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PREPARATION OF PLUTONIUM METAL BY THE BOMB METHOD

by

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ABSTRACT

This report describes in detail the methods developed at Los Alamos for the preparation of plutonium metal by the bomb-reduction method. The experimental work on the development of the methods is given for all scales (grams of metal) of reduction. The larger-scale-reduction techniques which are described are now used for the routine production of plutonium metal.

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The problem of preparing plutonium metal of high purity by the so-called bomb method was started at this laboratory in August, 1943. The objective was to develop small-scale methods (0.5 to 500 grams of metal) for the preparation of plutonium metal. At the time the research was started there was no plutonium available for reduction research, and nothing was known concerning the physical properties of the metal. This being the case, and also since this laboratory had the problem of developing methods for the reduction of U-235 when it became available, uranium was first used as a stand-in for plutonium. Successful bomb techniques were developed by which uranium could be prepared with high yields (90-99%) on the 1 g, 10 g, 25 g, 250 g, 500 g, and 100 g (of metal) scales from the tetraflouride and trichloride by reduction with calcium metal.

At the time the problem was started, only the large scale (25 lbs of metal) reduction technique for UF_4 as developed at Ames, Iowa, and the possible use of iodine as a booster, was known. This large scale method was in no way applicable to small-scale work where high yields and high purity were needed. The problem here thus involved the development of refractory crucibles for the reaction, the design of suitable bombs, the investigation of raw materials for the reaction, and the development of techniques for each scale of reduction studied.

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Shortly before plutonium became available for 0.5 to 1 g. scale reduction research at this laboratory, the melting point of the metal was reported to be ~1800°C. Firing or heating procedures were thus studied, using UF_4, which should work for such a high-melting metal. In April, 1944, the first reduction of PuF_4 with Ca in the stationary bomb and on the 1-gram scale was run. A heating procedure was used which carried the bomb to a top temperature of 1380°C in 51 seconds. A magnesium oxide liner fired to 2200°C in graphite was used. The reduction reaction took place, but the heating time was too short to allow for the coagulation of the plutonium metal. There was also very large absorption of the reaction products by the refractory crucible.

Very shortly after this, it was reported that the melting point of the metal was ~800°C. This made the use of uranium (m.p. 1100°C) as a stand-in undesirable. About the same time, the chemists at this laboratory were making the chloride of plutonium in place of the fluoride. In view of these facts, $LaCl_3$ was used as a stand-in for plutonium (m.p. of La, 826°C). The use of the chloride necessitated the use of liners much less porous than those previously used in order to hold the $CaCl_2$ slag produced. A method of making "vitrified" magnesium oxide liners was thus developed and is outlined in this report. Successful techniques were developed for the preparation of La metal from the chloride on the 1-gram scale. This technique was used to make the first successful reduction of $PuCl_3$ in the stationary bomb on the 0.5-gram scale.

It was soon found that the melting point of plutonium metal was

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600°C, and cerium was chosen as a more suitable stand-in (m.p., 640°C). Techniques for the reduction of $CeCl_3$ and CeF_4 on the 1-g, 10-g, 25-g, and 160-g scales were developed and applied successfully to $PuCl_3$ on the 1-g and 10-g scales, and to PuF_4 on all scales reported here. The use of uranium as a stand-in was also of great value in learning the reduction techniques, especially those used on the 160-g, 320-g, and 500-g scales for the reduction of PuF_4. The tribromide of plutonium was also successfully reduced with calcium on the 0.5-gram scale. Reductions of PuO_2 with calcium on the 10-gram scale were unsuccessful.

The work reported here is for all scales of reduction used, and all variations tried are given. Complete investigations on each scale reported were not possible due to the very urgent need of metal for remelting, fabrication, and physical measurement researches. The techniques do, however, give very good yields and leave little to be desired for the production of plutonium metal.

The following table gives a summary of the optimum conditions for the reduction of $PuCl_3$ and PuF_4 with Ca in MgO crucibles on the six scales studied.

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Nominal Scale, grams Pu	Halide	Charge Composition	Heating Time (min:sec)	Max. Crucible Temp. (without charge) °C	Yield in Single Butto of Clean Metal (%)
1	$PuCl_3$	25% excess Ca	2:00	975	90.3
1	PuF_4	0.25 mole I_2 per mole Pu. Layers of I_2 + Ca on top and bottom of charge. 25% excess Ca	2:00	975	95.0
10	$PuCl_3$	25% excess Ca. 1 g I_2 + 0.16 g Ca on top of charge	2:45	975	95.3
10	PuF_4	0.25 mole I_2 per mole Pu. 25% excess Ca. 1 g I_2 + 0.16 g Ca on top of charge	0:40	470	97.9
25	PuF_4	0.15 mole I_2 per mole Pu. 25% excess Ca	4:10	460	98.0
160	PuF_4	0.3 mole I_2 per mole Pu. 25% excess Ca	11:00	325	98.8
320	PuF_4	0.3 mole I_2 per mole Pu. 25% excess Ca.	11:00	325	99.0
500	PuF_4	0.3 mole I_2 per mole Pu. 25% excess Ca.	11:00	325	99.0

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The following men aided in the development of the 160-500 gram scale reductions: B. R. Hayward and H. Raich. C. Hull and A. R. Weiss aided in the development of the "vitrification" process for the magnesium oxide liners.

I. Introduction:

The reaction between a metal halide and an alkaline earth metal as used in the so-called bomb reduction is of the thermite type. The fundamental requirement for a successful bomb reduction is that a dense, coherent piece of pure metal giving a yield close to the theoretical be obtained. The reactions used for the preparation of plutonium metal as reported here are as follows:

(1) $PuF_4 + 2Ca \longrightarrow Pu + 2CaF_2$

(2) $2PuCl_3 + 3Ca \longrightarrow 2Pu + 3CaCl_2$

When adapting these reactions to the bomb reduction, several considerations must be studied:

A. The melting points of the products of the reaction, the heat liberated by the reaction, and the heat loss to the container are important. It is necessary that the reduction be carried out in such a manner that the products of reaction are in the molten state long enough, and that the slag has a sufficiently low viscosity to allow the metal to collect in a coherent piece. In the reduction of the fluoride with calcium (reaction 1), the combination of the melting points of the products ($CaF_2 = 1330^\circ C$, $Pu = 627^\circ C$) and the heat of reaction is not such as to allow for the best collection of metal. Three possible ways of overcoming this difficulty are: (a) supply more heat to the bomb by additional external heating; (b) lower the

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melting point of the slag by the addition of another substance (c) increase the amount of heat liberated in the charge by having a reaction of high heat take place along with the reduction reaction. It is known that external heating must be carried out at such a rate that the products of the reaction do not solidify before separation of the metal has taken place. If this does happen, it is not possible to collect the metal by subsequent heating even at temperatures well abo above the melting points of the products. The application of very rapid heating of the bomb and its contents, especially when applied to the larger scales (160 to 500 grams of metal), is very difficult and impractible. With the small scale reductions (1 to 25 grams of metal), the application of rapid external heating is necessary because of the greater effect of heat loss to the container. Even with the smaller scales, the rapid external heating is not sufficient to compensate for the combined effects of the heat loss to the container, the heat of reaction, and the melting points of the products of reaction. In the reduction of plutonium tetrafluoride, points (b) and (c) are combined by producing by a concurrent reaction a substance which will lower the melting point of the slag while at the same time the reaction supplies additional heat. The reaction used is as follows:

$$I_2 + Ca \longrightarrow CaI_2$$

The formation of the CaI_2 supplied additional heat to the charge, and the CaF_2-CaI_2 slag has a lower melting point than the CaF_2 alone.

In the reduction of the chloride (reaction2) with calcium, the melting point of the $CaCl_2$ (772°C) is much lower, than that of CaF_2 and the addition of iodine is not necessary to lower the melting point of the slag. In the 1-gram and 10-gram scale reductions of the

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chloride it was found that it was not necessary to use iodine for additional heat but that this could be supplied by external heating. Although no large-scale (160 grams of metal) reductions of plutonium trichloride were made, it was found with $CeCl_3$ that additional heat was required to compensate for the heat loss to the container. This was accomplished by using iodine in the charge.

The use of an inert atmosphere, such as argon, in the bomb (with both reactions 1 and 2) aids in the separation of the slag from the metal and gives a much better formed piece of metal. This is probably due to the lowering of the viscosity and/or the melting point of the slag by the elimination of calcium oxide and calcium nitride. If air or nitrogen is used much of the slag freezes on the liner walls, and the metal button is apt to be poorly formed and difficult to clean.

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B. A knowledge of the starting temperatures of the reactions and reaction mixture is important in the development of a successful heating or firing procedure for a bomb reduction. A method of determining the starting temperatures of the calcium halide mixtures was developed on a 50-mg scale. Values obtained by this method using uranium halide-calcium mixtures checked those determined on a 10-gram scale. The small-scale method consists of placing the mixture in a small refractory liner contained in a small steel bomb. A chromel-alumel thermocouple of No. 28 gauge is placed in the center of the charge and sealed through the screw cap of the bomb by means of a two-hole insulator. The loaded bomb is then heated in a high-frequency induction coil at a desired rate, usually that employed in the actual reduction; time versus temperature readings being taken. When the charge fires there is a rapid increase in temperature and,

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in some cases, the thermocouple is burned out. The data on the starting temperatures of various halides with calcium metal are given in Table I, together with heats of reaction, where known, for the purpose of discussion. In all cases the amount of calcium used was in 25% excess over that required to react with the halide and, if used, the iodine present.

TABLE I

Starting Temperatures for Halide-Ca Mixtures
(50 mgs Scale)

Mixture	Heat of Reaction ($-\Delta H$) K cal/mole halide*	Starting Temp. $^{\circ}C$	Remarks
$2UCl_3 + 3Ca$	73.0	649	Thermocouple burned out
$2CeCl_3 + 3Ca$	24.4	624	Thermocouple did not burn out
$2LaCl_3 + 3Ca$	32.8	675	Thermocouple did not burn out
$2PuCl_3 + 3Ca$	---	645	Thermocouple did not burn out
$PuCl_3 + Ce$	---	---	No reaction occurred
$UF_4 + 2Ca$	126	515	Thermocouple burned out
$CeF_4 + 2Ca$	---	575	Thermocouple burned out
$PuF_4 + 2Ca$	---	595	Thermocouple burned out
$I_2 + Ca$	128.5	398	Thermocouple burned out
$UF_4 + 0.3I_2 + Ca$	164.6	410	Thermocouple burned out (10 gram scale)
$PuF_4 + 0.3I_2 + Ca$	---	~325	Estimated on the 160 gram scale

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*Data from - The Thermochemistry of the Chemical Substances, Bichowsky, F. R. and Rossini, F. D. Reinhold Publishing Co. (1936)

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The above data show that all the chlorides listed have about the same starting temperatures with calcium metal. The same is true of the fluorides, but this temperature is definitely lower. It is significant that in reduction of UCl_3 the thermocouple is always destroyed, while in $PuCl_3$, $CeCl_3$, and $LaCl_3$ reductions this does not occur. As shown in Table I, $-\Delta H$ for the rare-earth reductions is considerably less that that for the corresponding uranium reaction. Although rate of reaction will also influence the minimum temperature, these data provide strong indication that the heat of reaction for $PuCl_3 + Ca$ is closer to that of $CeCl_3 + Ca$ than to that of $UCl_3 + Ca$. Using a mixture of $PuCl_3$ + cerium metal, no starting temperature was obtained, and the cooled mixture after heating to a maximum temperature of 967°C showed no sign of a reaction having taken place. The heat of formation of $PuCl_3$ is therefore probably greater or equal to that of $CeCl_3$. The data on the fluorides indicate that the heat or rate of reaction for $PuF_4 + Ca$ is higher than that for $PuCl_3 + Ca$. It should also be noted that the starting temperature for the $PuF_4 + 0.3I_2 + Ca$ mixture was estimated from firing data on the 160 gram scale and is below the starting temperature of the $I_2 + Ca$ mixture. In the case of the same mixture with UF_4 this is not the case; the $I_2 + Ca$ starting temperature determines the starting temperature of the $UF_4 + I_2 + Ca$ mixture. This starting temperature, as determined on the 10 gram scale, agrees well with the one estimated in the same manner as was the $PuF_4 + I_2 + Ca$ starting temperature. The reason for the starting temperature of the $PuF_4 + I_2 + Ca$ mixture being lower than that for the $I_2 + Ca$ mixture is not known.

