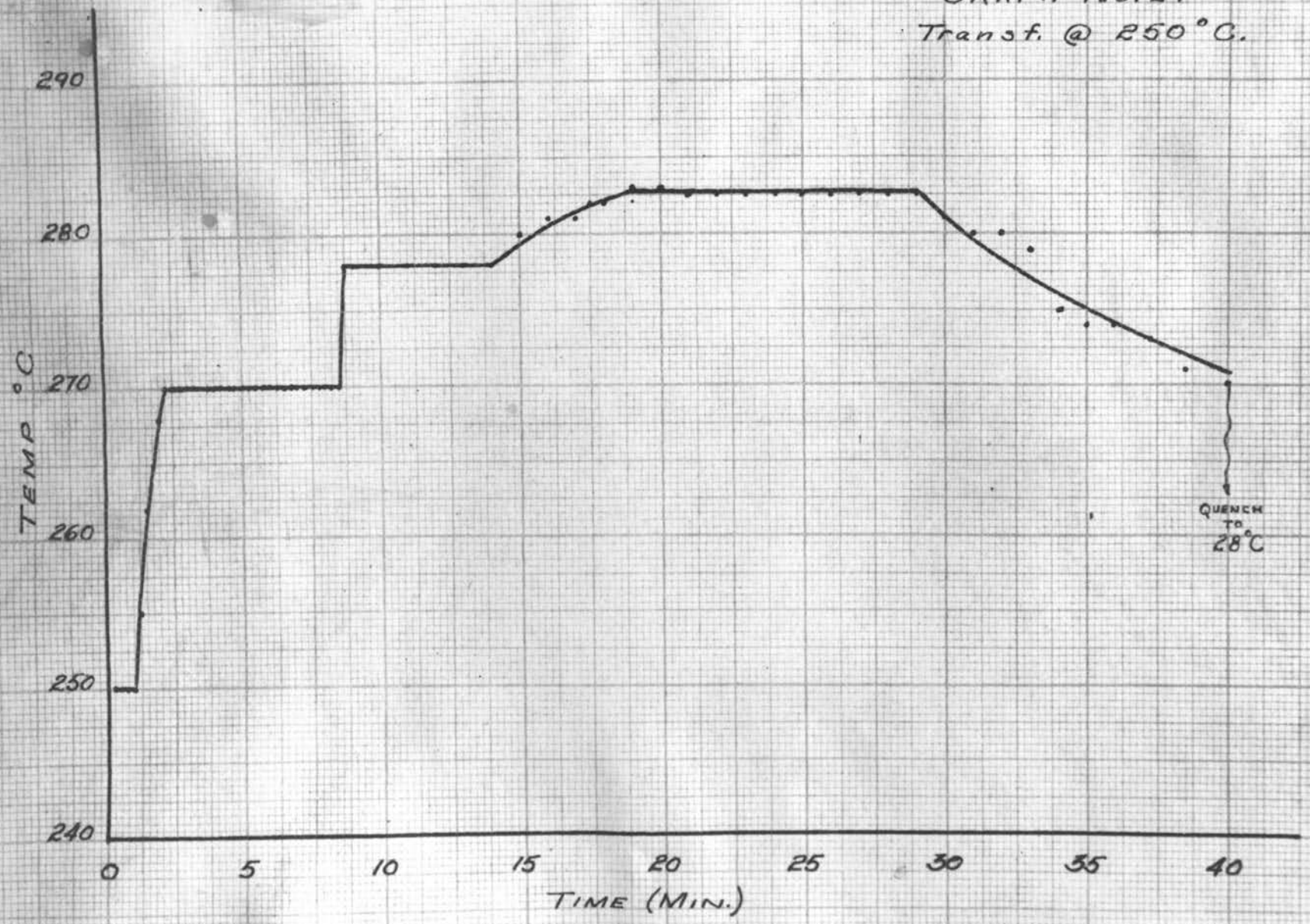


FIGURE B5

TABLE IIITHERMAL ANALYSIS DATA

Figure Number	Graph Number	Quenching Medium	Transformation Temperature	Transformation Start	Transformation Finish	Total Required Time
7	1	Water	0°C	4.50 min.	10.00 min.	5.50 min.
7	2	"	"	1.50 "	8.00 "	6.50 "
8	3	"	"	3.50 "	8.00 "	4.50 "
8	4	"	"	2.50 "	9.50 "	7.00 "
9	4a	"	"	3.75 "	10.50 "	6.75 "
9	4b	"	"	1.25 "	5.25 "	4.00 "
			Average	<u>2.83 min.</u>	<u>8.54 min.</u>	<u>5.71 min.</u>
10	5	Water	28°C	0.75 min.	4.00 min.	3.25 min.
10	6	"	"	1.00 "	4.00 "	3.00 "
11	7	"	"	1.00 "	4.00 "	3.00 "
11	8	"	"	0.75 "	4.00 "	3.25 "
12	9	"	"	0.50 "	3.75 "	3.25 "
12	10	"	"	0.75 "	4.75 "	4.00 "
			Average	<u>0.791 min.</u>	<u>4.08 min.</u>	<u>3.29 min.</u>

TABLE III (CONTINUED)

Figure Number	Graph Number	Quenching Medium	Transformation Temperature	Transformation Start	Transformation Finish	Total Time Required
13	11	Water	50°C	0.5 min.	3.00 min.	2.50 min.
13	12	"	"	0.5 "	3.75 "	3.25 "
14	13	"	"	0.5 "	3.75 "	3.25 "
			Average	<u>0.5 min.</u>	<u>3.33 min.</u>	<u>3.00 min.</u>
14	14	Water	100°C	0.5 min.	3.50 min.	3.00 min.
15	15	"	"	0.5 "	4.25 "	3.75 "
15	16	"	"	0.5 "	4.50 "	4.00 "
16	17	"	"	0.5 "	5.00 "	4.50 "
			Average	<u>0.5 min.</u>	<u>4.31 min.</u>	<u>3.81 min.</u>
17	18	Crisco	150°C	0.75 min.	3.75 min.	3.00 min.
17	19	"	"	0.75 "	2.75 "	2.00 "
18	20	"	"	0.75 "	3.75 "	3.00 "
			Average	<u>0.75 min.</u>	<u>3.42 min.</u>	<u>2.66 min.</u>

TABLE III (CONTINUED)

