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REDUCTIONS IN THE MANUFACTURING CYCLE FOR THE FLUORINATION PROCESS OF THE 234-5 BUILDING

By

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Separations Section

Manufacturing Department

October 11, 1954

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I. INTRODUCTION

In the dry chemistry process of the Metal Fabrication Building, plutonium oxalate as received from the Isolation Building is converted to plutonium tetrafluoride and the fluoride is then reduced to the metal. The oxalate-fluoride conversion involves oxidation of the oxalate and subsequent fluorination of the oxide, utilizing anhydrous HF gas. Batch operation is practiced. The standard batch for the period covered by this report was 400 g. Pu.

II. SUMMARY

Since startup of the RMA Line in the 234-5 Building, the time to effect the oxalate-fluoride conversion in Task II has been steadily reduced. The initial Task II time cycle of 8.25 hours has been cut to 4.33 hours primarily by reducing the temperature of the fluorination cycle and the time required at that temperature. Both of these variables were reduced under controlled conditions in a stepwise manner. The use of preheated process gases aided materially in accomplishing these cycle reductions. The overall effects on the process have been a large decrease in the number of refluorinations required because of incomplete conversion and approximately a two-fold increase in production capacity for Task II. A moderate increase in the production of the trifluoride occurred but reduction yields have remained high and product purities have not been affected. The major cycle improvements and their effects are summarized in Table I below:

Table I

Improvement	Date of Improvement	Effects of Improvement
1. Reduced the fluorination period at 600C from 2 hours to 1 hour.	December 1952	Improvements 1, 2, and 3 reduced the time cycle from 8.25 hours to 5.25 hours.
2. Reduced the drying period at 190C from 1 hour to 15 minutes.	December 1952	
3. Reduced the furnace purging period after fluorination from 1¼ hours to 15 minutes.	January 1953	
4. Combined the drying and oxidation steps.	September 1953	Reduced the time cycle from 5.25 hours to 4.42 hours.
5. Instituted the use of preheated process gases.	February 1954	Reduced the refluorination rate by about 35%.
6. Reduced the fluorination temperature from 600C to 450C.	April 1954	Reduced the refluorination rate by about 50% and decreased the time cycle from 4.42 hours to 4.33 hours.

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III. DISCUSSION

Chemistry of the Process

The original cycle was arranged so as to effect the following steps during the conversion of plutonium oxalate to plutonium tetrafluoride: (1) Drying of the oxalate cake; (2) Oxidation of the oxalate; (3) Fluorination of the oxide. Heat and air were used to aid the drying step with some decomposition to the oxide occurring. Additional heat in conjunction with the air was applied to complete the oxidation. During the last part of the cycle, the oxide was converted to the tetrafluoride by contact with anhydrous HF gas. A small amount of oxygen was combined with the HF to insure an oxidizing atmosphere and prevent reduction of Pu^{+4} to Pu^{+3} by any reducing atmosphere which may have been present. The amount of HF supplied during the cycle was approximately ten times that necessary to stoichiometrically convert an average size batch of the plutonium oxalate (400 g. Pu) to the tetrafluoride. Production of PuF_4 could be visually confirmed by the pink color normally associated with tetrafluoride powder. In the event any PuO_2 remained after completion of the cycle, as evidenced by a green color, the run was reprocessed under an abreviated fluorination procedure.

Equipment

The fluorination equipment consists of furnaces equipped with service lines for supplying HF, O_2, and drying air (drying air is also used for furnace purging after fluorination). External resistance windings supply heat to the furnaces. The furnaces and windings are surrounded by cooling jackets through which cooling air can be forced to aid in cooling down from the fluorination temperature. The oxalate is contained in platinum lined boats, which have sintered platinum discs in the bottom portion of the liners. Water jets supply vacuum to the furnaces through offgas lines connected to the bottom of the boats. Process gases which are controlled by rotameters, enter the furnaces at the furnace door and are drawn down through the cake, out through the sintered discs, and are then exhausted through the jets.

Original Cycle

An overall fluorination cycle of 8.25 hours was in effect at startup of the RMA Line in March of 1952 (see Fig. 1). It consisted of a 1.00 hour drying period at 190C, a 1.25 hour oxidation period at 300C, and a 2.00 hour fluorination period at 600C. The HF-O_2 mixture was admitted after the indicated furnace temperature had been at 300C for approximately one hour. After fluorination had been completed and cooling had started, jacket cooling air was turned on at 550C. The HF and O_2 was turned off at 175C and a furnace air purge was started. Furnace unloading was not performed until a 1¼ hour purge period had elapsed. This cycle was utilized for eight months.

When, on several occasions water from the water jets backed up into the boats, an attempt was made to eliminate the practice of drawing the process gases down through the boat, but merely introducing the gases into the furnaces and fluorinating by diffusion was not very successful. In spite of increasing the fluorination period to 4 hours at 600C, poor HF-cake contact resulted and the refluorination rate seldom dropped below 25%. By December of 1952 the practice of drawing the process gases down through the boat had been resumed.

CHRONOLOGY OF CYCLE REDUCTIONS

Initial Reductions

In December of 1952 the first changes in the cycle were made. Portions of the cycle were considered excessively long when combined with the drawing of the process gases through the cake. The oxalate cake as charged to the furnace in most cases was of firm consistency and appeared to contain little moisture. This suggested that a shorter drying period might be feasible. In view of the large excess of HF utilized during the cycle, a cut in the high temperature fluorination period was planned as was a reduction in the long furnace purging period after fluorination. The relative stability of PuF_4 toward air at temperatures up to 300C indicated that no ill effects would be observed by furnace purging and unloading at 250C.(1) First the drying period at 190C was reduced from one hour to 15 minutes and the furnace purging period was reduced from 1¼ hours beginning at 175C to a 15-minute purge beginning at 250C. No increase in the refluorination rate was observed, and a month later in January of 1953 the high temperature fluorination period at 600C was cut one hour resulting in the 5.25 hour cycle pictured in Fig. 2.

Cake Temperature Study

No changes were made in the cycle for the next five months. While no adverse effect was noted on the refluorination rate utilizing the reduced cycle, neither was there any improvement. In an effort to more clearly understand the changes in the cake that occurred during the cycle, in June and July of 1953 a series of cake temperature measurements were carried out. A platinum-rhodium (90%Pt-10%Rh) thermocouple was placed directly in the cake and plots were made (Figs. 3-7) of cake temperature versus furnace temperature during the cycle. From these plots it was obvious that: (1) There was a considerable variation in the degree of wetness of the individual cakes. In all cases even when the furnace temperature had risen to above 200C, the cake temperature was below 100C and in most cases leveled off at 75C for variable amounts of time during the drying period; (2) During the 300C oxidation period (furnace temperature) of the standard cycle (Figs. 3, 6 & 7) the cake temperature actually never reached 300C. Only when the oxidation period was extended for 80 minutes (Fig. 4) did the cake temperature reach 300C in time for the $HF-O_2$ admission; (3) Providing the cake temperature had reached about 250C a rapid cake temperature rise occurred on $HF-O_2$ admission indicating an exothermic reaction within the cake. This temperature rise decreased progressively with lower cake temperatures at the time of $HF-O_2$ admission.

Fast Drying and Oxidation Cycle

On the basis of the cake temperature data a "fast drying" cycle was tried out in an attempt to rapidly dry and oxidize the cake before $HF-O_2$ admission. From the results described above it was decided that when the cake temperature reached 250C it had dried sufficiently for $HF-O_2$ admission. A rapid heating

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period to approximately 450C (furnace temperature) was employed followed by a drop to 300C in order to prevent the formation of high temperature plutonium oxides during the cake temperature rise occurring after $HF-O_2$ admission. High temperature plutonium oxides are difficult to fluorinate(2).