C. The container in which the reaction takes place is a steel

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bomb with a liner of refractory material. This refractory liner is a very important consideration in bomb reduction development. The following points are important when considering a reduction liner.

(1) Reaction between the electropositive reductant, the reduced metal, or the slag produced should be as small as possible.

(2) It should be sufficiently impervious to retain the reaction products, and should be of such purity as to not contaminate the metal produced.

(3) It should be capable of withstanding the thermal shock of the rapid heat evolution accompanying the reaction.

(4) If a given rate of heating of the reduction charge is to be repeated on every run, the thermal conductivity of the liner must be reproducible; also, the rate of heat transfer from the bomb to the liner must be duplicable; therefore, the fit of the liner to the bomb must be controlled.

The most satisfactory liners for plutonium reductions on all scales have been found to be prefired, magnesium oxide crucibles. The liners used will be discussed in more detail under the various scales of reduction.

II. Raw Materials:

1. Calcium:

The choice of calcium metal used in the thermite reactions under consideration is of primary importance. The reductant must be low in light-element impurities so as not to contaminate the plutonium metal produced. It must also be free of oxide and low in nitrogen.

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It has been found with uranium reductions that calcium containing 0.40% N_2 or less is satisfactory when the bomb is argon-filled, while with air-filled bombs the nitrogen content must be 0.04% or less. If the nitrogen content is too high, the metal buttons (uranium) are poorly formed and the yield of metal tends to be lower. The effect of nitrogen on the calcium for plutonium reductions is not known, low-nitrogen calcium having always been used. The calcium used in the work reported here was redistilled-electrolytic calcium manufactured by the Electro-Metallurgical Corporation. The calcium was received as muffs. These were ground or sheared to - 1/4" pieces, after which they were ground in a Wiley mill and screened, the -20, +80 mesh fraction being used. This grinding and screening removes much of the oxide and leaves a clean shiny product. The ground calcium was stored under argon. A typical analysis of the calcium used is given in Table II.

TABLE II

Analysis of Ca Used

Element	ppm
N_2	400
B	<0.5
Al	≤ 10
Mn	<10
Mg	<1000
Fe	50

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2. **Tetrafluoride**:

The PuF_4 was prepared by the Building D Dry Conversion Process; the details of the methods used being given in LA-   . It was found that fluorides made by the hydrofluorination of oxides ignited from the oxalate at 1000°C or 600°C were comparable with respect to reduction yields, but that the bulk density of the fluoride obtained from the 600°C oxide was lower. Fluoride made by the direct hydrofluorination of the dried oxalate did not give as high yeilds on reduction as the fluorides made from the oxides. The bulk density was also higher than either of the oxide-fluorides. The effects of bulk density on the reduction of the tetrafluoride are not definitely known, but a high bulk density is of value in putting the mixed charge into the bomb liners.

The percent conversion of the fluoride from the oxide is important. It has been found that the average yield does not drop off appreciably if the fluoride is 90+% converted from the oxide. Reductionson the 160-gram scale giving yields of 92% have been made on fluorides with conversions as low as 75%. It is recommended, however, that in order to obtain consistent high yields on all scales, the fluoride should be 90+% converted from the oxide. Further discussion of the percent conversion of the fluoride will be given under the larger-scale reductions.

3. **Trichloride**:

The $PuCl_3$ was prepared by the Building D Dry Conversion Process; the details of the methods used being given in LA-112. It was found that chlorides made from the oxalate were superior to those

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made from the oxide. It was also found that chloride made from the oxalate could be improved by sintering at 725°C for 2 to 3 hours. All of the chlorides were 100% converted from either the oxide or oxalate.

4. Iodine:

Reagent-grade, redistilled iodine manufactured by Mallinckrodt Chemical Works was used. For the small scale reductions (1-25 grams of metal) it was ground to -30, +80 mesh, but was used as received for the larger scale reductions.

III. 1, 10, 25 gram (of metal) Scale Reductions:

1. General

(a) Apparatus: The apparatus consists, in general, of a bomb or external container with a pre fired refractory liner for the charge, and a high frequency convertor and furnace to heat the loaded bomb under controlled conditions. Fig~~ure~~ I is a photograph of the bombs and liners used. Fig~~ure~~ II gives cross sectional drawings with dimensions of the bombs and liners. The bombs are machined from cold-rolled steel rod and have threaded caps with a lip on the inside which makes a seal with the copper gasket held in a groove in the body of the bomb. The screw in the cap of the bomb is to enable filling the loaded bomb with an inert gas.

The most satisfactory liners were found to be pre-fired crucibles made of magnesium oxide. The MgO used was an electrically fused product (Vitrofrax) ground to pass a 300 mesh sieve. Unfortunately, this material, made from mined magnesite, is no longer available. Later shipments of powder from the same supplier were found to behave

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quite differently. This powder will be discussed after the use of the mined magnesite is described.

The mined magnesite had the following analysis:

Fe	0.05%
SiO_2	1.58
R_2O_3	0.39
CaO	0.50
B	<20 ppm

The liner was formed in a graphite mold using either a graphite or metal plunger. The procedure was to jar a bottom layer of MgO in the mold, center the plunger (which determined the shape of the inside of the liner) in the mold; and add powder in small amounts, the mold being jarred on the bench after each addition. When the height of the liner was reached, the plunger was carefully removed. The formed liner was then fired in the mold to 2200°C by induction heating. This firing took about twenty minutes. After cooling, the liner was removed from the mold. Liners made in this manner, and with the mined magnesite, were hard and dense, and were satisfactory for fluoride reductions. They were, however, too porous to be used for chloride reductions. The "vitrification" of the liner at still higher temperatures for use in both fluoride and chloride reductions was accomplished as follows: A large MgO crucible (4" OD, 3.5" ID and 6" high) which had been fired to 2300°C was placed in a graphite crucible which was 6" OD, 5" ID and 9" high. The cover of this crucible had a center vent hole and a pyrometer sight tube at an angle of 45 degrees. The liners prepared as above were placed in the large MgO crucible which was covered with an MgO lid. The graphite crucible was heated in a 7" ID induction furnace powered by a 20 KW

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Ajax converter. The "vitrification" cycle was to heat the liners to 2300°C in 1.5 hours and hold at this temperature for 30 minutes.

Calcium oxide liners were also made and vitrified by this method, except that the first firing temperature was 1700°C and the vitrification conditions were 2100°C for 30 minutes. Electrically fused CaO was used. The CaO liners made by this method were very dense and non-porous, but were inferior to the MgO liners for reduction, probably because of a reaction between the slag and the CaO.

As stated above, the mined magnesia was later substituted by a product which could not be used for the making of liners by hand tamping the dry powder. The use of the powder was taken over by Group CM-7. A method was developed using machine tamping and pressing of the moist powder to form the liner. The formed liner was then dried and fired using the same "vitrification" cycle as described above. The liners obtained were satisfactory for both chloride and fluoride reductions. The powder had the following analysis:

Fe	0.17%
SiO_2	2.35
R_2O_3	0.38
CaO	0.94
B	300 ppm

(b) Loading of the Bomb: All loading operations are carried out in a stagnant-air box to avoid endangering the health of the operator. Rubber gloves and a respirator are worn by the operator during all reduction operations. The halide is mixed with the reducing metal and iodine in a closed bottle and the mixed charge poured into the liner, covered with the refractory lid, and the bomb

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cap ~~is~~ screwed on and tightened. The closed bomb is then placed in a vacuum jar (see Fig[illegible]), through the lid of which a screw driver passes by means of a Wilson seal. The screw in the cap of the bomb is then run out, it being held by means of a clip on the screw driver. The jar is then twice evacuated and twice filled with argon, the screw replaced and tightened in the cap, and the bomb removed from the jar ready for firing.

(c) Firing of the Charge: In the firing of the reaction mixture a controlled and reproducible rate of heating is necessary, and a knowledge of the top temperature reached is important. This is especially true in the case of the small scale reductions where the heat generated by the reaction itself is not sufficient to keep the reaction products in the molten state long enough for the metal to collect in one coherent piece. The rate of heating of the reaction mixture is also important because if the temperature rise is not fast enough through the firing temperature, the products may solidify, and subsequent heating to temperatures above the melting points of the products will not coagulate the metal satisfactorily. A method of heating the bombs was developed where the rate of temperature rise and top liner temperature (without the charge) reached were known and could be varied.

Data for the above method of firing were obtained by taking time temperature data on the inside of the liner without a charge. Fig~~ure~~ 4 ~~IV~~ is a graph showing these data for MgO liners on the 1-gram, 10-gram, and 25-gram scales. These rates have been found best for firing the bombs, having been ascertained in most cases by trying both slower and more rapid rates of firing. The converter, coil, location of

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bomb, etc., used to obtain these curves will be given in the discussions of each scale. The use of these curves can be explained with an example. Consider the 1 gram scale bomb with an MgO liner. A reduction of PuF_4 with Ca is to be run. It has been found that firing to a liner temperature of 975°C at the rate given by curve 1 is satisfactory (not considering the heat of reaction). The time of heating would be two minutes (See Fig[redacted]), the temperature being known to rise 25°C after the power is turned off.

The above method of firing was used to locate the optimum firing conditions for cerium halides. The conditions arrived at with cerium were found, in general, to apply to the corresponding halides of plutonium.

(d) Unloading of the Bomb and Cleaning of the Metal: All unloading and cleaning operations are carried out in a stagnant air box to avoid endangering the health of the operator. The liners are usually easily removed from the bomb. They are then broken and the button of metal removed. Slag and excess calcium which may be on the metal is best removed by placing the button in concentrated nitric acid (plutonium metal is passive to conc. HNO_3). After pickling, the button is washed in water and dried in acetone. Glacial acetic acid may also be used for cleaning the metal. In this case a thin layer of oxide is formed on the surface of the metal.

2. 1-gram-Scale Reductions

The bomb and liner for this scale of reduction have been described. Curve 1 of Fi[redacted] 4 gives the heating rate which was found to give the most satisfactory and consistent reduction results

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for both the chloride and fluoride. A 7.5-KW high-frequency Lepel converter was used with the following coil: 1 1/4" ID, 2" high, and 10 turns of 1/4" copper tubing flattened to a thickness of 1/8". The converter settings were as follows:

Coarse Inductance Setting:	Left S; Right M.
Fine Inductance Setting:	16
Power Set:	1

The bomb was centered in the coil.

(a) Reduction of $PuCl_3$ with Ca: The first successful reductions of plutonium in the stationary bomb were made on the 0.5-1-gram scale, using the trichloride and calcium metal. In a successful reduction of the trichloride, the calcium chloride slag is down over a well formed button of metal, and very little of the slag is absorbed by the liner. The button of metal has a "Ca cap" which is easily broken loose from the button. This "Ca cap" contains about 50% Ca and 50% Mg. The use of "vitrified" MgO liners was found necessary for the chloride reductions. Liners fired at 2200°C absorbed most of the slag and some of the metal. When this happened the buttons were poorly formed and the yields were low.

The data on 0.5-1-gram-scale chloride reductions are given in Table III. Entries 1 through 7 are the first group of 0.5-1 gram scale reductions made in vitrified MgO liners. The liner temperatures were varied; 975°C giving the best results. The chlorides used in these runs were made from the oxide, and many of the variations in the data are believed to be due to differences in the various batches of chloride. In entry 7, 0.14 mole I_2/mole Pu was added and found to be of no advantage.

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Entries 8 through 23 are for reductions of chloride made from the oxalate. Entries 14 and 15 are for the chloride made from the oxalate and then sintered at 725°C for 2-3 hours. Entries 19, 20, and 21 are for distilled chloride. Reductions of the sintered chloride were the best; giving the best formed metal buttons and the best collection of slag above the metal. In addition to the better reductions, the sintered chloride had a higher bulk density, this being an advantage in that a larger charge may be reduced in a given liner.

Entries 15 through 18 list the results of a study of iron pickup from iron bombs and nickel plated bombs with and without iodine. The metal from all four reductions was low in iron, and no significant differences in the iron contents were apparent (See Table IV).

Entry 24 is for a reduction of a chloride which had been allowed to hydrate to the $PuCl_3 \cdot \frac{1}{2}H_2O$ formula. The results of this reduction indicate that some hydration of the chloride does not interfere with the reduction reaction. Reductions of the oxychloride of plutonium with calcium were tried. Only a cokey mass was formed, no coherent metal being obtained. This indicates that the oxygen when present in water as in $PuCl_3 \cdot \frac{1}{2}H_2O$ is not detrimental, but is harmful to the reduction reaction when it is as the oxide of the metal.