Figure Number	Graph Number	Quenching Medium	Transformation Temperature	Transformation Start	Transformation Finish	Total Time Required
18	21	Crisco	200°C	0.50 min.	5.00 min.	4.50 min.
19	22	"	"	0.50 "	5.00 "	4.50 "
19	23	"	"	0.50 "	4.00 "	3.50 "
			Average	<u>0.50 min.</u>	<u>4.67 min.</u>	<u>4.17 min.</u>
20	24	Crisco	235°C	1.00 min.	14.00 min.	13.00 min.
21	25	"	"	0.75 "	12.00 "	11.25 "
22	26	"	"	0.75 "	14.00 "	13.25 "
			Average	<u>0.835 min.</u>	<u>13.35 min.</u>	<u>12.50 min.</u>
23	27	Crisco	250°C	1.00 min.	Unknown	-----

(See Discussion)

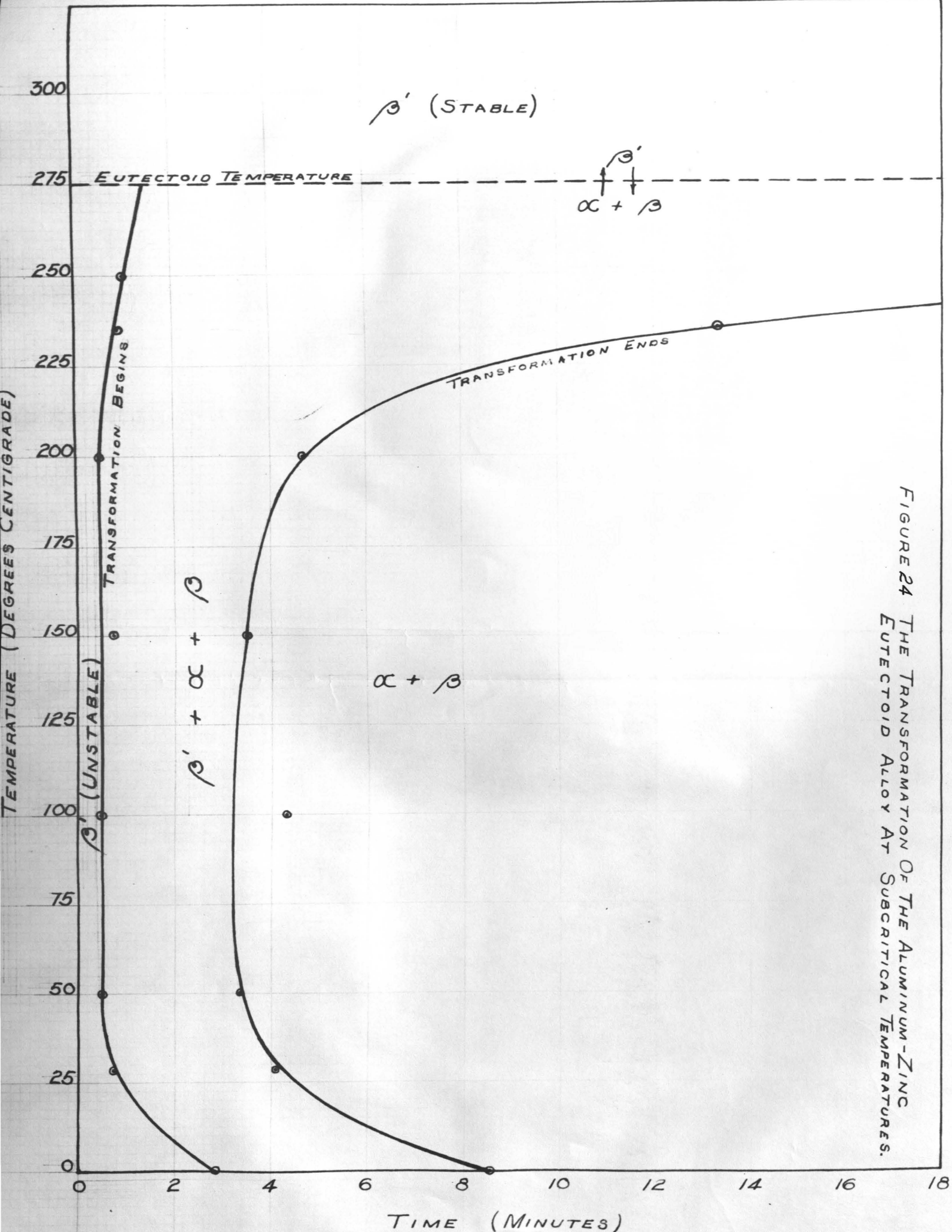


FIGURE 24 THE TRANSFORMATION OF THE ALUMINUM-ZINC EUTECTOID ALLOY AT SUBCRITICAL TEMPERATURES.