Figures 8 and 9 are plots of the cake temperatures versus furnace temperatures obtained during this cycle. The cake temperature rose steadily to the point of $HF-O_2$ admission where it then rose more rapidly. After the completion of the cycle both powders exhibited the characteristic pink color of PuF_4 and reduced with good yields. The net time savings of the new cycle was 30-45 minutes. Nine more runs were processed utilizing the "fast drying" cycle without cake temperature measurements. The data obtained were satisfactory and are presented in Table II below:

Table II

Run No.	Powder Color	Reduction Yield %	Remarks
RMX 13-07-164	Pink	97.3	
166	Pink	95.9	
170	Pink	95.3	
177	Green	95.6	Refluorinated to Pink
181	Pink	86.1	
184	Pink	98.4	
187	Pink	—	Reduced in the Development Laboratory.
192	Pink	97.6	
196	Pink	99.3	

The good results suggested the possibility of further cycle reductions by using an even more rapid drying and oxidation cycle. Four runs which were heated directly to 600C followed. On all runs the cake temperatures rose to at least 650C after $HF-O_2$ admission and on three of the runs some oxide remained unfluorinated at the end of the cycle. It was apparent from the oxide produced in the runs heated directly to 600C that some limiting factor had been exceeded. High temperature oxides could have been formed when the cake temperature rose past 600C.

It was next decided to run a control study on the "fast dry" cycle depicted in Fig. 10. The results obtained during August and September of 1953 are summarized in Table III. (The Standard Cycle is the one described earlier in Fig. 2).

Table III

	Fast Cycle	Standard Cycl
No. of Runs	33	104
No. of Refluorinations	7	23
Percent Refluorinations	21.2	22.1
Fluorination Time/Run (min.)	265	315
Refluorination Time/Run (min.)	145	200
Average Processing Time/Run (min.)	296	359

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While both cycles produced comparable refluorination rates, an average savings of 63 minutes per run was used as the basis for adopting the "fast drying" cycle. This was done in September of 1953.

Preheated Process Gases

At the same time that cycle reduction tests were being made, an attack on the refluorination rate was carried on from a different direction. It was felt that during fluorination more efficient use could be made of the HF gas if polymers which are known to exist at temperatures below about 60C(3) could be dissociated by heating prior to furnace entry. Accordingly, a gas preheater was designed and fabricated. The design is pictured in Fig. 13. Monel had to be substituted as the material of construction because Hastalloy was unavailable at the time of fabrication. Calibration tests of the heater using process gas flows and air as a stand-in gas revealed an exit gas temperature of about 450C. The heater was evaluated in conjunction with the cycle pictured in Fig. 10. All gases entering the furnace were preheated. Out of fifty runs processed during September and October of 1953, only two required refluorination. This was a drastic improvement over the refluorination rate of about 20% experienced during the same period through furnaces not utilizing preheated process gases.

Initial Fluorination Temperature Reduction

The success experienced with preheated process gases offered hope of solving another problem which was causing concern in the fluorination operation. High temperature HF corrosion had begun to show its effects on the equipment. Flange welds on the furnace faces were principally affected. Expensive repairs and loss of production time were the result. It was felt that since PuF_4 obtained by fluorinating at 500C had been successfully reduced in the Development Laboratory(4), a lower fluorination temperature in conjunction with preheated process gases would be feasible and would aid in reducing furnace corrosion.

On a test basis, in November of 1953, fifteen runs were fluorinated under the cycle pictured in Fig. 11. Two refluorinations resulted. The preheater then failed due to a weld separation. The test was continued for 49 runs, however, without the preheaters and only one refluorination resulted. Plans were immediately made to equip all furnaces with preheaters capable of heating the gases to about 500C and to reduce the fluorination temperature below 500C. In the interim the cycle in Fig. 10 was retained as standard. The improved preheater design is depicted in Fig. 14. Calibration runs showed an exit gas temperature of about 520C. For information purposes two heaters were connected in series during one of the tests resulting in a 45C exit temperature increase.

Effect of the Preheaters

In February of 1954 all furnaces were equipped with preheaters. Their effect on the process was immediately noticeable. A decrease in the refluorination rate of 42% occurred on the first 66 runs processed. At this time considerable scaling of the preheater internal surfaces was discovered and in order to reduce the scaling problem, the power input to the heating elements was reduced to effect a calculated drop of about 180C in the fin temperature. The resulting fin temperature of about 420C was approximately 60C below the maximum recommended temperature for monel exposed to HF and O_2(5).

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Further Reduction of the Fluorination Temperature

Now that the preheaters had proven themselves to be of value and a 500C fluorination temperature had been tested with good results, a further reduction in this temperature was made. Laboratory work on a small scale reductions had previously shown that if fluorination takes place at too low a temperature, a significant increase in bomb pressure occurs during reduction to the metal(6). This increase was noted during the reduction of 300C and 400C fluorides. For this reason a 450C fluorination temperature was decided upon. By April of 1954 all runs were being processed under the cycle in Fig. 12. For comparison purpose data covering an extended period of time from runs processed under the cycles in Figs. 10 and 12 are presented in Table IV. The effect of preheaters is also brought out. All runs are normal 400 g. Pu batches.

Table IV

	Cycle - Fig. 10 No Preheater	Cycle - Fig. 10 With Preheater	Cycle - Fig. 12 With Preheater
No. Runs	240	189	421
Refluorination Rate	20%	14%	6%

The new cycle virtually eliminated reprocessing caused by unfluorinated PuO_2. An increase did occur, however, in the production of PuF_3. This was not considered important in that Laboratory work had shown the reduction of PuF_3 to metal in good yields to be feasible(7). This was borne out in actual operation.

During the period covered by Table IV intermittent double batches (800 g. Pu) of oxalate were processed through Task II. A refluorination rate of about 35% was experienced on these runs. Because future production will consist of an increasing number of double batches, some cycle changes will have to be made, but it is not felt that big changes will be necessary. Slightly increased HF flows and/or furnace time will probably suffice. The net effect of the described cycle reductions, refluorination rate improvement, and batch changes will eventually become a four-fold increase in productive capacity for the fluorination step of the 234-5 Building.

RBGuenther

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Manufacturing Department

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References:

1. Facer, J. F., Lyon, W. L., Weidenbaum, B., The Preparation of Plutonium Tetrafluoride by Direct Hydrofluorination of Plutonium Oxalate, HW-20164, February 1951.

2. Garner, C. S., Chemistry of Uranium and Plutonium, Chapt. IV, LA-1100, April 20, 1950.

3. Technical Service Bulletin No. 30A, General Chemical Company, New York, N. Y., 1945.

4. Cooper, V. R., Separations Technology Sub-Section Monthly Report, April 1953, HW-27932-H.

5. The Technical Editor Speaks, International Nickel Co., Inc., New York, N. Y., 1945.

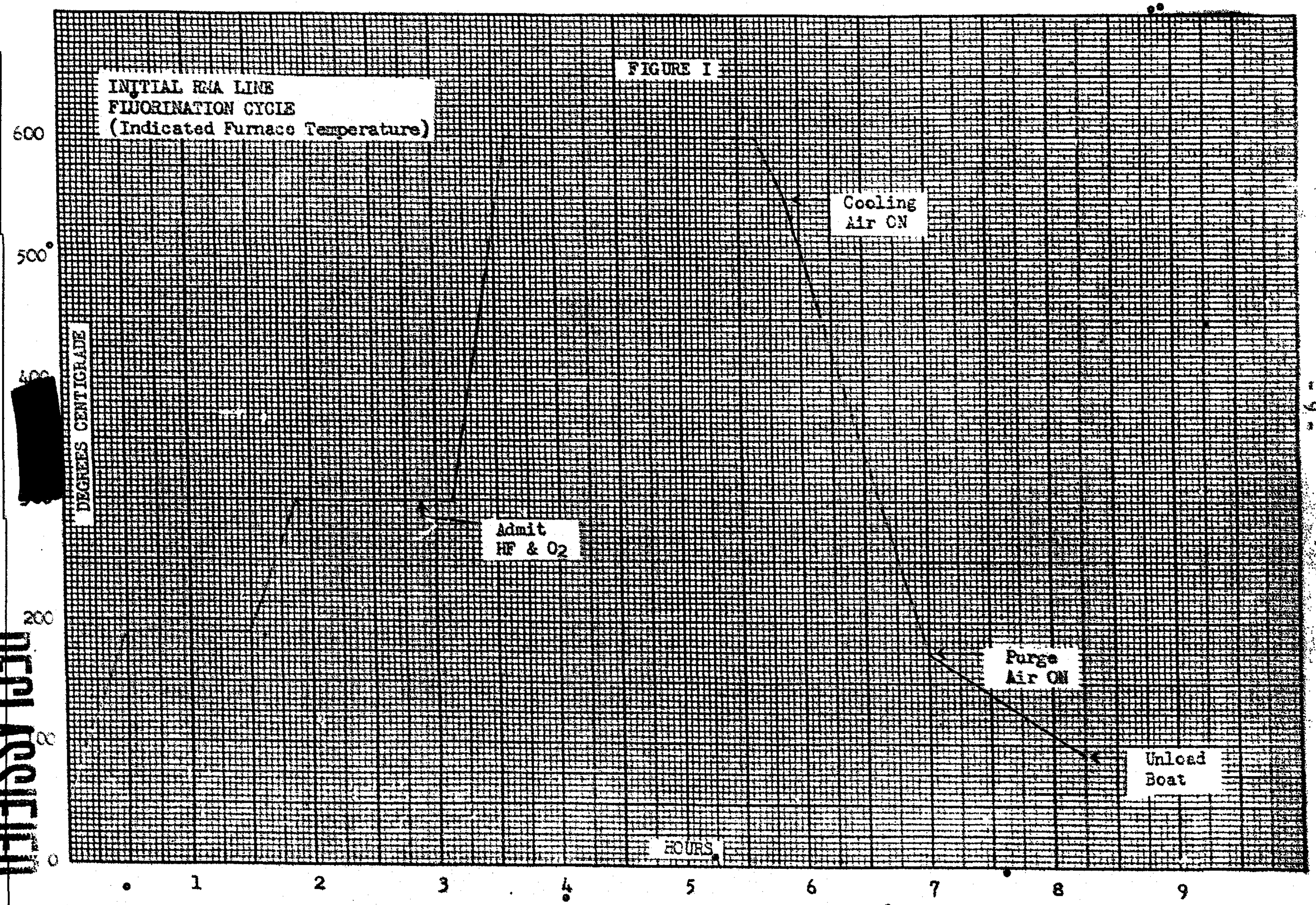
6. Cooper, V. R., Separations Technology Unit - Process Progress Report for February 1953, HW-27739.