Entries 25 through 26 are for reductions of the chloride in vitrified CaO liners. These liners absorbed the slag and gave poorly formed buttons, thus being inferior to MgO liners for chloride reductions.

One reduction of $PuCl_3$ with Ca was made in a CeS liner. This liner absorbed all of the slag and part of the unreduced chloride, giving a poorly formed button of low yield.

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Representative analytical data on plutonium metal made by the reduction of $PuCl_3$ with Ca are given in Table IV. The colorimetric iron determinations are more reliable than the iron values determined spectrographically.

(b) Reduction of $PuBr_3$ with Ca: Only one reduction of the tribromide was made. This was on the 0.5-gram scale in a vitrified MgO liner. The metal obtained was in two pieces, a yield of only 53.4% being obtained. A satisfactory technique for the reduction of $PuBr_3$ could no doubt be developed.

(c) Reduction of PuF_4 with Ca: Data on reductions of PuF_4 with Ca on the 0.5-1-gram scale are given in Table V. As has been discussed in the Introduction, the reduction of a fluoride with Ca on a small scale offers one difficulty not encountered when dealing with a chloride. This is the high melting point of the CaF_2 slag (1330°C) as compared with that of $CaCl_2$ (772°C). Iodine is therefore used in the fluoride reductions to give a lower melting slag and at the same time to furnish more heat to the reaction mixture. The general technique for the 0.5-1-gram-scale reductions of PuF_4 was developed at first with UF_4 and then later and more satisfactorily with CeF_4. The charge consisted of a layer of 0.15 g I_2 and 0.02 g Ca on the bottom, the PuF_4-I_2-Ca, and another layer of 0.15 g I_2 + 0.02 g Ca on the top. It was found from the stand-in work with UF_4 and CeF_4 that the layers of I_2 + Ca were very important; the same amount of I_2 mixed with the PuF_4 did not give the desired results. The firing procedure for the fluoride reductions was the same as with the chloride reductions, that is, firing to a liner temperature of 975°C. The fluoride reductions gave very well formed buttons with the "Ca cap". The

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yields were higher than with chloride reductions on the same scale. This is due to the fact that there is less slag absorption by the liner in the case of the fluoride reductions.

Entries 1 through 7 (Table V) are for reductions using the same charge (0.64 mole I_2/mole Pu) but fluorides prepared in different ways. The fluoride prepared from 1000°C oxide seemed to be the best. It also had a higher bulk density which is desirable in that a larger charge (grams of metal) may be used in a given liner. Entries 8 and 9 are for reductions using 0.25 mole I_2/mole Pu with the fluoride and the I_2 + Ca layers. <u>This was found to be the best charge</u> because the slag absorption by the liner was less and the buttons were always very well formed.

Analytical data on plutonium metal made by the reduction of PuF_4 with Ca on the 0.5-to 1-gram scale are given in Table VI.

3. 10 gram Scale Reductions:

The bomb and liner for this scale of reduction have been described. Curve 2, Figure IV, gives the heating rate which was found to give the most satisfactory and consistent reduction results for both the chloride and fluoride. A 7.5-KW high-frequency Lepel converter was used with the following coil: 2" ID, 3" high, and 8 turns of 1/4" copper tubing flattened to a thickness of 1/8". The converter settings were as follows:

Coarse Inductance Setting:	Left M, Right M.
Fine Inductance Setting:	6
Power Set	6

The bomb was centered in the coil.

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(a) <u>Reduction of $PuCl_3$ with Ca</u>: Three reductions of $PuCl_3$ with Ca on the 10 gram scale were made. The data on these reductions are given in Table VII. "Vitrified" MgO liners were used. The heating rate used is given by curve 2, Figure IV. The 975°C liner temperature (without charge) was obtained by using a heating time of 2 minutes, 45 seconds; the liner temperature being known to increase 35°C after the power was turned off. The button of metal obtained had a "Ca cap" (50% Ca, 50% Mg) as in the case of the 1 gram scale reductions. The method used for these reductions was studied using $CeCl_3$ as a stand-in.

Entry 1, Table VII, is for a reduction of chloride made from the oxalate. Entries 2 and 3 are for reductions of chloride made from the oxalate and sintered at 725°C for 2 to 3 hours. The layer of I_2 + Ca on top of the charge was used to avoid having a bridge of unreduced chloride formed at the top of the charge. It is believed, along with the 1 gram scale results, that the sintered chloride is best for the 10 gram scale reductions.

(b) <u>Reduction of PuF_4 with Ca</u>: Data on reductions of PuF_4 with Ca on the 10 gram scale are given in Table VIII. The heating rate used is given by curve 2, Figure IV. The buttons of metal obtained had the usual "Ca cap". All development work on this scale was done with CeF_4 as a stand-in.

Entry 1, Table VIII, is for a reduction where 0.5 mole I_2/mole Pu was used in the charge; 2 grams of I_2 + 0.32 grams Ca on top; and a liner temperature of 975°C (2 minutes, 40 seconds, curve 2, Figure IV). This reduction was fired to too high a temperature and contained too much iodine, thus causing all the slag and some of the metal to be

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absorbed by the liner. Entry 2 gives the results of reductions using 0.25 mole I_2/mole Pu and 1 gram I_2 + 0.16 gram Ca on top. The liner temperature was 750°C (1 minute, 40 seconds, curve 2, Figure IV). These reductions gave somewhat erratic yields, and a noticeable amount of slag was absorbed by the liner. Entry 3 gives the results of reductions using the same charge but MgO liners made by CM-7. These liners were formed by pressing the MgO powder, using a wax as a binder. The liners were fired to 2100°C in graphite and appeared to be vitrified. They did, however, show high slag absorption.

Entry 4 is for reductions, using what was found to be the <u>optimum conditions</u>: 0.25 mole I_2/mole Pu; 1 gram I_2 + 0.16 gram Ca on top; and a liner temperature of 470°C (40 seconds, curve 2, Figure IV). This reduction procedure gave very consistent results with very slight slag absorption by the liner. Fluorides prepared from 1000°C oxide were found to be best (see Entries 5 and 6). The percent conversion from the oxide of the fluorides used in the reductions reported in Entry 4 varied from 82 to 100%. It is, however, recommended that for the most consistent reduction results the fluoride be at least 90% converted from the oxide.

Representative analyses of metal obtained from the 10 gram scale reductions of PuF_4 with Ca are given in Table IX.

(c) <u>Reduction of PuO_2 with Ca</u>: Two reductions of PuO_2 with Ca were tried using the 10 gram scale liner and bomb (see Table VIII, Entry 7). The heating rate used was that given by Curve 2, Figure IV. A top liner temperature of 570°C was used with a charge which contained 2.0 mole I_2/mole Pu. There was no apparent reduction of the oxide, it not being possible to find even beads of metal upon leaching the charge with water. UNCLASSIFIED [redacted]

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4. 25 gram Scale Reductions:

The bomb and liner used for this reduction scale have been described. Curve 3, Fig~~ure IV~~ 4, gives the heating rate which was found to give the most satisfactory and consistent reduction results for the fluoride. A 3-KW high-frequency Ajax converter was used with a standard Ajax coil; 4" ID and 4" high. The bottom of the bomb was located 1/4" above the bottom of the coil. The total heating time for the 460°C liner temperature was 4 minutes and 10 seconds. The converter settings for this heating cycle were: angle 25 for 2.5 minutes and angle 0 for 1 minute and 40 seconds. All development work was done with CeF_4 as a stand-in. No plutonium chloride reductions were made on the 25 gram scale.

Entry 1, Table X, is for reductions using 0.25 mole I_2/mole Pu and vitrified MgO liners. Entry 2 is for reductions using 0.15 mole I_2/mole Pu and vitrified MgO liners. This charge gave slightly better formed buttons than the higher-iodine charge (Entry 1). Entry 3 is for reductions using MgO liners which were fired to 2100°C in graphite and not vitrified. These liners proved to be as satisfactory as the vitrified MgO liners. The conversions from the oxide of the fluorides used were between 90 and 100%.

Representative analyses of the metal obtained from the 25 gram scale reductions of PuF_4 with Ca are given in Table XI.

IV. 160, 320, 500 gram (of metal) scales:

1. General

(a) Apparatus: The apparatus consists, in general, of a bomb or external container with a pre-fired refractory liner for the charge, and a high-frequency converter and furnace to heat the bomb under controlled conditions. Two types of bombs have been used for reductions in the 160-gram and 320 to 500-gram scales; one with a double flange, and one with a solid bottom. The two-flange bombs are desirable where the liners do not fit well and may stick in the bomb after firing. Figures V and V (a) are photographs of these 160-gram bombs and liners, while Figures VI and VI (a) are cross-sectional drawings with dimensions. Figures VII, VII (a), VIII and VIII (a) are for the 320 to 500 gram scale; the same bomb and liner being used for both scales. All bombs are made of cold-rolled steel. The screw and gasket in the lid of the bomb is to enable filling the loaded bomb with an inert gas. The thermocouple well is for the purpose of following the heating cycle. The lids or covers of the bombs have a lip which if forced into the annealed copper gasket.

The most satisfactory liners were found to be pre-fired crucibles made of electrically fused magnesium oxide. The liners were made at M.I.T. or by Group CM-7. The powder used by M.I.T. had the following analysis:

Fe	0.02 %
SiO_2	2.00
R_2O_3	0.23
CaO	0.69
B	30 ppm

The analysis of the powder used by Group CM-7 was as follows:

Fe	0.17 %
SiO_2	2.35
R_2O_3	0.38

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CaO	0.94%
B	300 ppm

The boron content of this powder is higher and, as will be discussed later, the boron content of the metal made in these liners was higher than that of metal made in M.I.T. liners.

Briefly, the method used at M.I.T. for the manufacture of the liners was as follows. The magnesium oxide was mixed with 7% water and working tamped and pressed into steel dies. The formed liner was then extruded from the die, dried, and fired in a gas furnace at 1700°C for three hours. The only essential difference from the above procedure and that used by CM-7 was that the dried liners were induction fired to 2100°C using graphite as a heater. With both methods the resultant body was hard and had a porosity of less than 22%.

(b) Loading of the Bomb: All loading operations are carried out in a stagnant-air box to avoid endangering the health of the operator. Rubber gloves and a respirator are worn by the operator during all reduction operations. The halide is mixed with the reducing metal and iodine in a closed bottle, and the mixed charge poured into the liner, covered with the refractory lid, and the space between the liner and bomb wall and above the liner lid and the gasket groove filled with 40 mesh electrically fused magnesia powder. The gasket groove is then brushed free of magnesia and the annealed copper gasket put in place. The bomb lid is then bolted on. A stopcock assembly (Fig~~ure~~ ¶ III) is then screwed into the hole in the bomb lid and the bomb twice evacuated and filled with argon. The stopcock assembly is then removed and quickly replaced with the screw and copper gasket.

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(c) Firing of the Charge: The essential difference between the firing technique used for the larger-scale reductions and that used for the small scales is that the large-scale charges are heated just to the starting temperature and the heating stopped, while on the smaller scales the heating is continued past the starting of the reaction mixture. The heating of the bomb and its contents to the starting temperature of the reaction mixture is very important. It has been found in this laboratory that the charge requires a definite preheat period before the starting temperature is reached. If the bomb is heated rapidly, the reaction starts at the surface between the charge and liner, while the center of the charge is at a much lower temperature. In this case more of the heat of reaction is dissipated in heating the charge, thus allowing the products to solidify more rapidly than if a preheat is used. If the preheat period is too long, the calcium particles are coated with a layer of CaI_2 which presumably lowers the rate of reaction with the fluoride. This allows more heat to be dissipated to the liner and bomb before the reaction is complete, thus again causing poor collection of metal. The heating or firing procedures used for the 160-, 320-, and 500-gram scales are the same and were arrived at by experiment, using several different heating cycles to locate the optimum conditions. Uranium tetrafluoride was used as a stand-in for the development of the firing procedure. When developing a heating cycle, three thermocouples are placed on the inside surface of the liner, one near the top, one at the center, and one on the bottom. The temperature of the liner can then be correlated with the temperature of the outside thermocouple well. It is important that the bomb be located in the coil so that the entire length of the liner heats at nearly the

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same rate (±75°C). For example, if at the time of firing, the bottom portion of the liner is well below the firing temperature, the metal button is poorly formed and a lower yield is obtained.