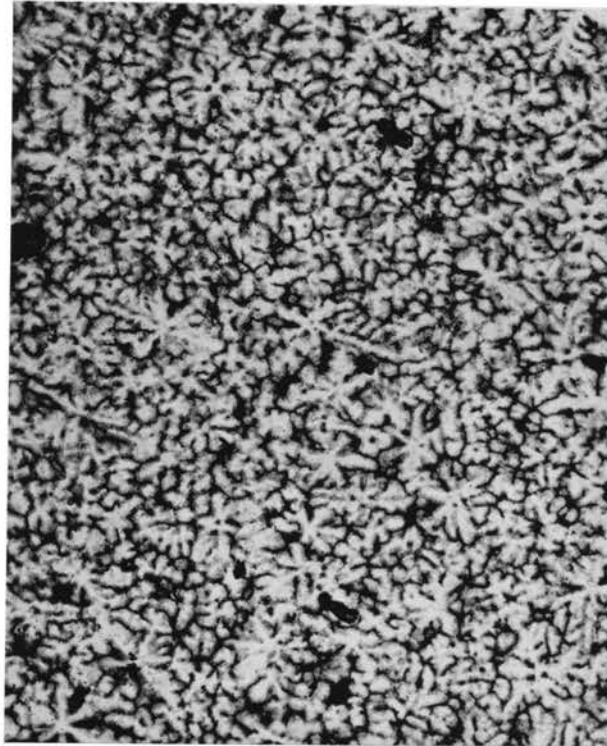


Figure 25

100 x

Al-Zn Eutectoid Alloy in the "As Chill
Cast" Condition. Etched with 3 % Nital

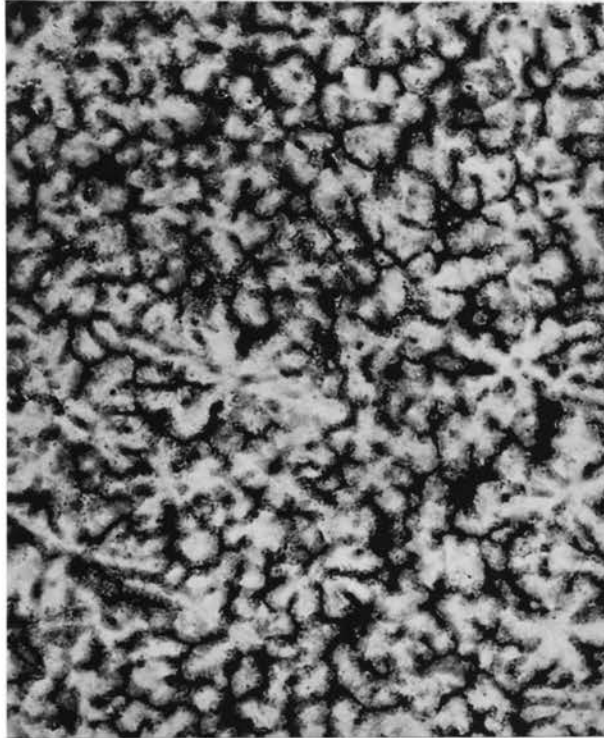


Figure 26

200 x

Al-Zn Eutectoid Alloy in the "As Chill
Cast" Condition. Etched with 3 % Nital

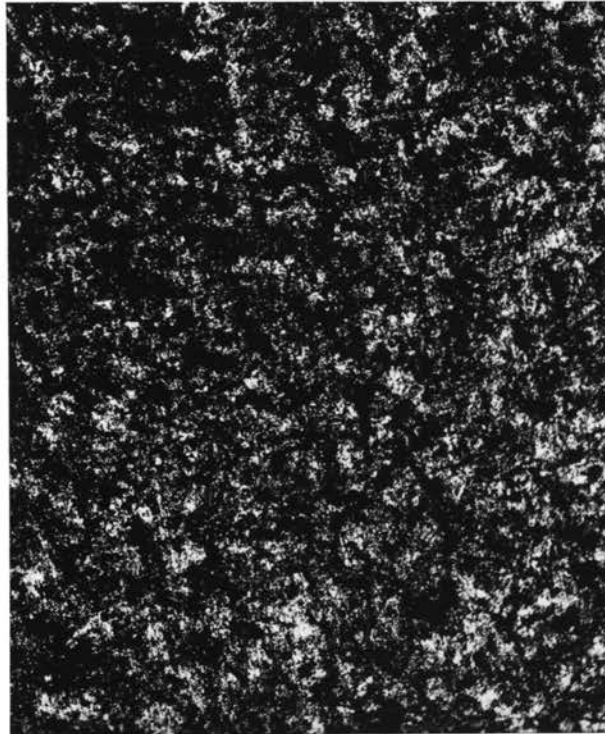


Figure 27

100 x

Al-Zn Eutectoid Alloy Annealed 105 hours at 360°C, then 210°C for 15 hours, then furnace cooled to room-temperature. Dark etching constituent is the unresolved "pearlitic" structure. Etched with 3 % Nital.

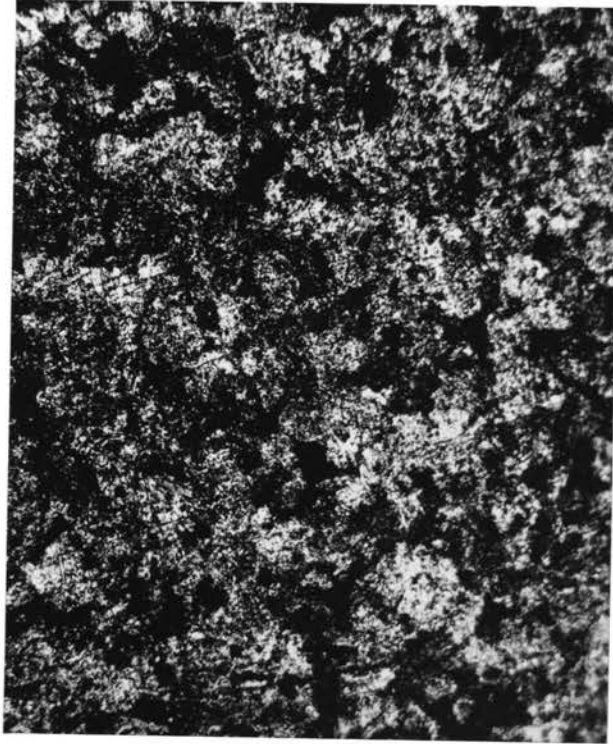


Figure 28

200 x

Al-Zn Eutectoid Alloy Annealed 105 hours at 360°C , then 210°C for 15 hours, then furnace cooled to room-temperature. Dark etching constituent is the unresolved "pearlitic" structure. Etched with 3 % Nital.

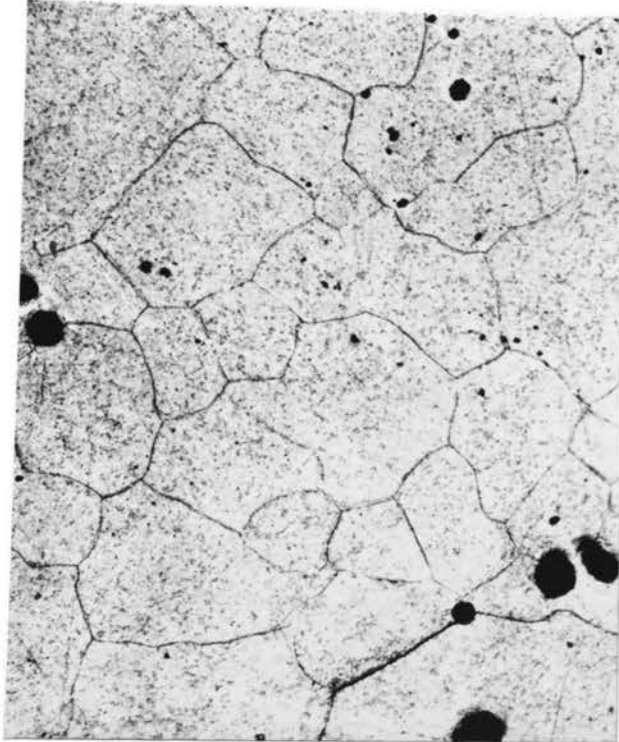


Figure 29

200 x

Beta-prime solid solution thirty-
seconds after quenching in ice-water.
Etched with 3 % Nital 30 seconds
after quenching.