7. Cooper, V. R., Separations Technology Sub-Section Monthly Report, July 1953, HW-28906-H.

[redacted]

FIGURE I

INITIAL RMA LINE
FLUORINATION CYCLE
(Indicated Furnace Temperature)



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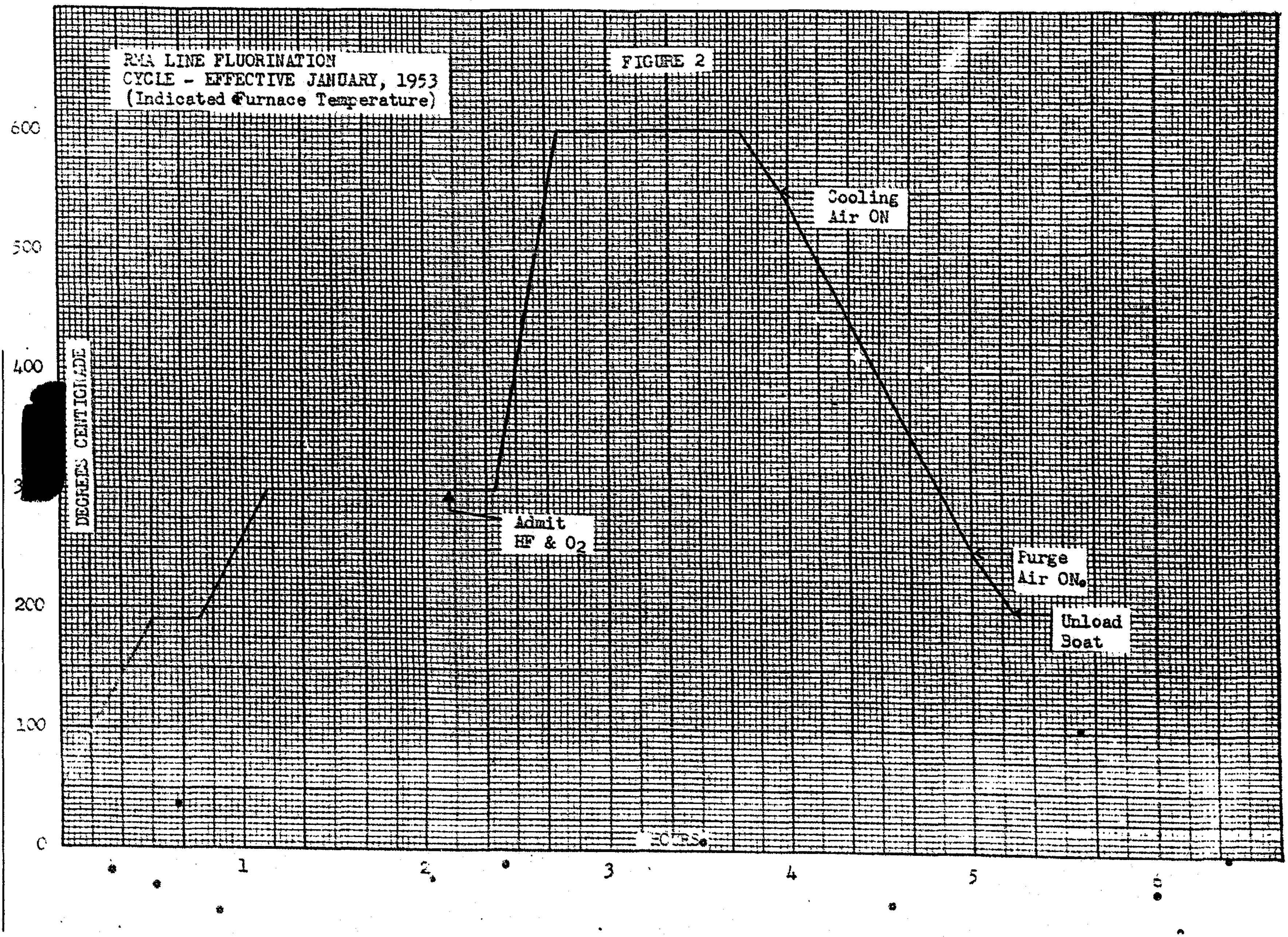
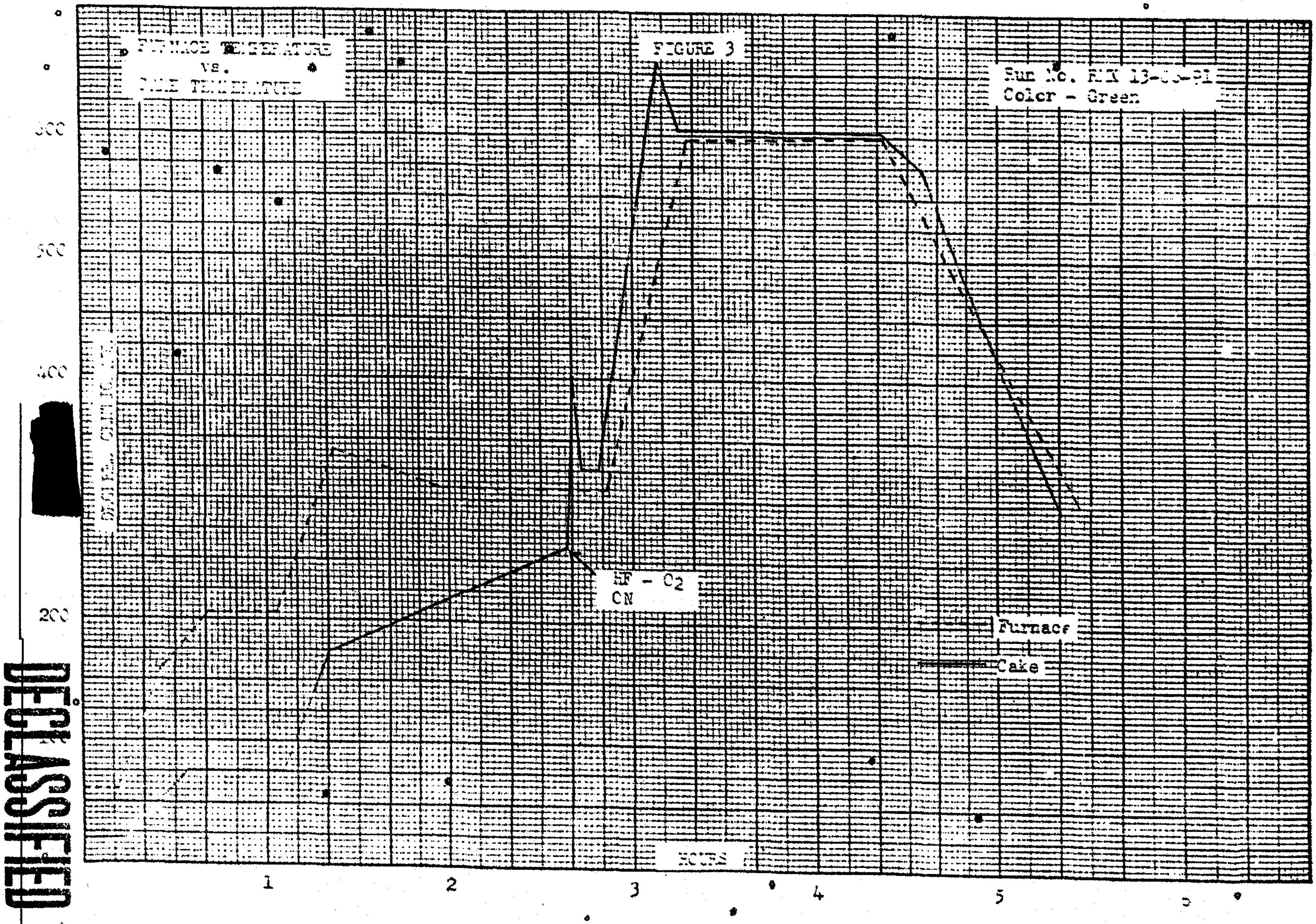