In the actual firing procedure used for the 160, 320, and 500 gram scale reductions, the loaded bomb is placed in an induction furnace which is powered by a 20-KW high-frequency converter. The 160 and 500 gram bombs are placed in a 7" ID, No. 312 Ajax furnace so that the bottom of the bomb is 1" above the bottom of the coil. The coil is protected by a silica sleeve which fits on the inside of the coil. After the bomb is placed in the coil, the thermocouple (chromel-alumel) is then placed in the well on the bomb and the heating cycle given in Table XII followed. The liner temperature given is an example and will vary ±75°C depending on the fit of the liner. The heating cycle for the thermocouple well is the one recommended for the bombs used; however, if different bombs, liners, etc. were used, the liner temperature should be duplicated and not the thermocouple-well cycle. When the charge reaches the starting temperature, which is between 10 and 12 minutes, there is a sudden increase in temperature with time. When this increase occurs, the power is turned off and the bomb allowed to stand in the coil until the thermocouple well is at a temperature of ~400°C. The bomb is then removed from the coil and cooled in front of a fan. Fig[redacted] is a photograph of the firing cubicle, coil, and converter used.

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TABLE XII

Heating Cycle for 160 and 500 gram Bombs

Time (min)	Thermocouple Well (°C)	Liner Temperature (°C)
1	110	25
2	200	47
3	280	54
4	360	102
5	400	135
6	425	164
7	450	211
8	475	252
9	500	279
10	525	320
11	550	347
12	575	381
13	600	416
14	625	442
15	650	470
16	674	500

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(d) **Unloading the Bomb and Cleaning of the Metal**: All unloading and cleaning operations are carried out in a stagnant air box to avoid endangering the health of the operator. After the lid is removed, the outside of the bomb is tapped with a hammer until the contents of the bomb can be poured out. Slag and calcium which may be on the metal are removed by placing the button in concentrated nitric acid (plutonium metal is passive to conc. HNO_3). The metal button usually has a thin "Ca cap" which is made up of ~50% Ca and 50% Mg. After pickling, the button is washed in water and dried in acetone.

2. 160-gram-Scale Reductions

The bombs and liners for this scale of reduction have been discussed. The firing or heating cycle for the loaded bomb is given in Table XII. No reductions of plutonium trichloride were made on this scale, but reductions of UCl_3 and $CeCl_3$ showed that the same reduction technique as used for the fluoride was satisfactory.

Data for reductions of PuF_4 with Ca on the 160 gram scale are given in Table XIII. This table gives the percent conversion of the fluorides used as well as the yields. Entry 1 is for reductions using 0.2 mole I_2/mole Pu and fluoride made from oxide which had been ignited to 900°C. Entry 2 is for the same type of reduction using 0.3 mole I_2/mole Pu. These two entries show that there is little difference between the two iodine ratios, but it is believed that the 0.3 mole charge is the more reliable. Entry 3 is for reductions using fluoride made from oxide ignited to 600°C and 0.3 mole I_2/mole Pu. Entry 4 is for reductions using fluoride made by the direct hydrofluorination of the dried oxalate. The reduction yields are not

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significantly different from those using fluoride made from the oxide; however, the bulk density of fluoride made from the oxalate was very low, making it difficult to get the charge into the liners used. Entry 5 is for reductions using fluorides which had low conversions from the oxide and 0.5 mole I_2/mole Pu.

The data given in Table XIII and the plot given in Figure XI show that the percent conversion of the fluoride is not critical until it drops below 90%. This is very different than with UF_4 where the percent conversion of the fluoride must be 99+% for successful reductions. It is not known whether the oxygen is as plutonium oxide or plutonium oxyfluoride. Analytical data on metal from the 160 gram scale reductions are given in Table XV. It should be noticed that the metal made in liners made by Group CM-7 ran higher in boron than metal made in liners manufactured at M.I.T. This is due to the fact, as has been discussed, that the powder used by CM-7 contained 300 ppm of boron, while the powder used at M.I.T. contained only 30 ppm of boron.

3. 320-and 500-gram-Scale Reductions

The bombs and liners used for these scales of reduction have been described. The firing or heating cycle for the loaded bomb is given in Table XII. The same size bomb and liner was used for both scales of reduction.

Data for reductions of PuF_4 with Ca on the above scales are given in Table XIV. Entry 1 is for reductions using 0.2 mole I_2/mole Pu and fluoride made from 900°C oxide, while Entry 2 is for reductions using 0.3 mole I_2/mole Pu and the same type fluoride. While the data given show no significant difference between the

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iodine ratios, it is believed that the 0.3 mole I_2/mole Pu charge is more reliable, especially in view of the variations in the fluorides which may be received. Entry 3 is for reductions of fluorides made from 600°C oxide using 0.3 mole I_2/mole Pu. Entry 4 is for 500 gram reductions of the same fluoride.

The data given in Table XIV and the plots given in Fig~~ures~~ XII & XIII show that the percent conversion of the fluoride is not critical for these scales of reduction in the 90 to 100% range.

Analytical data on metal from the 320-gram-scale reductions are given in Table XV. Most of the Mg and Ca present is removed by vacuum remelting.

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TABLE III (1) [redacted]

Reduction of $PuCl_3$ with Ca
0.5 1 gram Scale

Entry	Run #	Amount, mg. metal in charge	Charge (25% excess Ca)	Refrac. tory	Liner Temp. °C	Yield %	Den. sity	Remarks
1	1706	500	$PuCl_3$ (from oxide)	Vitri. fied MgO	950	80.0	18.53	Well formed button. Small Ca cap on button.
2	1708	500	"	"	950	88.0	11.00	Button of metal porous
3	1785	990	"	"	1000	83.0	16.40	Fair button with Ca cap. Black slag.
4	1862	1258	"	"	975	76.8	16.3	Well formed button with Ca cap. Black slag.
5	1871	1183	"	"	975	93.4	18.9	Well formed button with Ca cap.
6	1897	1250	"	"	975	77.6	19.0	Well formed button with Ca cap. Black slag.
7	1895*	1220	" I_2 in charge	"	975	83.5	18.9	" "
8	1943	490	$PuCl_3$ (from oxalate)	"	975	77.0	17.6	Well formed button with Ca cap. Some unreduced $PuCl_3$ on top.
9	1946	450	$PuCl_3$ (from oxalate) Ca + I_2 on top	"	975	89.0	18.0	Well formed button with Ca cap.
10	5001	531	$PuCl_3$ (from oxalate)	"	975	80.9	18.0	" "
11	500[illegible]	510	"	"	975	74.3	18.9	Well formed button with Ca cap. Unreduced $PuCl_3$ on top.
12	5029*	485	"	"	975	86.4	18.7	Well formed button with Ca cap.
13	5032*	488	"	"	975	83.0	18.8	" "

TABLE III (2)

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Entry	Run #	Amount, mg. metal in charge	Charge (25% excess Ca)	Refractory	Liner Temp. °C	Yield %	Density	Remarks
14	5036*	484	$PuCl_3$ (from oxalate) and sintered	Vitrified MgO	975	94.8	18.1	Well formed button with Ca cap.
15	5037*	485	" "	"	975	90.4	19.6	" "
16	5028*	495	$PuCl_3$ (from oxalate)	"	975	78.0	20.0	Well formed button with Ca cap. Ni plated bomb.
17	5041*	506	$PuCl_3$ (from oxalate) I_2 in charge	"	975	91.4	18.5	Well formed button with Ca cap.
18	5040*	498	"	"	975	87.0	18.8	" " Ni plated bomb.
19	5048*	465	Distilled $PuCl_3$	"	975	94.2	18.5	Well formed button with Ca cap.
20	5049*	504	"	"	975	88.9	18.6	" "
21	5050*	454	"	"	975	89.7	18.6	" "
22	5062	491	$PuCl_3$ (from oxalate) Sintered	"	975	86.5	....	" "
23	5073	514	"	"	975	89.0	....	" "
24	5005*	501	$PuCl_3 \cdot \frac{1}{2}H_2O$ from oxalate	"	975	90.0	19.5	" "
25	1709	500	$PuCl_3$ (from oxide)	Vit. CaO	950	91.0	17.59	All of slag absorbed by liner. Poorly formed buttons.
26	1881	1250	"	"	975	76.5	19.5	All of slag absorbed by liner. Fair button, no Ca cap.
27	1894*	1250	"	"	925	68.4	18.9	" "

*Analysis of metal given in Table IV.

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TABLE IV

Analytical Data on Pu from $PuCl_3$
Values in ppm

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Entry	Run No.	Scale mg. metal	Reduction Conditions	Be	Mg	Al	Ca	Na	Cr	Fe	Ni
1	1894	1250	$PuCl_3$ from oxide, 25% excess Ca. Vit. CaO liner.	ND <20		ND <200			ND <400	400*	
2	1895	1220	$PuCl_3$ from oxide, 25% excess Ca. Vit. MgO	2	80	10	~600	15	ND <400	8000*	
3	5005	500	$PuCl_3 \cdot \frac{1}{2}H_2O$ from oxalate. 25% excess Ca. Vit. MgO liner.	≤0.5	<3	≤3	<5	<5		800*	
4	5010	9320	$PuCl_3$ from oxalate. 25% excess Ca. Vit. MgO liner.	<0.5	130	<10	200	40		400*	
5	5028	495	$PuCl_3$ from oxalate. 25% excess Ca. Vit. MgO. Ni plated bomb.	ND<2	<20	ND <200	≤200		ND <200	<1000*	≤20
6	5029	485	$PuCl_3$ from oxalate. 25% excess Ca. Vit. MgO. liner.	ND<2	<20	ND <200	100		ND <200	<1000*	
7	5032	488	"	ND<2	<20	ND <200	20		ND <200	1000*	
8	5036	484	"	ND<2	<20	ND <200	40		ND <200	<1000* 190	
9	5037	485	"	ND<2	~20	ND <200	200		ND <200	<1000* 350	
10	5040	498	" I_2 in charge.	ND<2	~20	600	200		ND <200	2000* 313	≤20

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TABLE IV (contd.)

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Entry	Run No.	Scale mg. metal	Reduction Conditions	Be	Mg	Al	Ca	Na	Cr	Fe	Ni
11	5041	506	$PuCl_3$ from oxalate. 25% excess Ca. Vit. MgO liner. I_2 in charge. Ni plated bomb.	ND<2	<20	ND <200	200		ND <200	<1000* 240	20
12	5048	465	Distilled $PuCl_3$. 25% excess Ca. Vit. MgO liner.	ND<2	20	100	100		ND <200	<400* 107	
13	5049	504	"	ND<2	40	100	10,000		ND <200	<400* 65	
14	5050	454	"	ND<2	60	100	6,000		ND <200	<400* 174	

*Spectrographic Fe, other values colorimetric.

Note: Zr, La, Ce, Bi, and Th were all below the "not-detected" limit.

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TABLE V

Reduction of PuF_4 with Ca
0.5-1 gram Scale

Entry	Run #	Amount, mg. metal in charge	Charge (25% excess Ca)	Refractory	Liner Temp. °C	Yield %	Density	Remarks
1	5104	504	PuF_4 from oxide; 0.64 mole I_2/mole PuF_4; 0.15 g I_2 + 0.02 g Ca, top and bottom	Vitrified MgO	975	93.4	18.40	well formed button with Ca cap.
2	5105*	480	" " "	"	"	95.5	19.50	" "
3	5109	514	PuF_4 from oxalate. Same charge as 1.	"	"	94.5	17.76	Button had hole inside; thus lower density.
4	5110*	511	" " "	"	"	95.5	19.16	Well formed button with Ca cap.
5	5113	510	PuF_4 from 1000°C oxide; same charge as 1	"	"	97.6	15.70	Button had small hole inside, thus lower density.
6	5114*	510	" " "	"	"	96.2	19.00	Well formed button with Ca cap.
7	5133	510	PuF_4 from oxalate; 0.64 mole I_2/mole PuF_4 0.15 g I_2 + 0.02 g Ca top and bottom	"	"	95.0	18.5	" "
8	5134*	514	PuF_4 from oxalate; 0.25 mole I_2/mole PuF_4 0.15 g I_2 + 0.02 g Ca top and bottom	"	"	96.1	18.10	" "
9	(14 runs)	~500	PuF_4 from 1000°C oxide. Same charge as 8.	"	"	Max. 97.0 Min. 91.0 Ave. 95.0	....	" "
10	5633	1470	" " "	"	"	96.9	....	" "

*Analysis of metal given in Table VI

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TABLE VI

Analytical Data on Pu from PuF_4
0.5-1 gram Scale
Values in ppm

Run No.	Amount mg. metal in charge	Reduction Conditions	Be	Mg	Al	Ca
5105	480	PuF_4 from 1000° oxide. 0.64 mole I_2/mole Pu. 0.15 g I_2 + 0.02 g Ca on top and bottom. Liner temp. 975o.	ND<2	ND<20	ND<400	100
5110	511	PuF_4 from oxalate. Same charge as 5105.	ND<2	ND<20	ND<400	40
5114	510	Same as 5105.	ND<2	ND<40	ND<1000	40
5134	514	PuF_4 from oxalate. 0.25 mole I_2/mole Pu. 0.15 g I_2 + 0.02 g Ca on top and bottom. Liner temp. 975°C.	ND<2	<20	ND<200	20

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TABLE VII

Reduction of $PuCl_3$ with Ca
10 gram Scale

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Entry	Run #	Amount, g. metal in charge	Charge (25% excess Ca)	Refractory	Liner Temp. °C	Yield %	Density	Remarks
1	5010*	9.32	$PuCl_3$ (from oxalate)	Vitrified MgO	975	86.5	18.9	Well formed button with Ca cap. Some unreduced Cl_3 near the top.
2	5063	9.53	$PuCl_3$ (from oxalate) sintered. 1 g I_2 + 0.16 g Ca on top	"	"	96.0	18.9	" "
3	5074	9.50	" "	"	"	94.7	18.9	" "

*Analysis of metal given in Table IV.