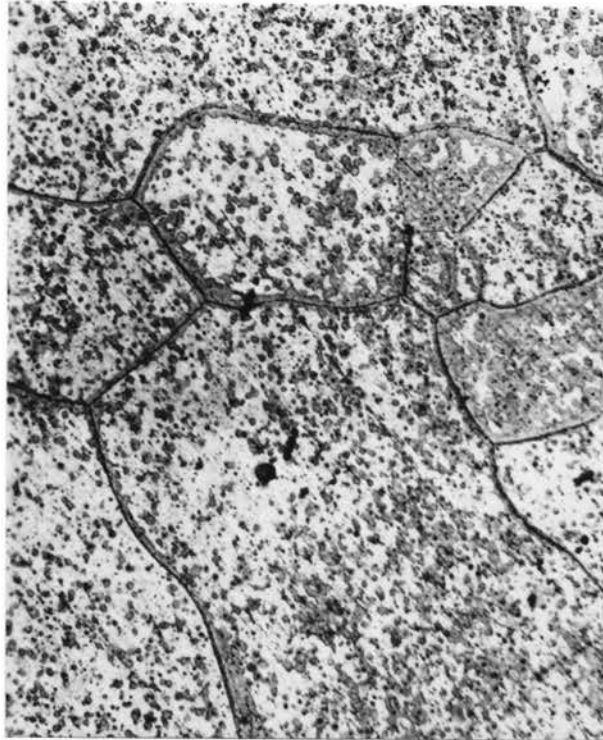


Figure 30

200 x

Al-Zn eutectoid alloy one minute after quenching in ice-water. Single phase beta-prime structure beginning to decompose into duplex structure of alpha plus beta. Etched with 3 % Nital.

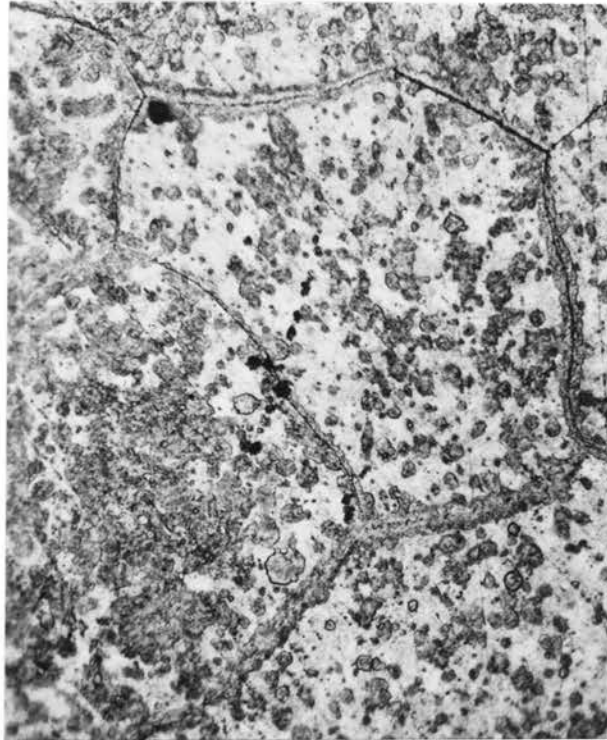


Figure 31

500 x

Al-Zn eutectoid alloy one minute after quenching in ice-water. Single phase beta-prime structure beginning to decompose into duplex structure of alpha plus beta. Etched with 3 % Nital.

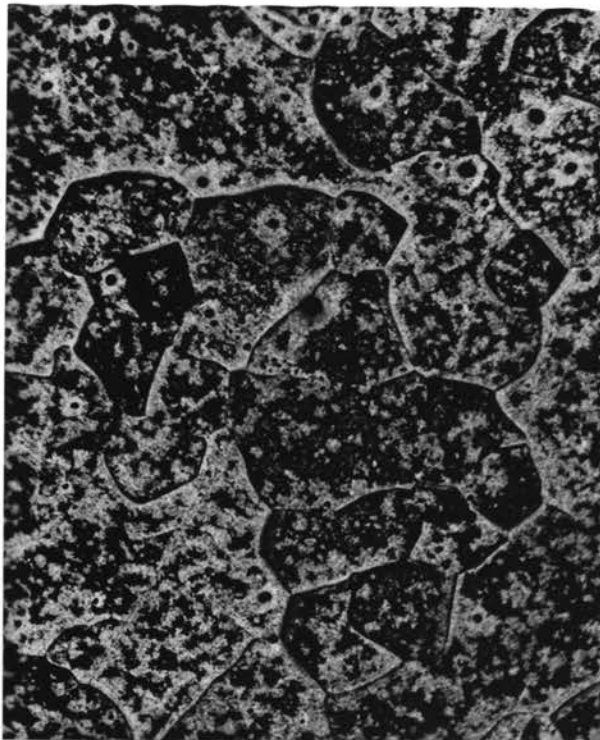


Figure 32

200 x

Al-Zn eutectoid alloy two and one-half minutes after quenching in ice-water. White areas designate unchanged beta-prime solid solution. Dark areas designate fine mixture of alpha and beta phases. Etched with 3 % Nital.