FIGURE 2

RMA LINE FLUORINATION
CYCLE - EFFECTIVE JANUARY, 1953
(Indicated Furnace Temperature)



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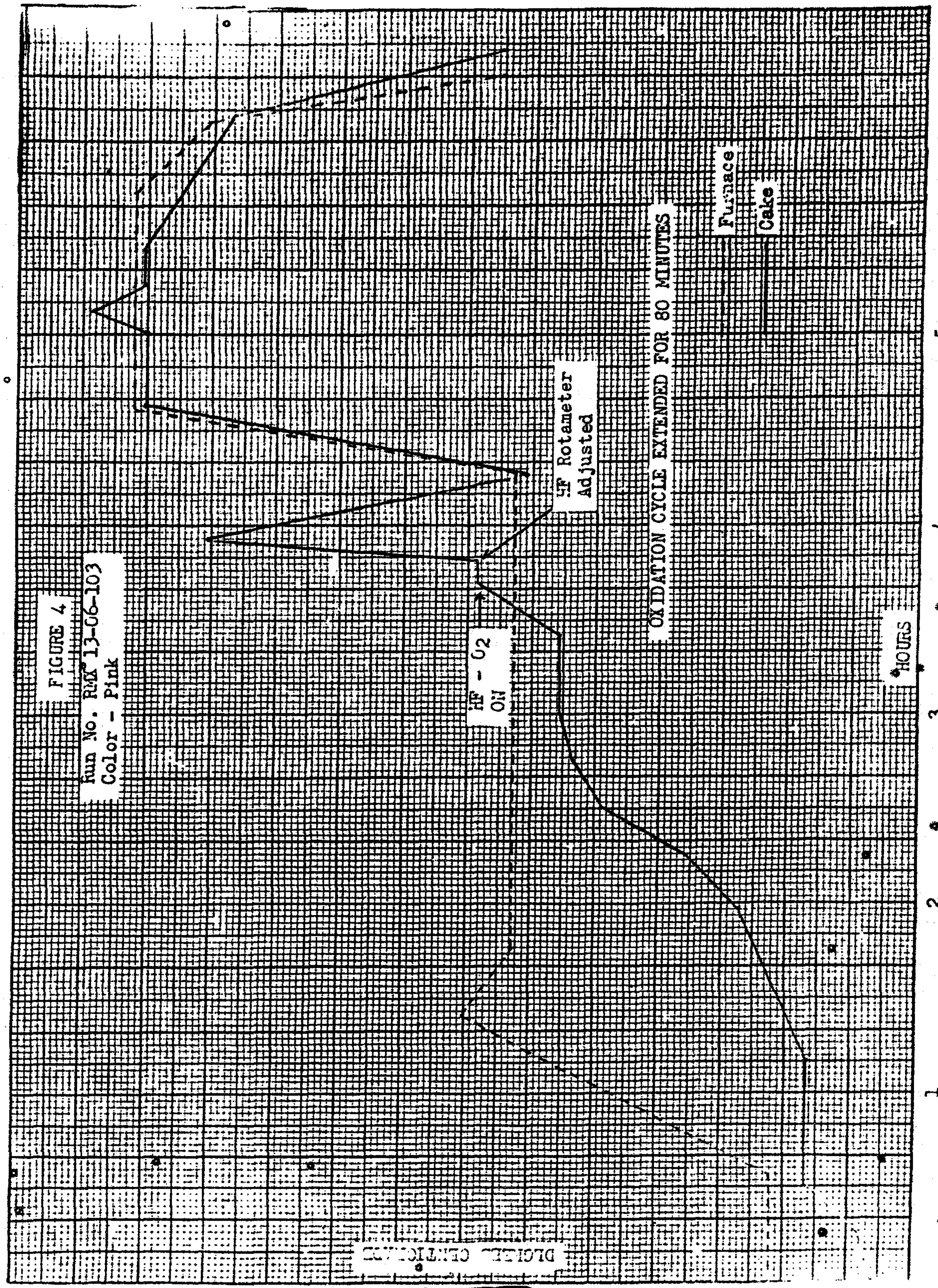

FIGURE 4
Run No. RMX 13-06-103
Color - Pink

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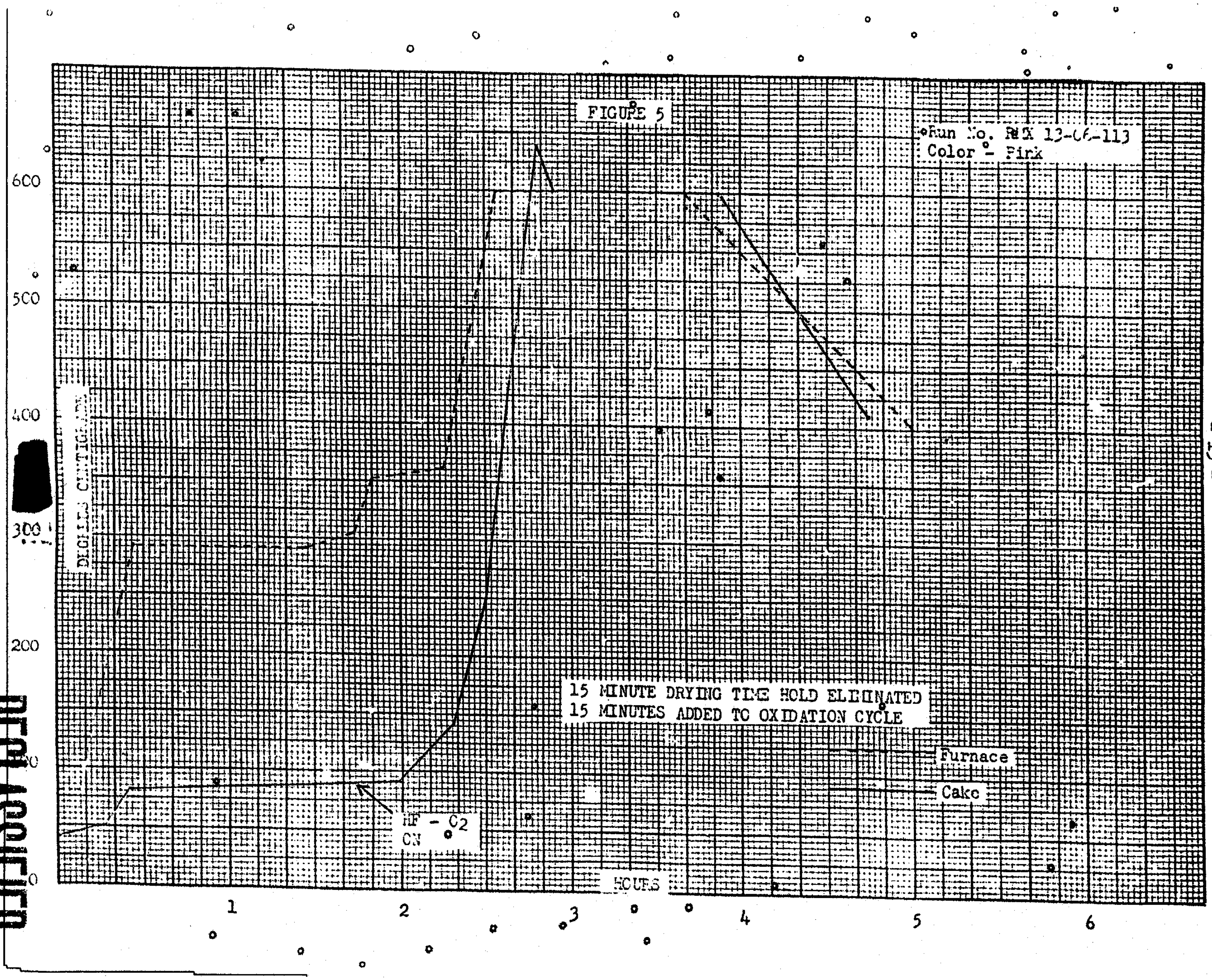