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TABLE VIII

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Reduction of PuF_4 with Ca
10 gram Scale

Entry	No. of Runs	Amount, g. metal in charge	Charge (25% excess Ca)	Refractory	Liner Temp. °C	Yield % Max.	Yield % Min.	Yield % Ave.	Remarks
1	1	6.52	PuF_4 from 1000°C oxide. 0.50 mole I_2/mole Pu. 2 g I_2 + 0.32 g Ca on top.	Vitrified MgO	975	---	---	86.3	Well formed button. All the slag absorbed by liner.
2	4	6.50-8.50	PuF_4 from 1000°C oxide. 0.25 mole I_2/mole Pu. 1 g I_2 + 0.16 g Ca on top.	"	750	97.3	93.1	95.7	Well formed buttons. Slight absorption of slag by liners.
3	2	"	" "	MgO, 2100°C firing	750	97.7	94.0	95.9	Poorly formed buttons. High absorption of slag by liners.
4	27*	"	" "	Vitrified MgO	470	99.1	96.6	97.9	Well formed buttons. Very slight absorption of slag by liners.
5	3*	"	PuF_4 from oxalate Same charge as 2	"	470	97.0	94.4	96.0	" "
6	3	"	PuF_4 from oxide made from peroxide ppt. Same charge as 2	"	470	99.1	94.9	96.9	" "
7	2	4.00	PuO_2 ignited to 900°C. 2.0 mole I_2/mole Pu	"	570	0.00	0.00	0.00	No apparent reduction of the oxide.

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*Analysis of metal given in Table IX.

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TABLE IX

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Analytical Data on Pu from PuF_4
10 gram Scale
Values in ppm

Run No.	Amount g. metal in charge	Reduction Conditions	Li	Be	B	C	O	Na	Mg	Al	Si	K	Ca	Fe
5700	7.60	PuF_4 from 1000°C oxide. 0.25 mole I_2/mole Pu. 1 g I_2 + 0.16 g Ca on top. Liner temp. 470°C	<5	<0.5	<6	120	<100	<5	93	47	250	<47	7	70
5702	7.48	"	<4	<0.4	---	115	105	29	74	<4	---	74	55	75
5706	7.09	"	<5	<0.5	<6	115	<100	14	23	5	30	<47	23	80
5710	7.30	"	<3	<0.3	---	220	<100	50	300	13	---	<100	17	75
5727	7.94	"	<4	<0.2	<6	95	<100	13	300	86	400	<45	17	100
5728	8.00	"	<4	<0.2	---	135	<100	17	220	44	---	<44	17	90
5756	8.06	PuF_4 from oxalate. 0.25 mole I_2/mole Pu. 1 g I_2 + 0.16 g Ca on top. Liner temp. 470°C	<5	<0.3	---	110	160	<25	225	20	---	<50	<5	---
5757	8.07	"	<5	0.24	1.7	105	<100	<5	280	95	---	<95	35	---

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TABLE X

Reduction of PuF_4 with Ca
25 gram Scale

Entry	No. of Runs	Amount, g. metal in charge	Charge (25% excess Ca)	Refractory	Liner Temp. °C	Yield % Max.	Yield % Min.	Yield % Ave.	Remarks
1	2*	24.0-25.0	PuF_4 from 1000°C oxide. 0.25 mole I_2/mole Pu.	Vitrified MgO	460	97.6	97.1	97.4	Well formed buttons. Slight absorption of slag by liners.
2	6*	"	PuF_4 from 1000°C oxide. 0.15 mole I_2/mole Pu.	"	460	98.6	96.5	97.8	"
3	3*	"	"	MgO fired at 2100°C	460	98.7	97.7	98.0	"

*Analysis of metal given in Table XI.

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TABLE XI

Analytical Data on Pu from PuF_4
25 gram Scale
Values in ppm

Run No.	Amount g. metal in charge	Reduction conditions	Li	Be	B	C	O	Na	Mg	Al	Si	K	Ca	Fe
5498	25.80	PuF_4 from 1000°C oxide. 0.25 mole I_2/mole Pu. Liner temp. 460°C.	<3	<0.3	---	120	<110	9	26	43	---	---	4	91
5536	23.00	PuF_4 from 1000°C oxide. 0.15 mole I_2/mole Pu. Liner temp. 460°C.	<4	<0.4	---	<100	145	7	2100	71	---	---	--	60
5588	25.00	"	<4	<0.4	---	<100	<100	7	230	11	---	---	7	70
5557	24.00	" 2100°C. MgO liner.	<4	<0.4	---	<100	153	31	154	77	---	---	4	120

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TABLE XIII

Reduction of PuF_4 with Ca
160 gram Scale

Entry	No. of Runs	Amount, g. metal in charge	Charge (25% excess Ca)	Fluoride from:	% Conversion of Fluoride Max.	% Conversion of Fluoride Min.	% Conversion of Fluoride Ave	Yield % Max.	Yield % Min.	Yield % Ave.
1	5	130-160	0.2 mole I_2 per mole Pu	900°C oxide	92.3	89.2	91.5	99.11	97.36	98.33
2	6	"	0.3 mole I_2 per mole Pu	"	90.9	89.1	90.7	98.82	97.93	98.56
3	10	"	"	600°C oxide	100.0	94.4	96.81	98.96	98.27	98.75
4	2	"	0.2 mole I_2 per mole Pu	oxalate	96.0	94.6	95.3	98.75	98.25	98.50
5	2	"	0.5 mole I_2 per mole Pu	900°C oxide	75.4	75.3	75.4	96.49	92.44	94.47

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TABLE XIV

Reduction of PuF_4 with Ca
320 and 500 gram Scales

Entry	No. of Runs	Amount, g. metal in charge	Charge (25% excess Ca)	Fluoride from:	% Conversion of Fluoride Max.	% Conversion of Fluoride Min.	% Conversion of Fluoride Ave.	Yield % Max.	Yield % Min.	Yield % Ave.
1	2*	250-320	0.2 mole I_2 per mole Pu	900°C oxide	93.3	91.4	92.4	98.91	98.70	98.80
2	6*	"	0.3 mole I_2 per mole Pu	"	94.7	90.0	91.2	98.90	98.73	98.95
3	39*	"	"	600°C oxide	99.7	88.8	95.8	99.50	97.90	98.97
4	23	420-480	"	"	99.8	94.4	96.7	99.41	98.10	99.00

*Analysis of metal given in Table XV.

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TABLE XV

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Analytical Data on Pu from PuF_4
160 and 320 gram Scales
Values in ppm

Run No.	Scale g. metal in charge	Reduction Conditions	Refractory Liner	Li	Be	B	Na	MG	Al	K	Ca
5784	160	PuF_4 from 900°C oxide 0.2 mole I_2/mole Pu	MgO OM-7	<2	<0.1	2.1	19	950	---	<100	15
5804	160	"	"	<2	<0.2	2.0	--	920	10	---	10
5871	160	PuF_4 from oxalate. 0.2 mole I_2/mole Pu.	"	<1	<0.1	2.5	23	70	35	<70	<7
5875	160	"	"	<1	<0.1	2.0	13	1000	15	<70	90
5857	160	PuF_4 from 900°C oxide 0.2 mole I_2/mole Pu	MgO MIT	<2	<0.2	<0.5	--	160	3	---	30
5956	160	PuF_4 from 900°C oxide 0.3 mole I_2/mole Pu	"	<1	<0.1	0.26	4	1000	4	<30	80
7076	320	"	"	<1	<0.1	<0.5	8	1000	20	<40	120
7097	320	PuF_4 from 600°C oxide 0.3 mole I_2/mole Pu	"	<1	<0.1	0.5	4	1000	6	38	115
7244	320	"	"	<1	<0.1	0.5	<7	100	25	<17	12

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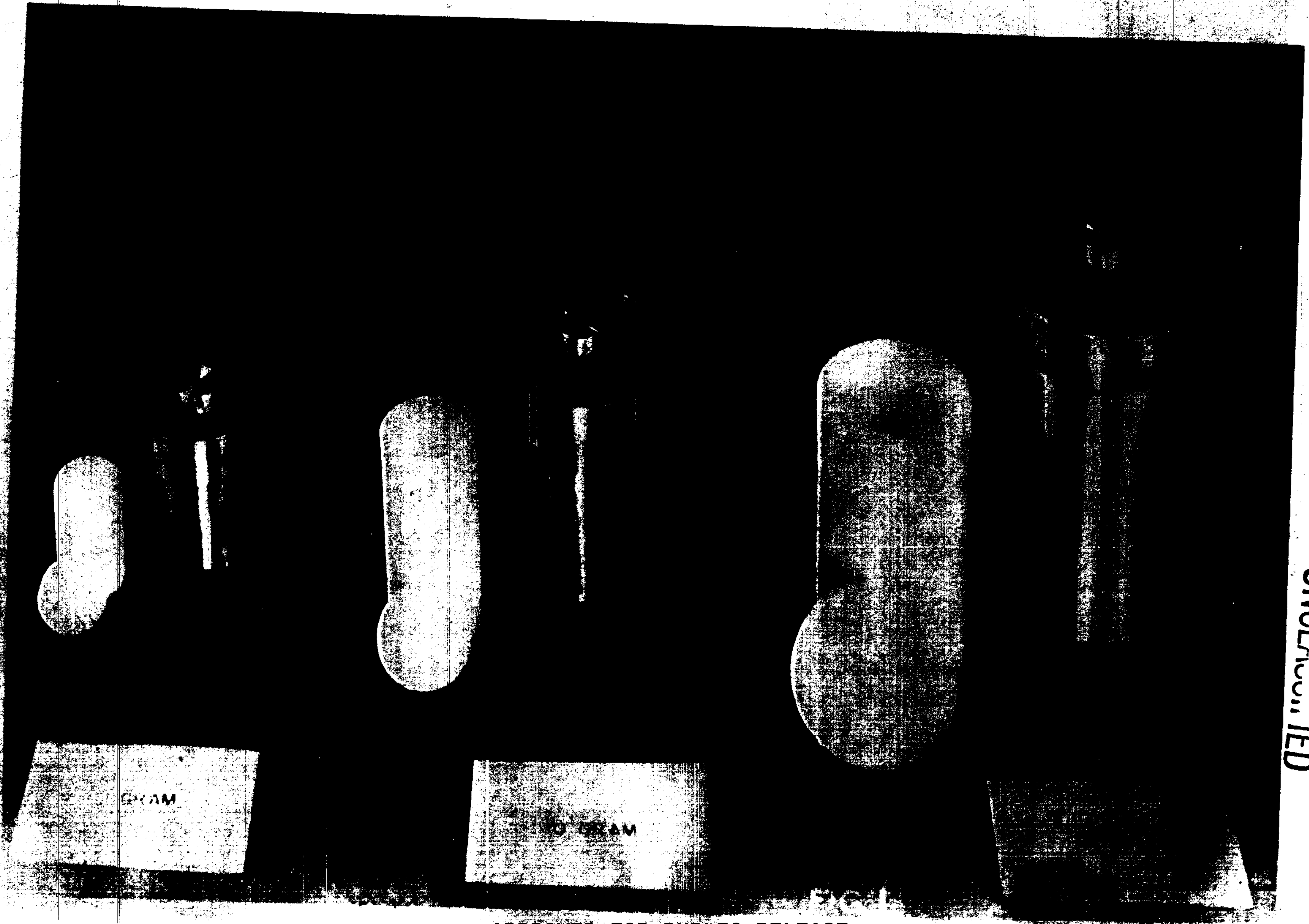