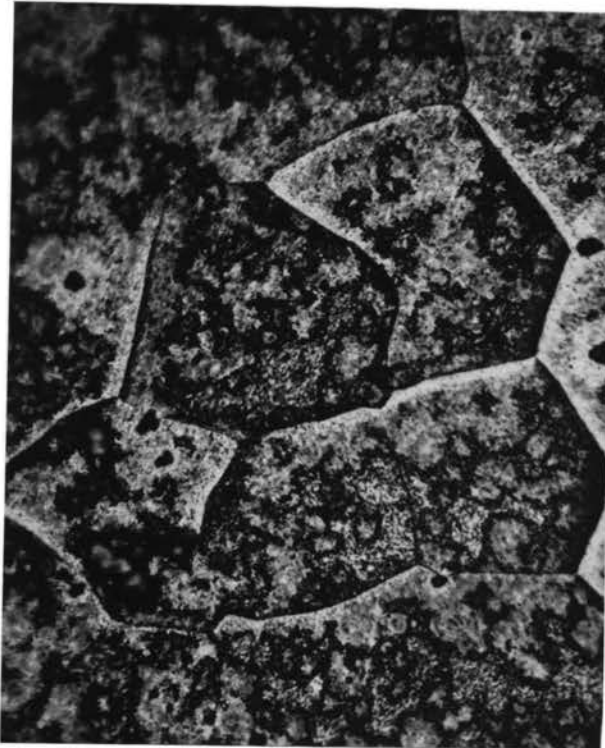


Figure 33

500 x

Al-Zn eutectoid alloy two and one-half minutes after quenching in ice-water. White areas designate unchanged beta-prime solid solution. Dark areas designate fine mixture of alpha and beta phases. Etched with 3 % Nital.

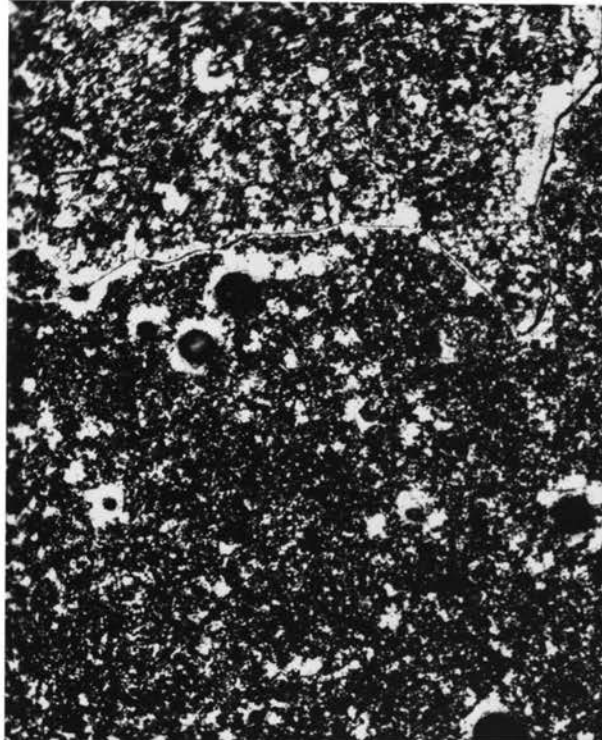


Figure 34

200 x

Al-Zn eutectoid alloy eight and one-half minutes after quenching in ice-water. White areas designate unchanged beta-prime solid solution. Dark areas designate fine mixture of alpha and beta phases. Etched with 3 % Nital.

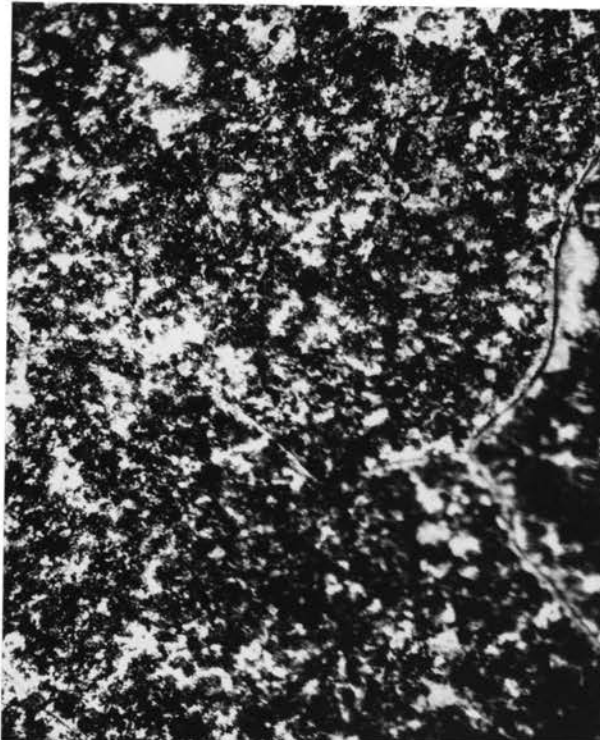


Figure 35

500 x

Al-Zn eutectoid alloy eight and one-half minutes after quenching in ice-water. White areas designate unchanged beta-prime solid solution. Dark areas designate fine mixture of alpha and beta phases. Etched with 3 % Nital.

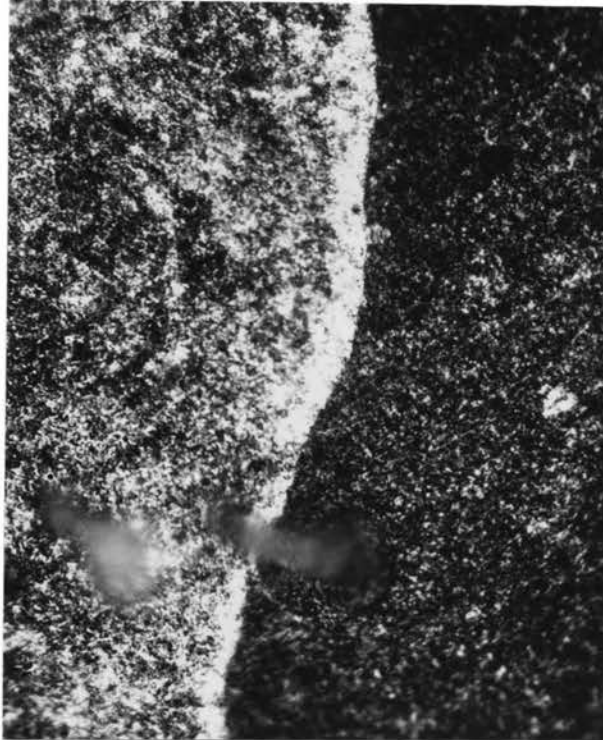


Figure 36

750 x

Al-Zn eutectoid alloy eight and one-half minutes after quenching in ice-water. The structure indicates the variation in the rate of transformation from grain to grain in the specimen.

THEORETICAL CONSIDERATION

The author believes that a detailed discussion of the theories of eutectoid transformation is beyond the scope of this investigation. However, it would seem appropriate to review a few of the characteristics of eutectoids as applicable to this research and to indicate the latest theory under consideration regarding the mode of transformation in these alloys.