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FIGURE 6

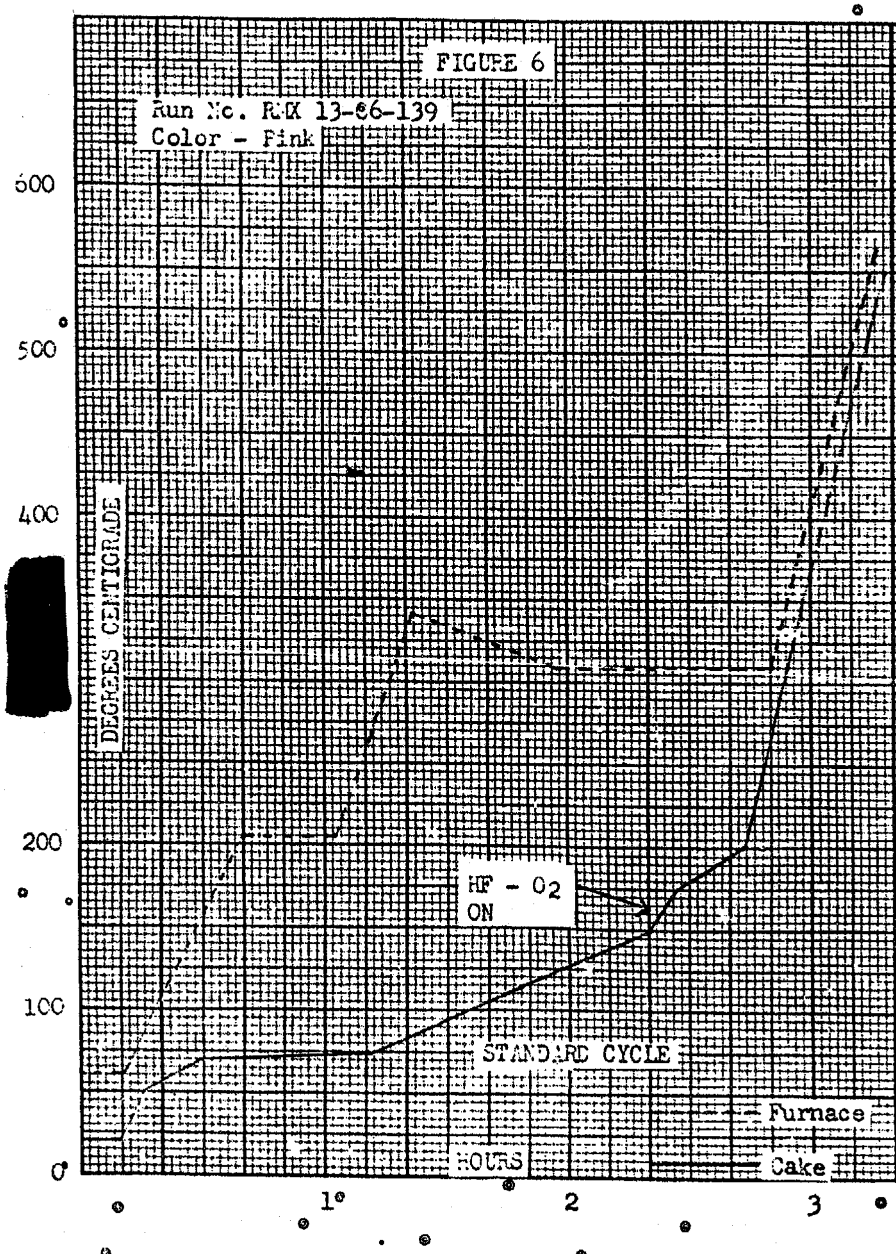

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FIGURE 7