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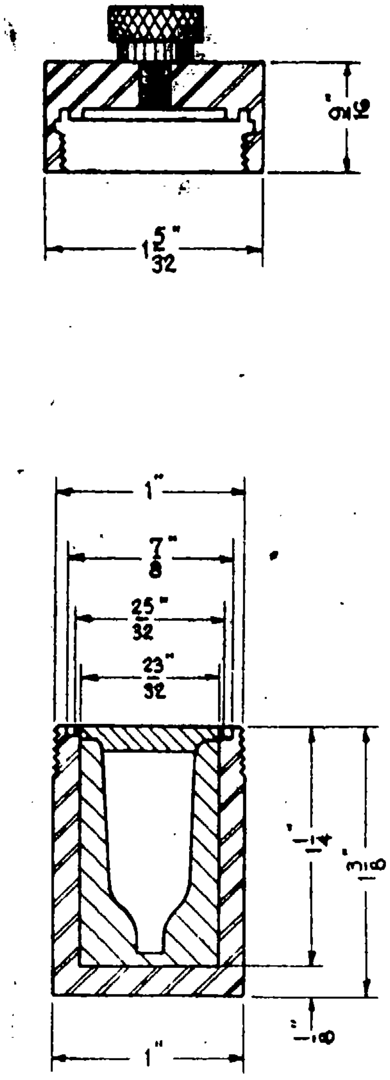
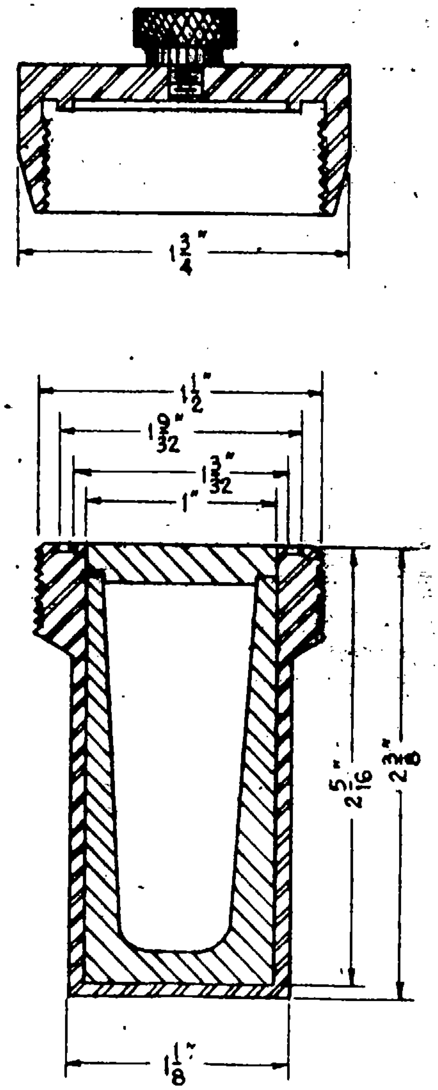
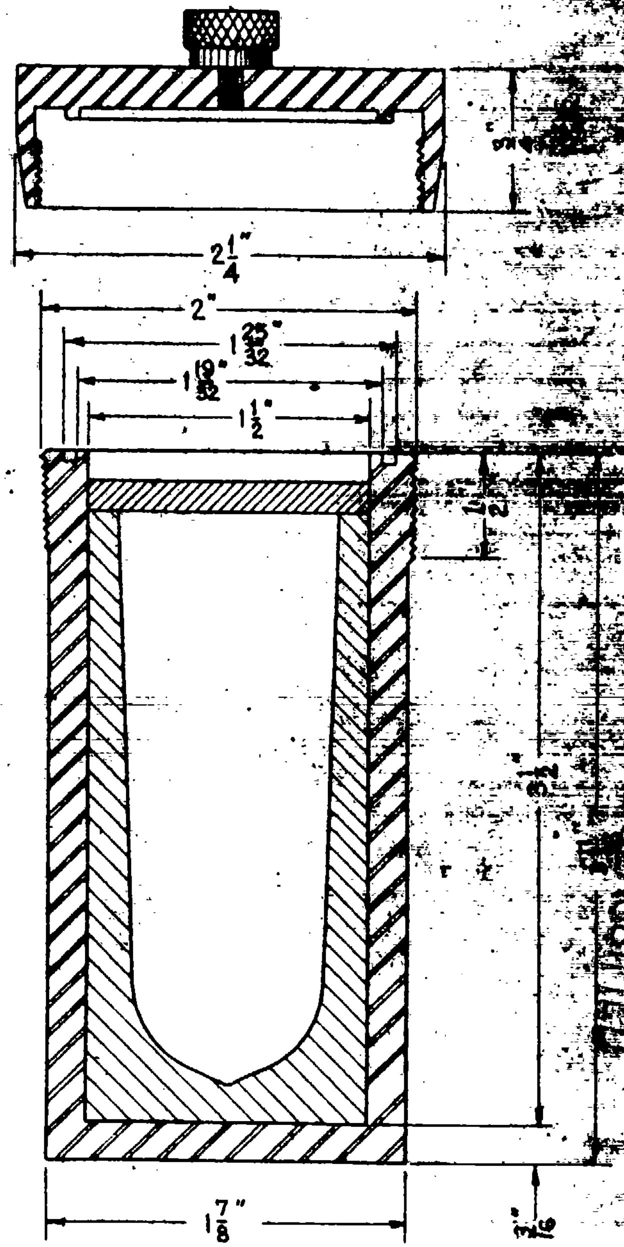


1 GRAM



10 GRAMS



25 GRAMS

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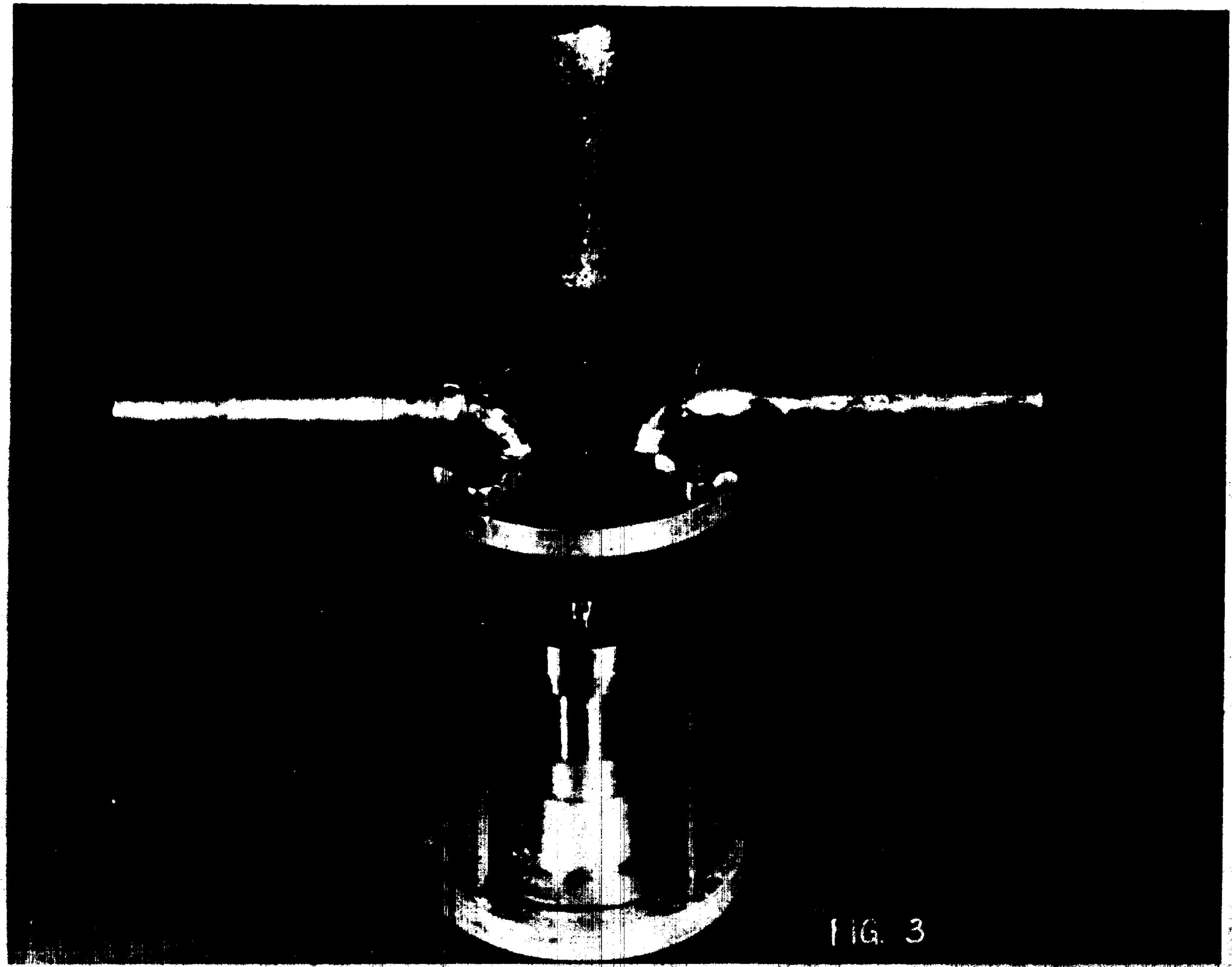

FIG. 3

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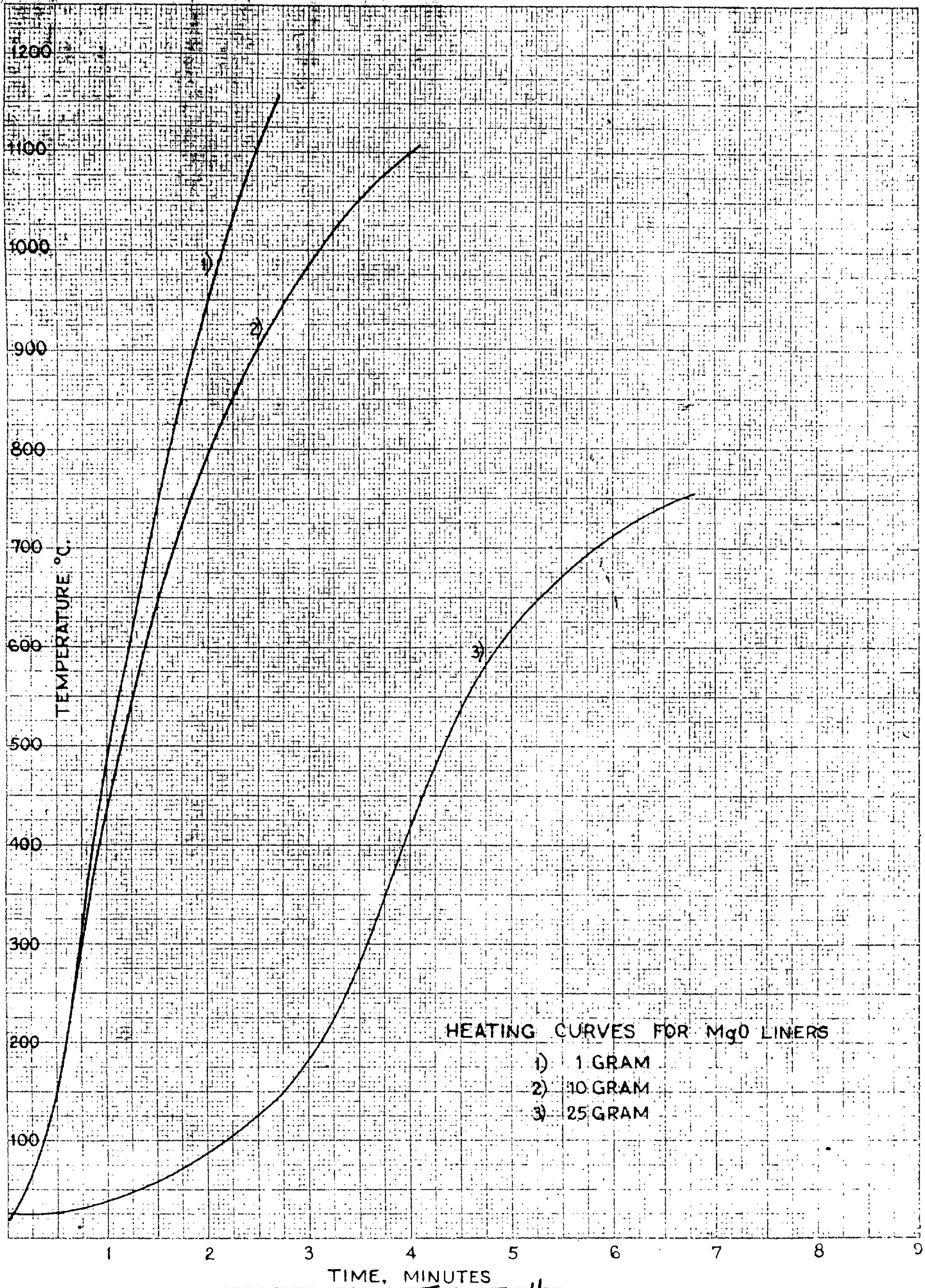
HEATING CURVES FOR MgO LINERS
1) 1 GRAM
2) 10 GRAM
3) 25 GRAM
1)
2)
3)
TEMPERATURE °C.
1200
1100
1000
900
800
700
600
500
400
300
200
100
TIME, MINUTES
1
2
3
4
5
6
7
8
9