The equilibrium diagram of a eutectoid alloy indicates a solid phase, which is stable only at high temperatures, and which on cooling converts itself into a heterogeneous mass of both neighboring solid phases. The eutectoid construction in the equilibrium diagram is denoted by the underlined "V" form similar to that construction found in the case of eutectics.

(52)
Doig, in his review of fundamental research,

(52) Doig, J. R., "Crystal Structure and Phase Transformations", Metals Review, Vol. 22, No. 12, December, 1949.

summarizes the latest accepted theories regarding transformation in the solid state. He treats the nucleation of phase transformations as follows: "A theory of transient nucleation, which appeared about 18 months ago, now makes it possible to explain all types of transformation in terms of nucleation and growth. This theory, first proposed by

(53)
Turnbull also explains why an incubation period is

(53) Turnbull, D., Metals Technology, Vol 15, June, 1948.

observed in such transformations as that from austenite to pearlite or bainite, while no incubation period is necessary for martensitic transformations.

"Over the past ten years or so, the isothermal transformation studies of Mehl and his co-workers established that pearlite forms by a process of nucleation and subsequent growth of the nuclei in the austenite matrix. They measured the rate of nucleation as a function of time. After the incubation period, during which no nuclei were detected, nucleation began at a low rate and gradually increased until it reached a steady - state rate.

"The theory of transient nucleation, as proposed by Turnbull, is an extension of the Volmer-Becker theory which had satisfactorily explained the rate of nucleation of droplets from condensed vapor but had failed to predict the incubation period for transformation in solids until it was revised by Turnbull. In this theory, it is assumed that there is a certain minimum or critical size of nucleus of a stable phase that is able to grow spontaneously in an unstable matrix phase. Nuclei of size smaller than this are always present because of chance arrangement of atoms, but they suffer continual fluctuation in size by gaining or

losing atoms through thermal motion. Hence, they are called embryos.

"For every temperature, there is a definite equilibrium size of embryo. Furthermore, the theory predicts that the rate of nucleation is proportional to the number of those embryos whose size is just smaller than the critical size. At this point, Turnbull injected his important revision that explained the incubation period. He pointed out that when the alloy is cooled from above the transformation temperature to a temperature not far below it, the equilibrium distribution of embryos does not take place immediately but requires time because the rate of growth of embryos by addition of atoms is limited by diffusion. Hence, the rate of nucleation is negligibly small at first and does not become appreciable until the concentration of embryos of near-critical size has been built up. As the distribution of embryo sizes approaches equilibrium, the nucleation rate increases until it, too, reaches a steady state.

"In a more quantitative study of transient nucleation, Hobstetter⁽⁵⁴⁾ considered that the chemical composition of

(54) Hobstetter, J. N., Metals Technology, Vol 15, Oct. 1948.

the embryos is important as well as their size, and was able to explain the shape of the C-curves in isothermal

transformation diagrams. In his calculations, he assumed a definite embryo shape and a decomposition within the solubility gap in an equilibrium diagram."

From what has been quoted above, it can readily be deduced that the transformation products of a eutectoid decomposition would be dependent upon the rate at which the phase which is stable at high temperatures is cooled. This point is best illustrated by the effect of increase in cooling rate on the decomposition products of austenite. When austenite is cooled at a very slow rate, but faster than the equilibrium cooling rate, the product of transformation will be coarse pearlite. As the cooling rate is increased, the structure of the pearlite changes. That is to say, the distance between the alternate plates of ferrite and carbide is reduced and causes the structure to appear finer. This process of transformation involves both time and diffusion. When however, the rate of cooling is increased considerably, so that it exceeds a certain "critical cooling rate", it is found that the transformation no longer is dependent wholly upon time and diffusion but also upon mechanical shear within the grains themselves. The product of transformation is then termed "martensite" and the rate of cooling necessary for its cooling is, of course, dependent upon the composition of the austenite. Attention must be called to the fact that intermediate transformation structures are to be found between coarse pearlite and

martensite and that the character and appearance of these structures are also dependent upon the rate of cooling and upon the time and diffusion factors.

Evidence indicates that this dependence of structure on cooling rate could easily be carried over from one eutectoid alloy in a given system and be made to apply, at least qualitatively, to other such alloy systems. This is borne out by the similarity between the transformation products of the copper-aluminum and the iron-carbon eutectoid alloys.

It would seem logical to assume that if the rate of transformation tends to exert such a strong influence on the structure and properties of the transformation products in one or two alloy systems, that the methods of study which are applicable to these two systems could be made to apply to a third, or even possibly to all eutectoid alloys. Previous investigation has shown that the study of the time-temperature relationship with regard to transformation have contributed much toward an insight concerning structural changes which take place during cooling at a variety of different rates. From this insight, much needed physical information has evolved.

At this point in the discussion, it seems appropriate to review some of the fundamental information regarding the eutectoid transformation as applied to a time-temperature-transformation study. For an alloy of eutectoid composition

there is a characteristic temperature found on the alloy equilibrium diagram which may be referred to as the "eutectoid temperature". Above this temperature the single solid phase will remain stable for an indefinite time. When, however, the temperature is lowered below this critical temperature and is held constant, the transformation of the single solid solution phase is not instantaneous, but requires for its onset and for its completion definite periods of time which should be characteristic of the temperature level at which the alloy is being held. The most convenient method of representing this phenomenon is by means of a time-temperature-transformation diagram. The time axis may be made logarithmic or straight time as best suits the rates of alloy transformation in question, the logarithmic scale being the most suitable for decompositions requiring excessively long periods of time. Temperature is usually plotted as the ordinate.

Past experience has shown that the time-temperature-transformation curves plotted for steels of various compositions and for the decomposition of the "beta" copper-aluminum alloy assume the shape of a "0" or "integral sign". Usually, the diagrams are, at any temperature level below the "eutectoid temperature", divided into three time zones: 1) that in which the high temperature phase, though unstable, has not yet begun to transform (this zone lies to the left

on the diagram); 2) that in which the transformation proceeds to completion at constant temperature; and 3) that in which the transformation is complete. It must be understood that these zones indicate the rate of transformation at temperatures where time and diffusion are the predominant factors in the transformation and do not constitute divisions in the diagram below the temperature at which martensite is formed.