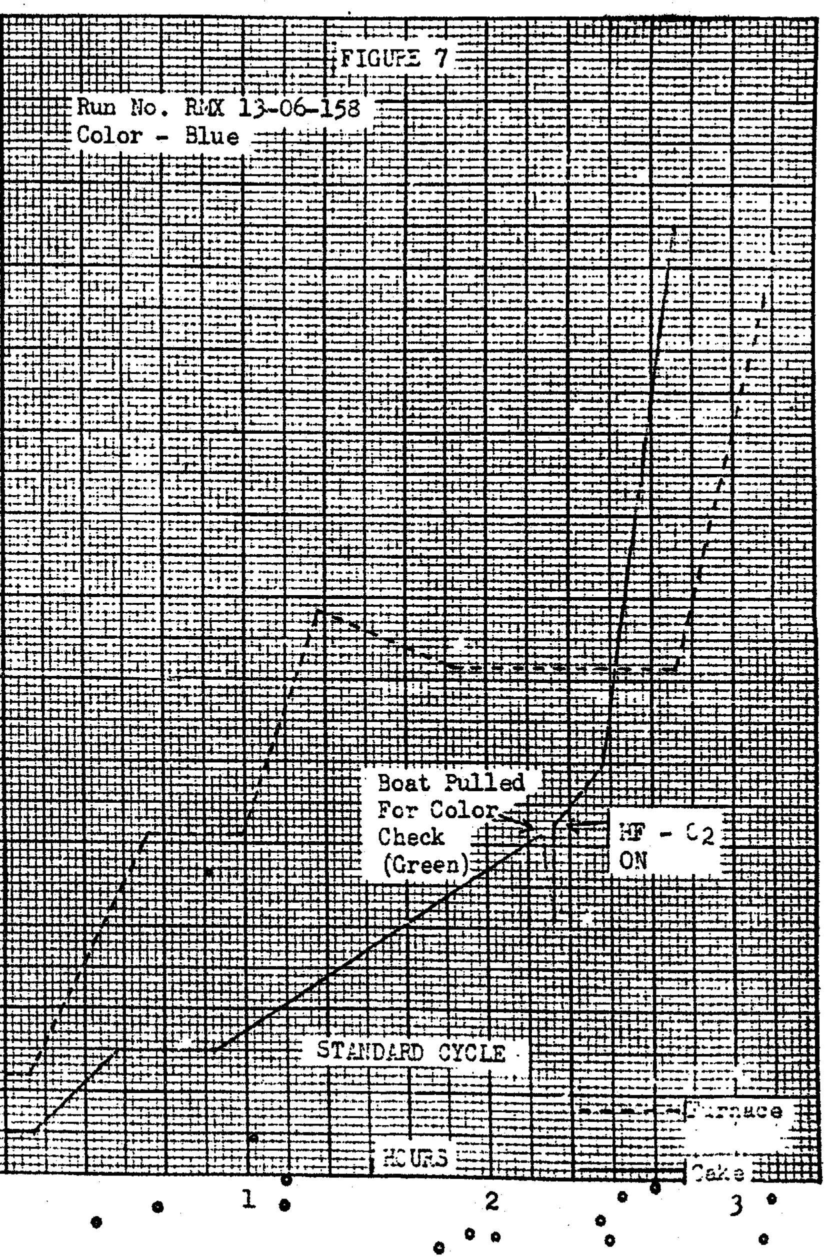


FIGURE 8

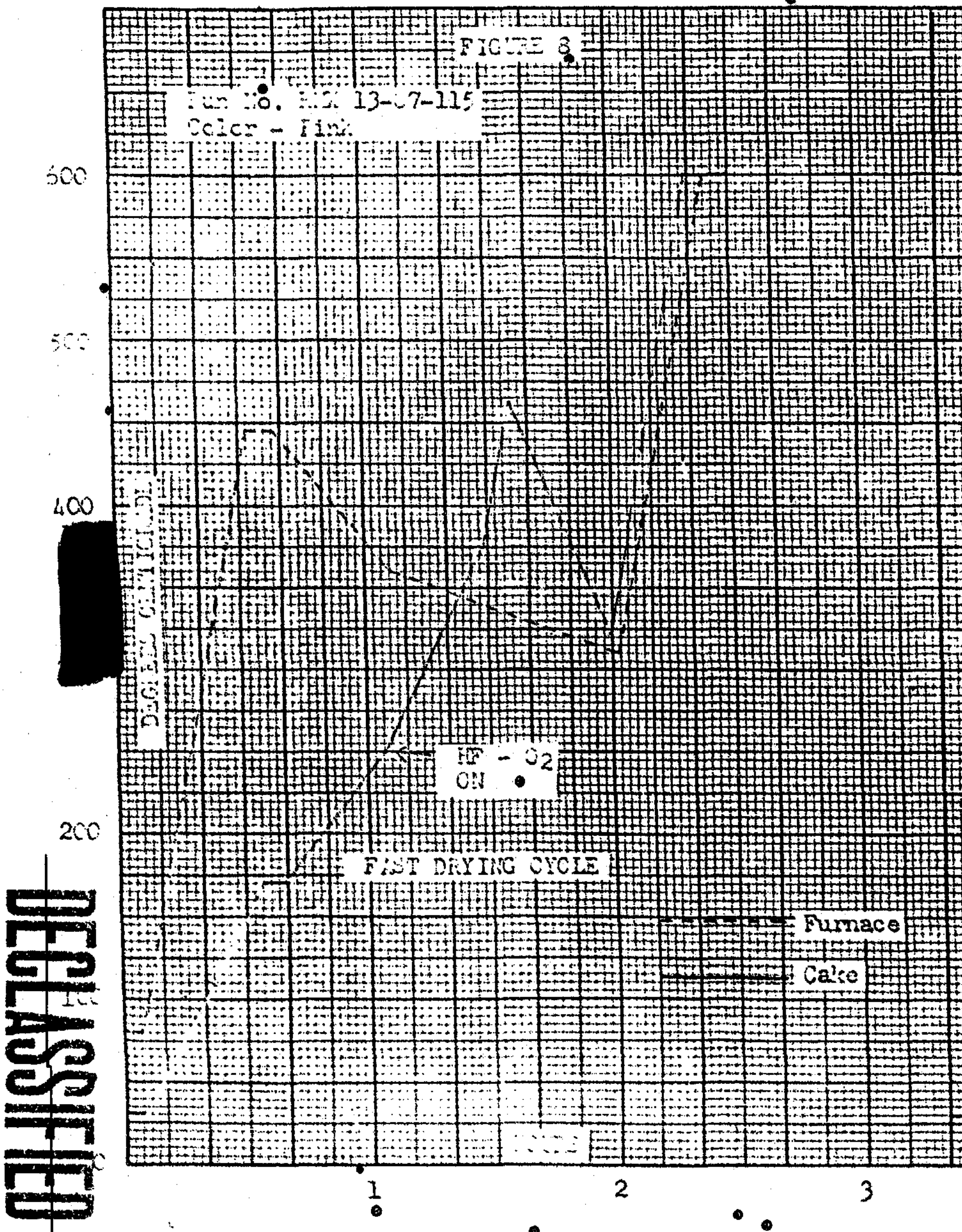
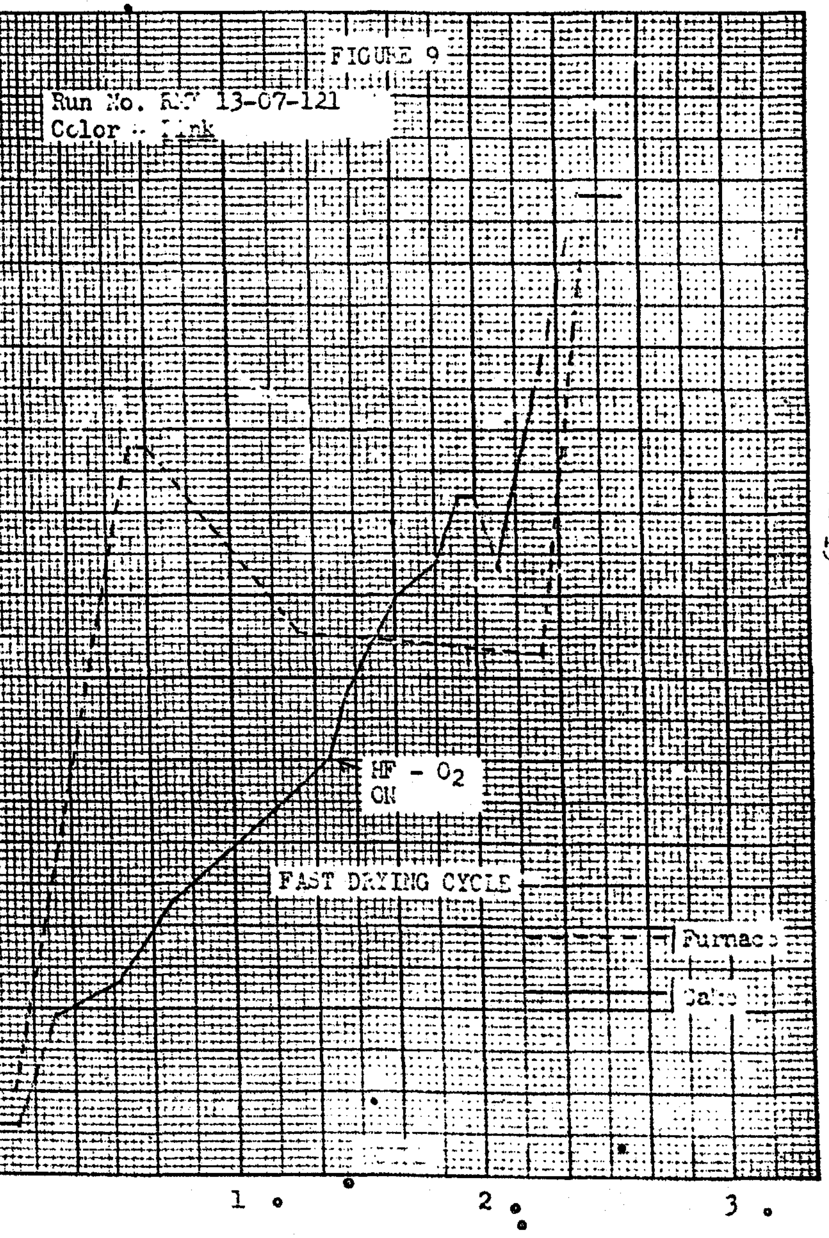