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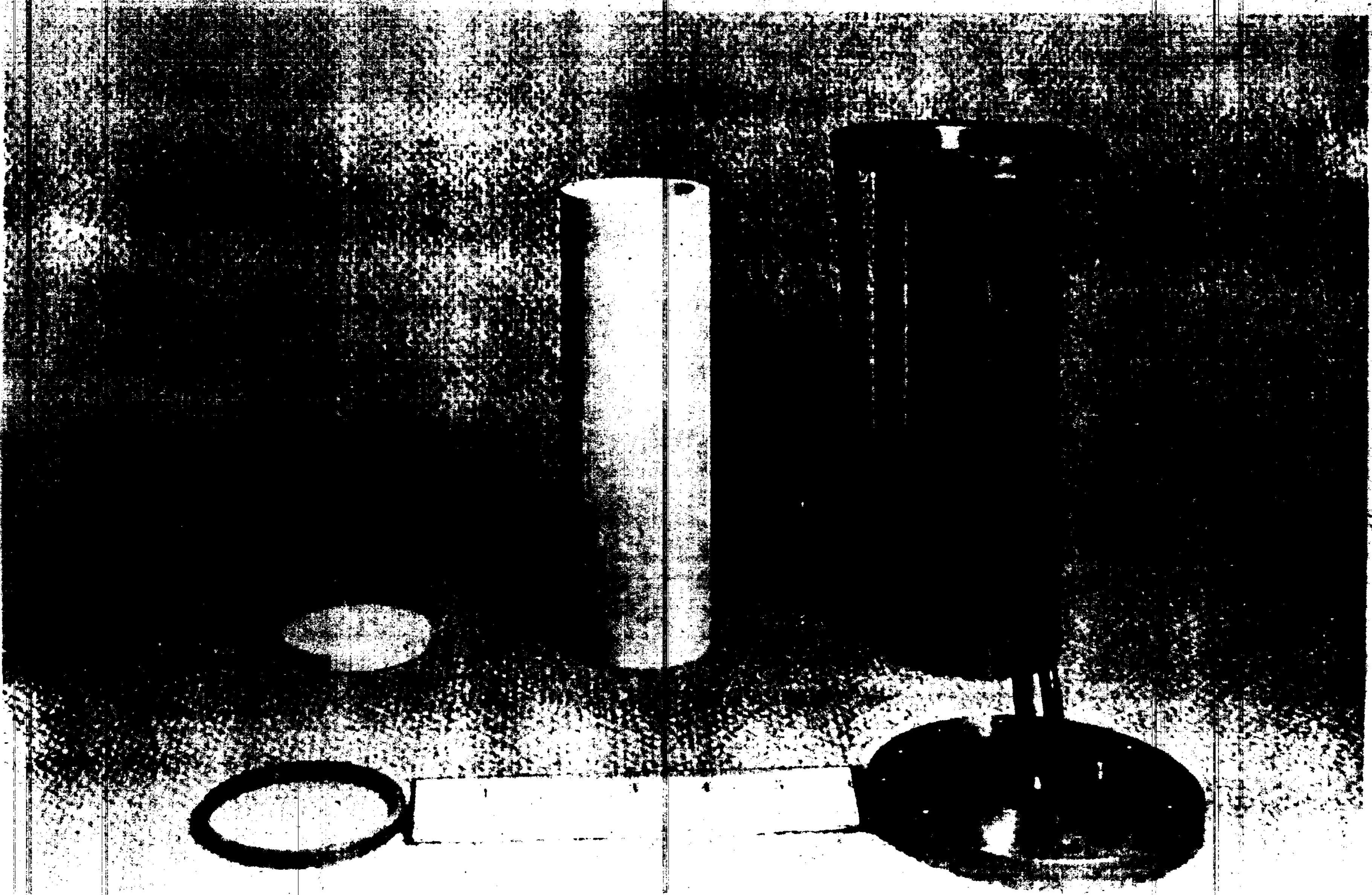

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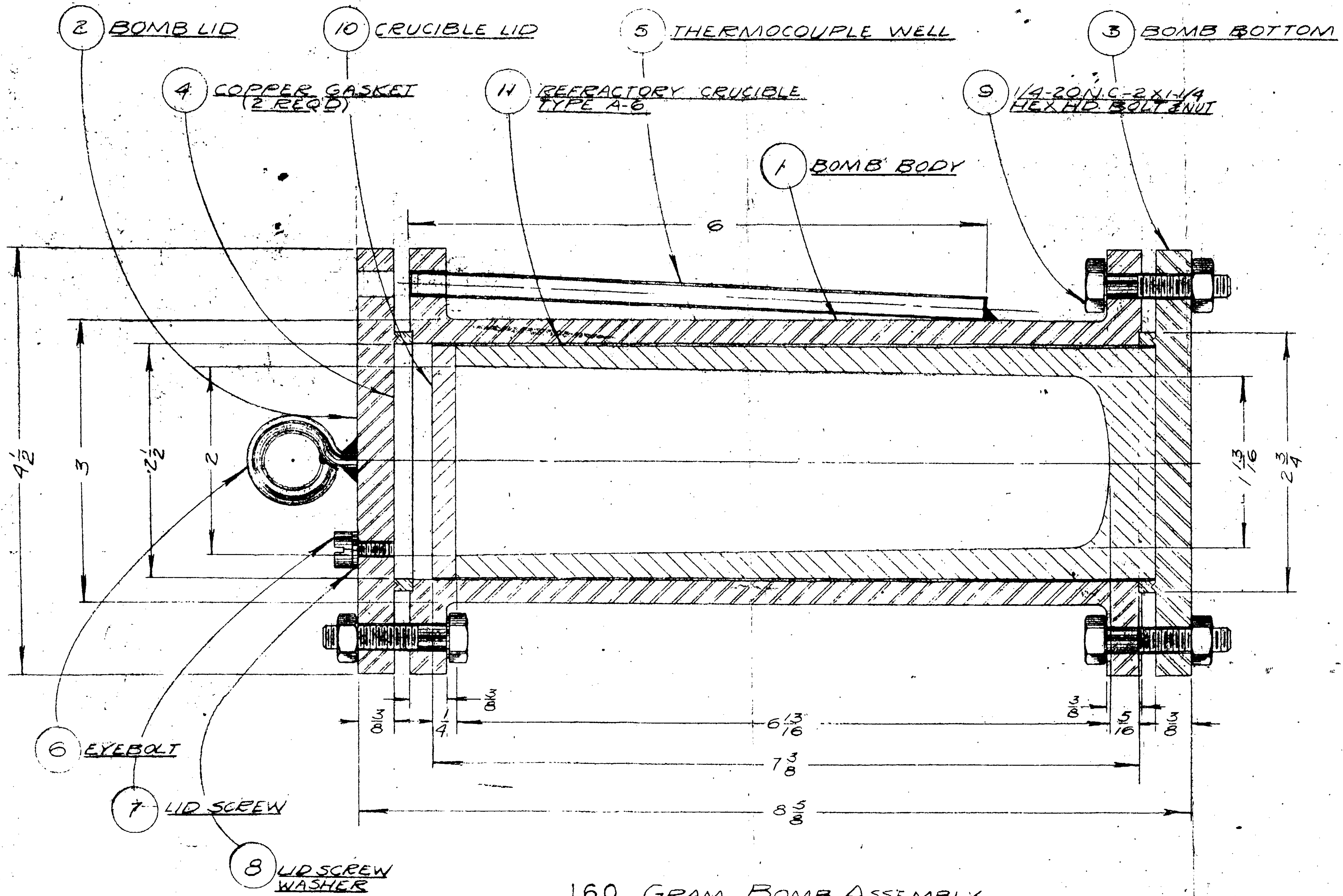
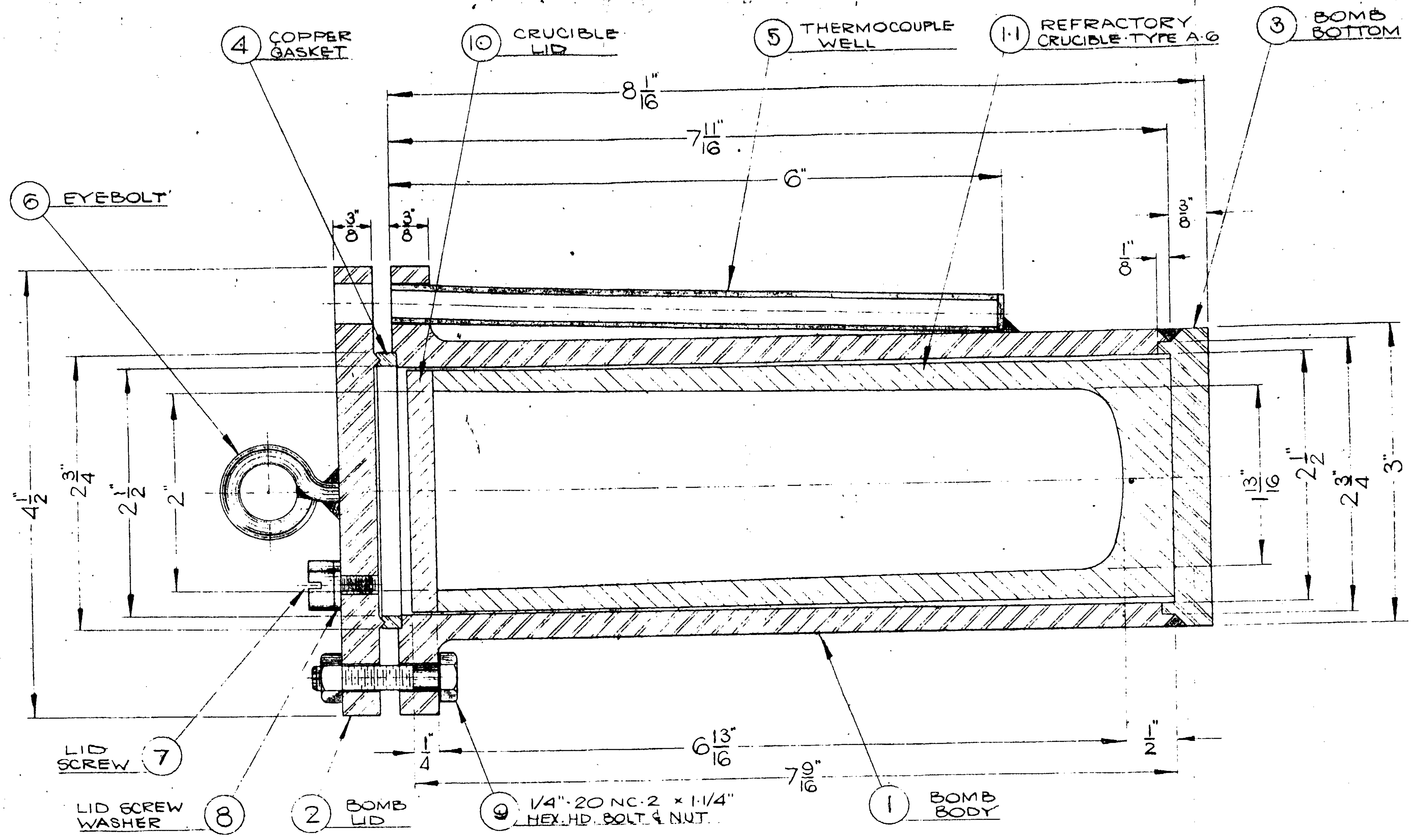