There would seem to be little doubt as to the existence of a proper theory to explain the shape taken by these time-temperature-transformation curves, provided the exact mechanism of transformation is known. The concept of incubation and formation of embryos, as proposed by Turnbull ⁽⁵⁵⁾,

(55) Turnbull, D., op. cit., p. 70

apparently is a recent step toward the understanding of the time required for the onset of nucleation. When this recent research is considered along with the voluminous work which has been completed in the past it can be seen that the proper answers to the mysteries involved in the phenomena of eutectoid transformation lie in the not too distant future. However, it must be kept in mind that the present knowledge of this mechanism has resulted from detailed study of only a small percentage of all possible eutectoid alloys, so that no hard and fast rules for the mechanism, as a whole, can be expected at this time. Complete knowledge and under-

standing could not be anticipated until all such systems were studied in detail and the similarities between individual alloys catalogued and explained.

DISCUSSION OF EXPERIMENTAL DATA

Examination of the experimental thermal analysis time-temperature graphs, which were established during transformation of the aluminum-zinc eutectoid alloy at subcritical temperatures, indicates certain changes in slope which require detailed consideration. For the purpose of discussion the individual curves may be divided into definite portions which are: 1) a flat zone, located at the left of the graph, which shows that the specimen temperature remained constant until the onset of transformation; 2) a rapid change in slope denoting a steep rise in temperature caused by a rapid generation of heat within the specimen and indicating the onset of transformation; 3) a second flat portion, or "plateau", indicating that the specimen temperature remained constant due to a balance in the rate of heating and rate of cooling of the test piece within the calorimeter or furnace; and 4) a portion showing the gradual cooling of the specimen as it approached the temperature of the calorimeter or furnace. (See Figure 7 to 26, inclusive.)

Time-temperature curves established in earlier published research do not contain the flat "plateau" regions found in this investigation. This variation in curve shape is due, no doubt, to the testing conditions set up for this experimentation. That is, the progress of alloy transfor-

mation had not been followed while the test piece was maintained at a constant temperature in an air-filled container. On the contrary, transformation data of this type had been recorded while the specimen was wrapped in a cloth and held at room temperature ^(55,56,57), or while

(55) Hanson, D. and Gayler, M. L. V., op. cit., p. 14

(56) Tanabe, T., J. Inst. Metals, op. cit., p. 16

(57) Kennedy, R. G., Metals and Alloys, op. cit., p. 18

the specimen was surrounded by some insulating material other than air ⁽⁵⁸⁾. Since the testing conditions vary from those

(58) Fuller, M. L. and Wilcox, R. L., op. cit., p. 18

reported in the literature, the time-temperature curves shown in this investigation could not be expected to agree in shape. Curves published earlier have shown no indication as to the formation of "plateaus", but rather, have shown a rapid increase in temperature to a rounded maximum with a subsequent rapid drop-off in temperature. The author believes that this shape is due to the rapid dissipation of heat from the specimen.

In the published work cited above, it has been the accepted policy to designate the onset of transformation

as the time at which a rapid change in slope of the curve took place and to designate the completion of transformation as the time at which the temperature reached a maximum. Owing to the different character of the curves plotted in this research, the author was forced to investigate the application of this accepted policy to the experimental graphs. It was found that the onset of transformation was indicated as the time of rapid rise in specimen temperature as shown by rapid change in slope. In order to determine when transformation was completed, the author first made a test run to determine the length of the "plateau" on the time-temperature curve for an individual specimen. The specimen was then re-heat-treated and time-temperature data collected a second time, but instead of allowing the reaction to go to completion, the specimen was quenched from the "plateau" temperature at some intermediate time. If the transformation had been completed at the time of this quenching, no subsequent heat generation or temperature rise from the specimen could have been expected. However, it was found that a temperature rise did take place, thus indicating that the "beta" decomposition had not gone to completion at the time of quenching. The possibility of some reaction remaining after the curve showed temperature drop-off from the "plateau" temperature (due to cooling of specimen toward the temperature of the air container) was then considered. This test was conducted in the same manner as the preceding

test and the results proved negative. This indicated that the decomposition had gone to completion in this range, so it was concluded that transformation ended when the temperature readings began to decrease from the "plateau" portion of the curve. This general procedure was repeated for each of the subcritical temperatures under consideration in this investigation and the results were identical in all cases. The writer then adopted the policy that the onset of transformation was indicated by a rapid rise in temperature or change in slope of the curve, and that the completion of transformation was indicated by the last time-temperature reading recorded in the "plateau" region of the curve.

Figure 23 requires explanation because the transformation at this temperature was not allowed to go to completion. This was done for the following reasons: when the air furnace was held at two hundred and fifty degrees centigrade and the test piece allowed to decompose at this temperature, the heat generation caused the temperature of the specimen to rise above the "eutectoid temperature" of the alloy. Theoretically, all things being equal the alloy would remain as single phase beta-prime under these conditions. However, this was not the case. The temperature of the piece dropped after twenty-nine minutes, thus indicating that transformation has gone to completion. The test piece was then quenched into water at twenty-eight degrees at forty minutes and almost immediately a heat generation

resulted. This showed that the transformation had not been completed at this time and that the time-temperature curve was of no value. The curve is included only to indicate the alloy behavior under these circumstances.

The reader's attention is called to Figures 15 and 16, Graphs 15, 16 and 17. It will be noted that the left portion of these curves is unique in that the expected plateau is replaced by a sharp drop in temperature to a minimum and then a sharp rise to the "plateau". This construction on each curve resembles in appearance the construction found in cooling curves of pure metals where a supercooling effect is present. The author can offer no explanation as to the meaning of this construction on the graphs.

Attention is called to those time-temperature curves which show no flat portion to the left of the graph. In cases such as these, there was an immediate rise in temperature following the first time-temperature reading. This indicates that transformation began immediately after quenching.

The Time-Temperature-Transformation curve as established from the time-temperature graphs is shown in Figure 24. It will be noted that the curve assumes essentially the same shape as curves established for the iron-carbon and copper-aluminum eutectoid alloys. Examination of the points plotted on this "C" curve appear to follow fairly well, with the exception of the point which indicates completion

of transformation at one hundred degrees centigrade. This particular point, it will be noticed, appears too far to the right. The author believes that this is due to the fact that the quenching medium was changed just above this temperature, that is to say, that the ability to extract heat from the alloy specimen varied in the water and in the Crisco. The change in quenching rate may possibly have some bearing on the time required for transformation.