FIGURE 9



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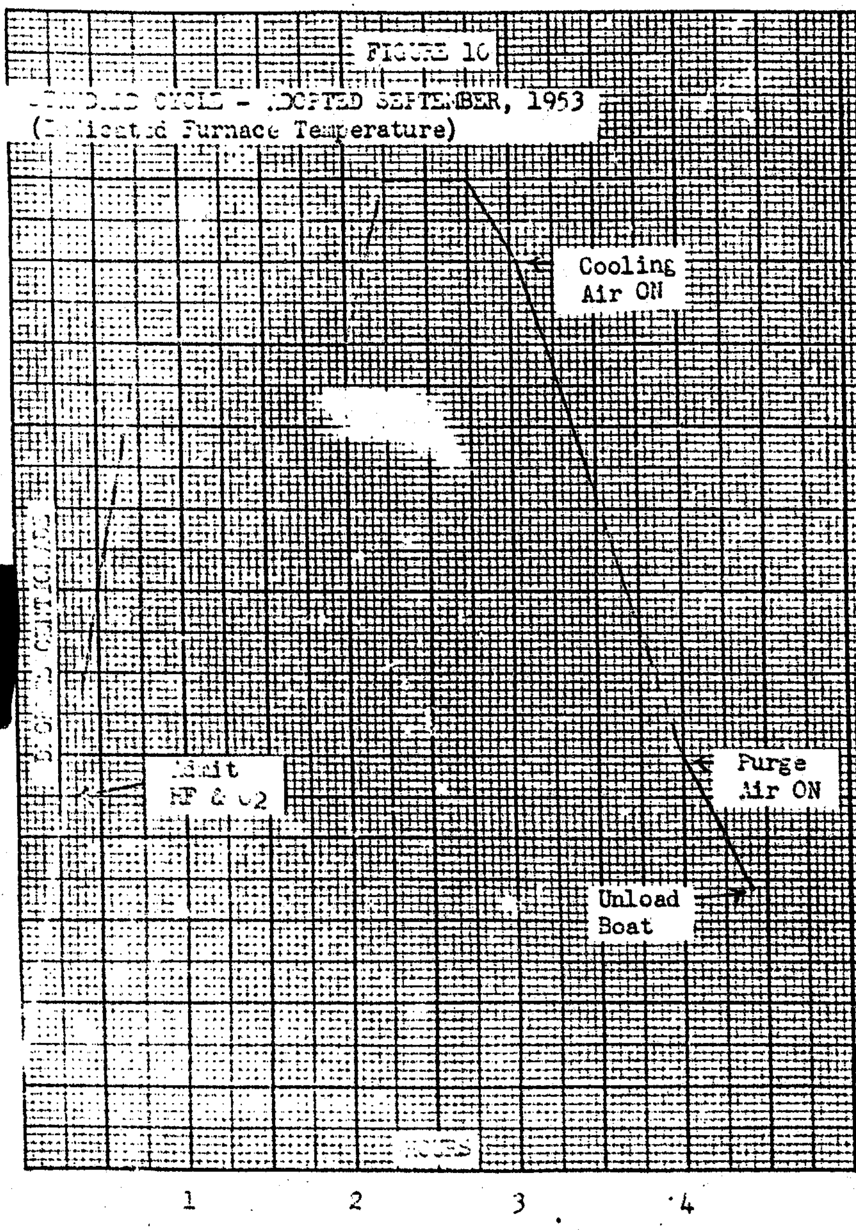

FIGURE 10

STANDARD CYCLE - ADOPTED SEPTEMBER, 1953
(Indicated Furnace Temperature)

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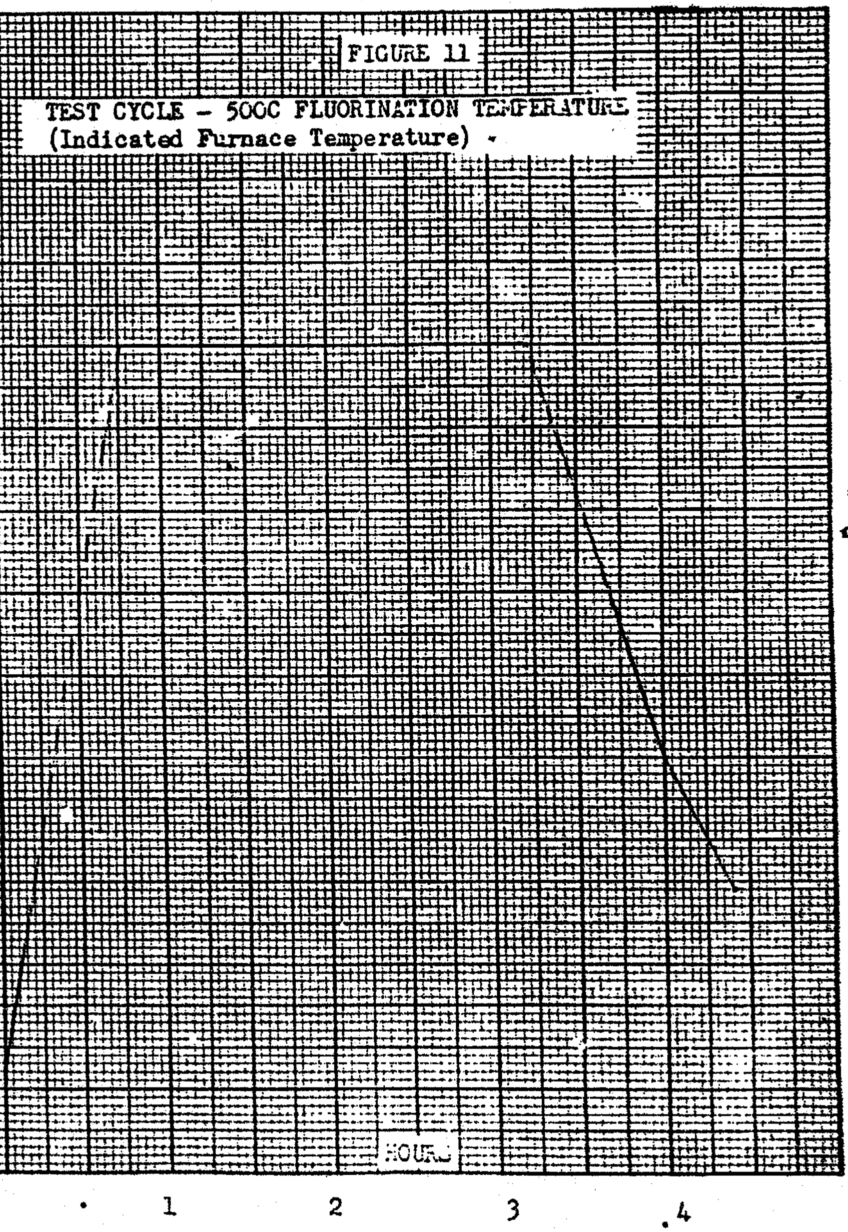

FIGURE 11

TEST CYCLE - 500C FLUORINATION TEMPERATURE
(Indicated Furnace Temperature)

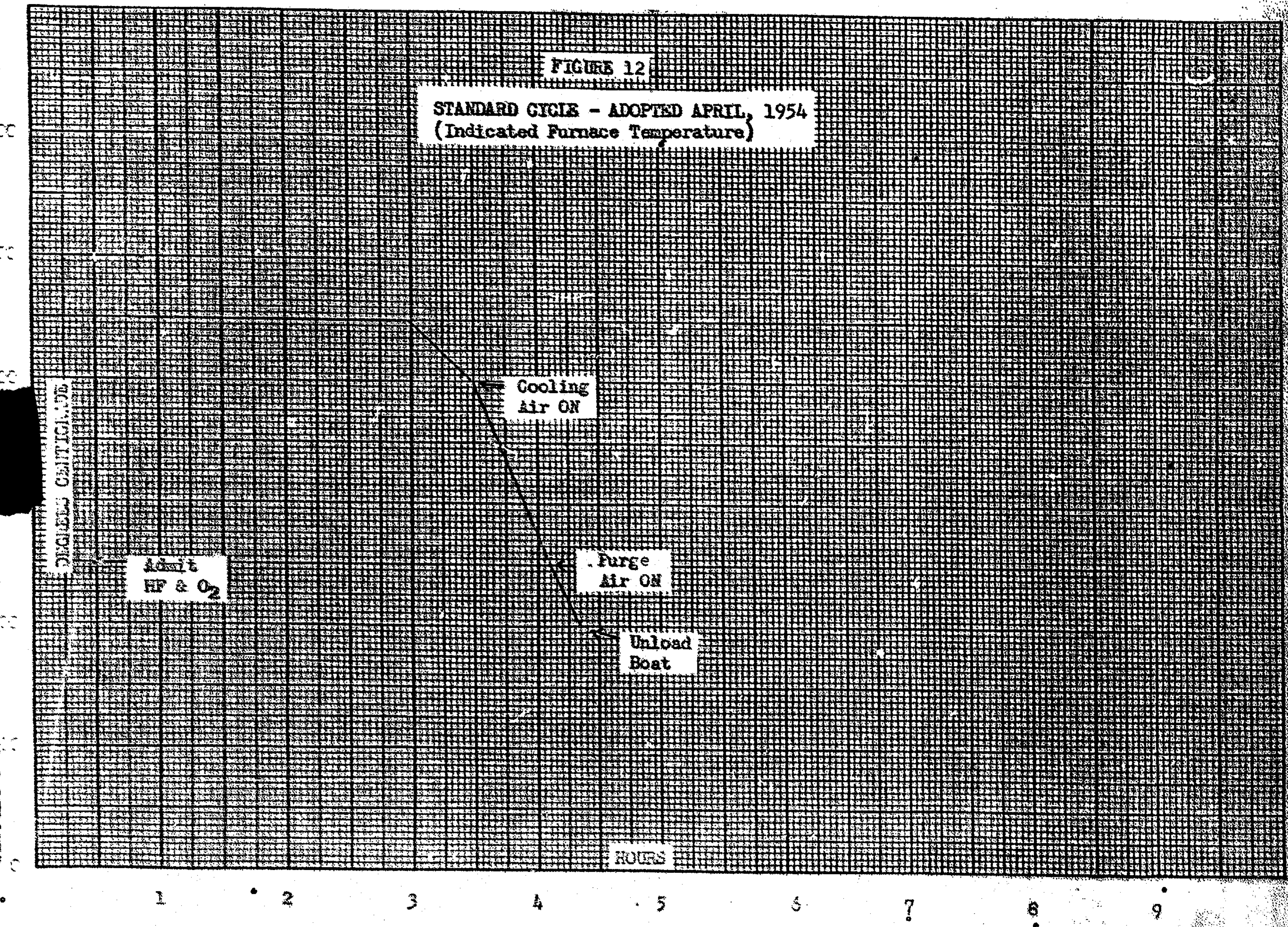

FIGURE 12

STANDARD CYCLE - ADOPTED APRIL, 1954
(Indicated Furnace Temperature)

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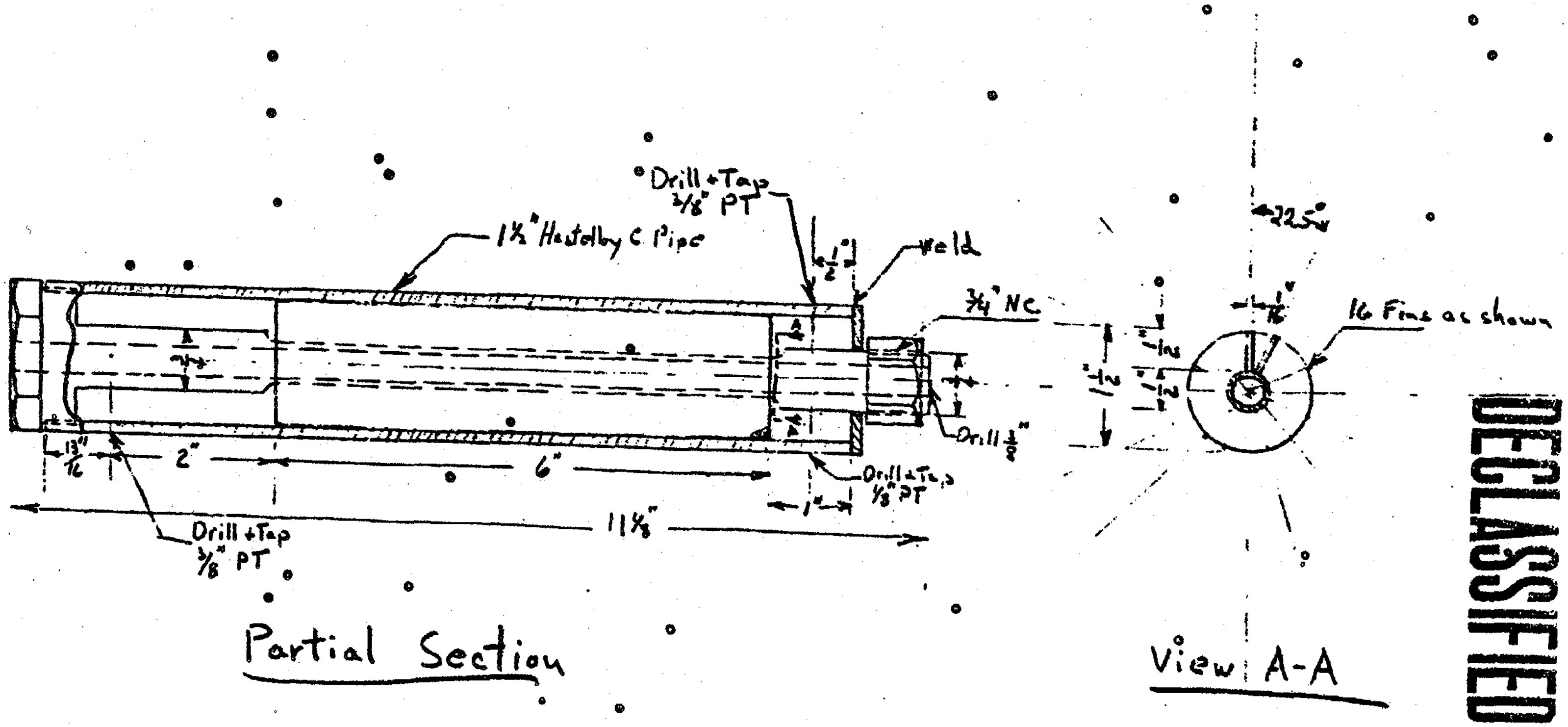
FIGURE 13



Mixed Gas Heater.

1/2-Scale

Material - Hastelloy C

1 Req'd

J.M. Hay
2-25-53
A-9521

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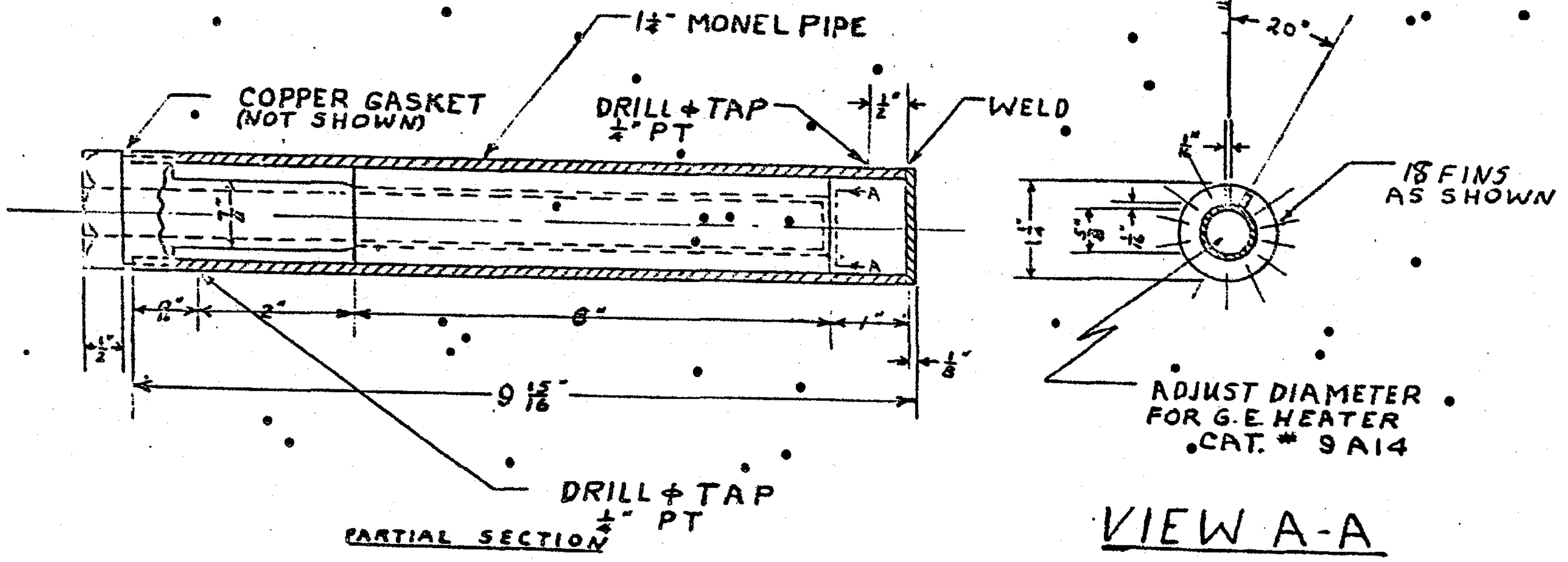
FIGURE 14



MIXED GAS HEATER
½ SCALE
MATERIAL - MONEL

M.N. RAILE
11-12-53

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