Examination of the photomicrographs (Figure 29 to 36, inclusive) indicates the structural changes which take place during transformation. It must be noted that the included micrographs should not be correlated with the Time-Temperature-Transformation curve, Figure 24, because the treatment of the metallographic specimens did not correspond to that of the thermal analysis specimens. The metallographic specimens were quenched from the heat-treatment temperature of three hundred and fifty degrees into ice-water and then allowed to transform at room temperature. This ice-water quench variation was performed in order that the transformation might be delayed long enough for necessary polishing and other manipulation of the sample to be accomplished.

Figure 29 shows the homogeneous structure of the beta-prime constituent thirty seconds after quenching. Figures 30 and 31 show this structure of the alloy one minute after quenching. It will be noted that the single phase structure is breaking down again into a duplex structure and that

transformation is beginning both at the grain boundaries and within the grains themselves. The darkening at the grain boundaries does not appear to be uniform even in an individual grain. Transformation appears to be taking place at the grain boundary on one portion of a single grain while no transformation has progressed in an adjacent portion of the same grain. Figures 32 and 33 show that transformation has progressed throughout the sample. It will again be noted that the transformation rate varies from grain to grain. The dark etching portions indicate an extremely fine mixture of the alpha and beta particles produced as a result of the beta-prime decomposition. Figures 34 and 35 represent the structure eight and one-half minutes after quenching. It can be seen that the decomposition or transformation has proceeded much farther and that almost all portions of the specimen have been affected. The white areas represent the beta-prime phase yet unchanged.

Figure 36 indicates the alloy structure eight and one-half minutes after quenching and shows the extent to which transformation at this time varies from grain to grain in the alloy.

The author wishes to call the reader's attention to the blurring which appears in many of the photomicrographs. This blurring is due to the uneven specimen surface which is caused by shrinkage of the alloy during transformation.

This shrinkage varies in magnitude from grain to grain and renders impossible the focusing of all portions of the microscope field at one time.

SUGGESTED FURTHER STUDY

The author realizes the improvement which could be made on this research, primarily, from the standpoint of method of measurement of the onset of the transformation at several subcritical temperatures. Temperature measurements are always accompanied by appreciable time lags, and a method of measurement which would eliminate the possibility of this source of error is to be recommended. The author feels that measurement of the rate of transformation of beta-prime by means of dilatometry, electrical resistivity or conductivity changes, etc. might eliminate this source of error.

The correlation of isothermal hardness changes at many subcritical temperatures with this thermal analysis study would probably shed much light on the mechanism of the transformation. Just such a study is now in progress in these laboratories under the direction of Dr. D. S. Eppelsheimer.

An extension of the research of Edmunds⁽⁵⁹⁾ on the

(59) Edmunds, G., op. cit. p. 17

study of beta-prime single crystals using the Laue method may perhaps shed much light on the mechanism of transformation and possibly explain the variation of the rate of transformation which appears to exist in each grain of a

polycrystalline mass of the beta-prime phase.

An extension of the research which has been done concerning the effect of additional elements on the rate of beta-prime transformation would be very interesting and also a consideration of the effect, if any, of grain size on the transformation.

CONCLUSIONS

The study of the rate of transformation of the aluminum-zinc eutectoid alloy by means of metallography and thermal analysis indicates the following conclusions:

1. There appears to be some relation in the appearance or shape of the Time-Temperature-Transformation curve of this alloy and the eutectoid iron-carbon and copper-aluminum alloys.

2. The portion of the Time-Temperature-Transformation diagram of this alloy between zero and two hundred and seventy-five degrees centigrade resembles the portion of the "C-curve" of the iron-carbon eutectoid alloy between four hundred and fifty degrees centigrade and the A_{c1} temperature. That is, the portion between the temperature range where upper bainite is formed and where coarse pearlite is formed.

3. The pearlitic or lamellar structure apparently is produced only when the alloy is slowly cooled. Rapid cooling by quenching produces a finely divided duplex structure composed of the alpha and beta solid solutions. This structure appears to resemble troostite or sorbite of steels.

4. Metallographic study shows considerable variation in the transformation rate from grain to grain in each sample examined.

APPENDIX
PROCEDURE FOR DETERMINATION OF ZINC IN
ALUMINUM-ZINC ALLOY

- 1.) Five grams of alloy sample dissolved in hot dilute HCl.
- 2.) Diluted to exactly 600 c.c.
- 3.) 25 C.C. taken for titration

$$\frac{25}{600} \times 5 = 0.2082 \text{ gm. alloy}$$
- 4.) Diluted the 25 c.c. sample to about 175 c.c. in a 250 c.c. beaker.
- 5.) Added 7 c.c. HCl; heated to about 90°C in preparation for titration.
- 6.) Prepared a 5 % Uranium nitrate solution for outside indicator, and placed numerous globules of this indicator on a sheet of white paper.
- 7.) Filled buret to zero with $K_4Fe(CN)_6$
 (1 c.c. = 0.00624 gm. Zn approx.)
- 8.) Approximately one-half of hot solution to be titrated was poured into a spare 250 c.c. beaker.
- 9.) Ferrocyanide solution was run slowly into the hot solution with frequent testing on spot paper indicator.
- 10.) Observed a change from greenish to a white cloudiness in beaker. (Sometimes this white color is not pronounced)
- 11.) End point in titration is encountered when faintest

brownish coloration is observed in the indicator globule.

- 12.) Spare solution was then mixed with that in the beaker under the buret; and about 50 c.c. of solution poured back into the spare beaker.
- 13.) Titration resumed until end-point reached
- 14.) Solutions mixed and 50 c.c. again poured back into spare beaker.
- 15.) Titration resumed, but more slowly than before. When brownish coloration appeared the solutions were again mixed.
- 16.) Solutions then poured back and forth twice from beaker to beaker to rinse out any incompletely titrated solution which may have adhered to spare beaker.
- 17.) Titration then resumed using 1/2 c.c. at a time and testing on spot paper after each addition.
- 18.) The end point appears after 2-5 seconds and the color should be faintly brown.
- 19.) 0.5 c.c then deducted from the total volume titrated from the buret for a blank.
- 20.) If 30.5 c.c. of $K_4 Fe (CN)_6$ were titrated, then:

$$30.5 - 0.5 = 30 \text{ c.c } K_4 Fe (CN)_6$$

$$\frac{30 \text{ cc (Value/cc)}}{0.2082} = \% Zn$$

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