160 GRAM BOMB ASSEMBLY
FULL SCALE
Fig ~~II~~ 6



160 GRAM BOMB ASSEMBLY

SCALE : FULL SIZE

Fig. ~~III (a)~~ 6(a)

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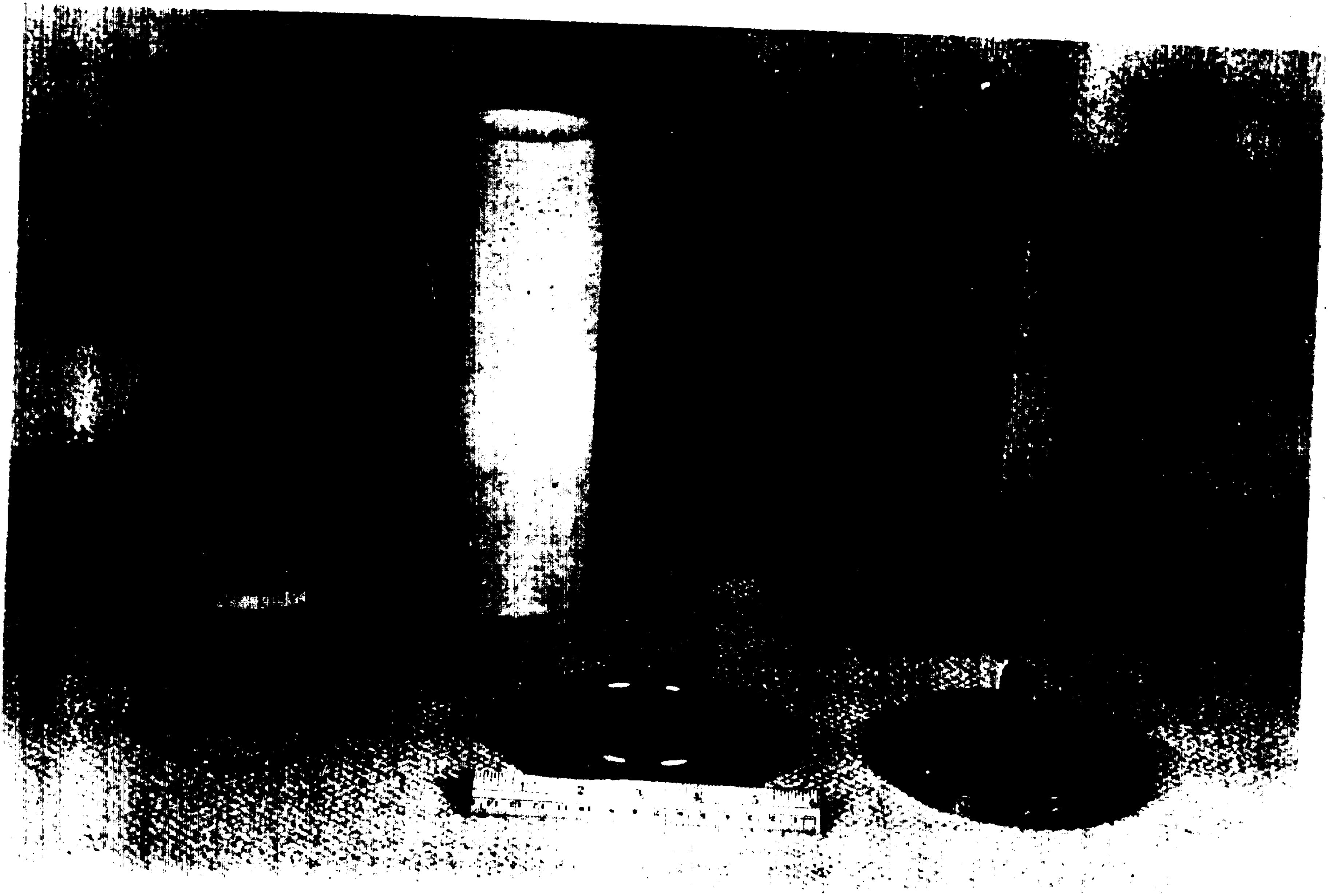

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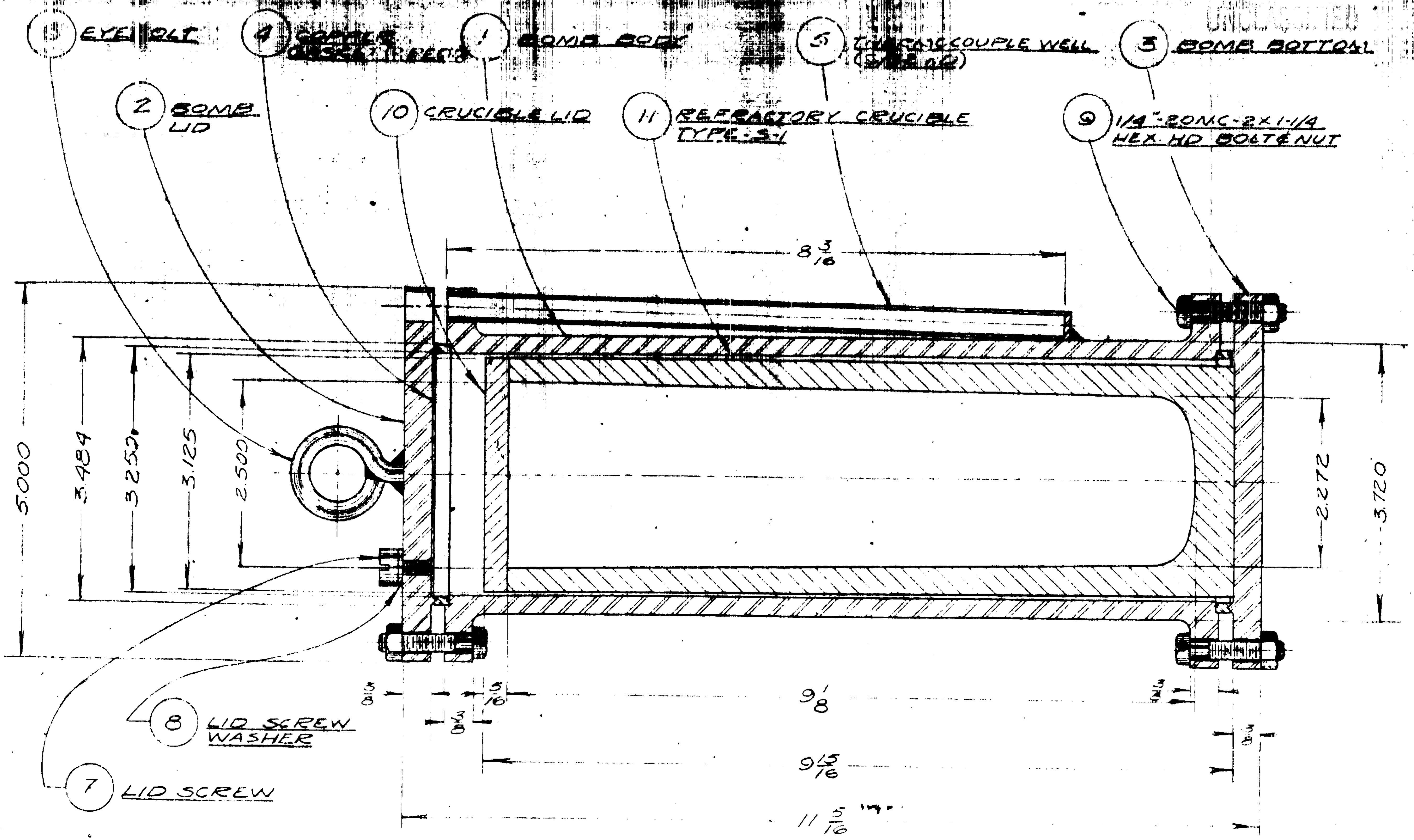

500 GRAM BOMB ASSEMBLY

SCALE 3/4"=1"

Fig. ~~III~~ 8

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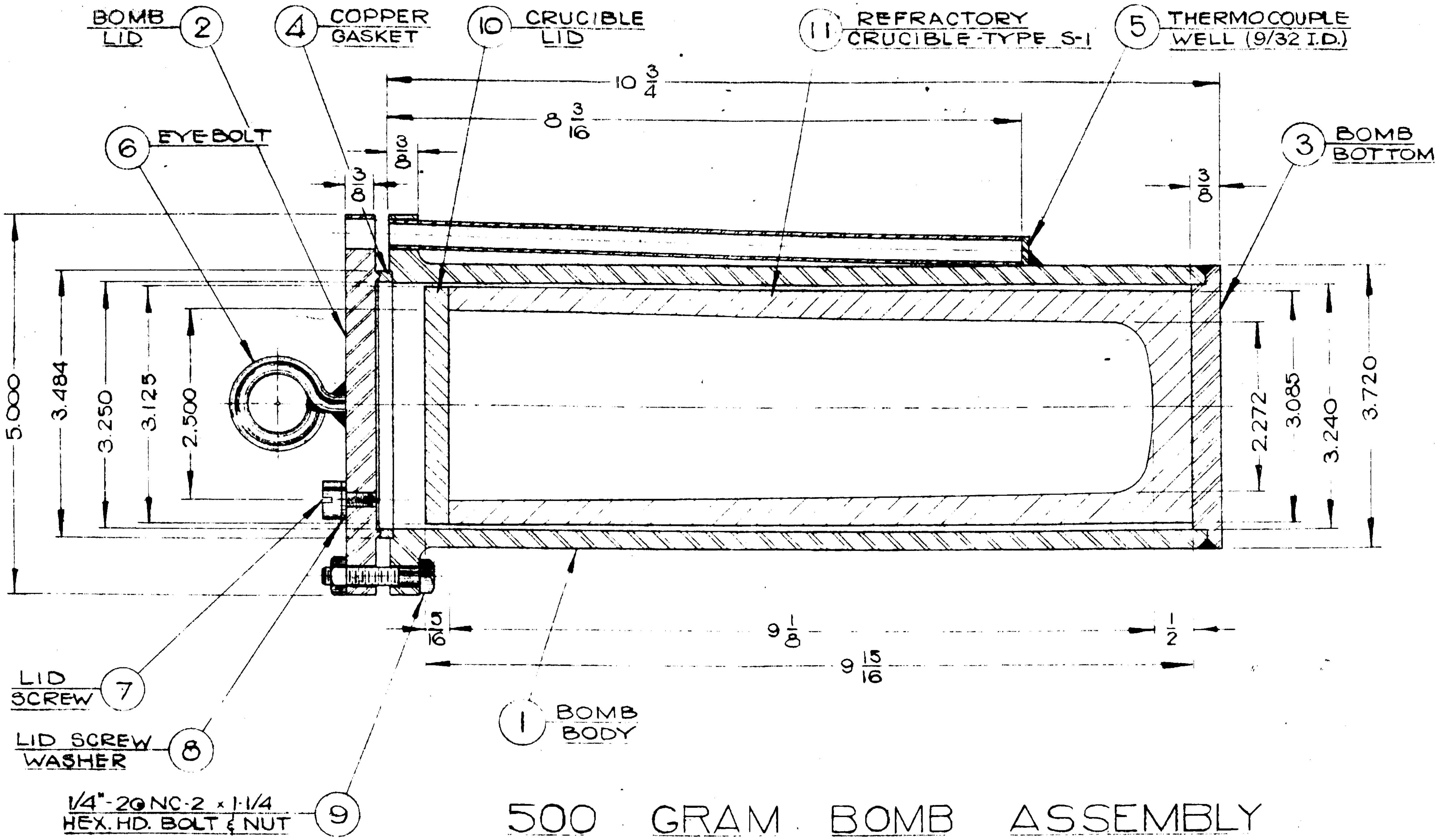

500 GRAM BOMB ASSEMBLY

SCALE: 3/4" = 1"

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Fig. ~~[illegible]~~ 8 (a)

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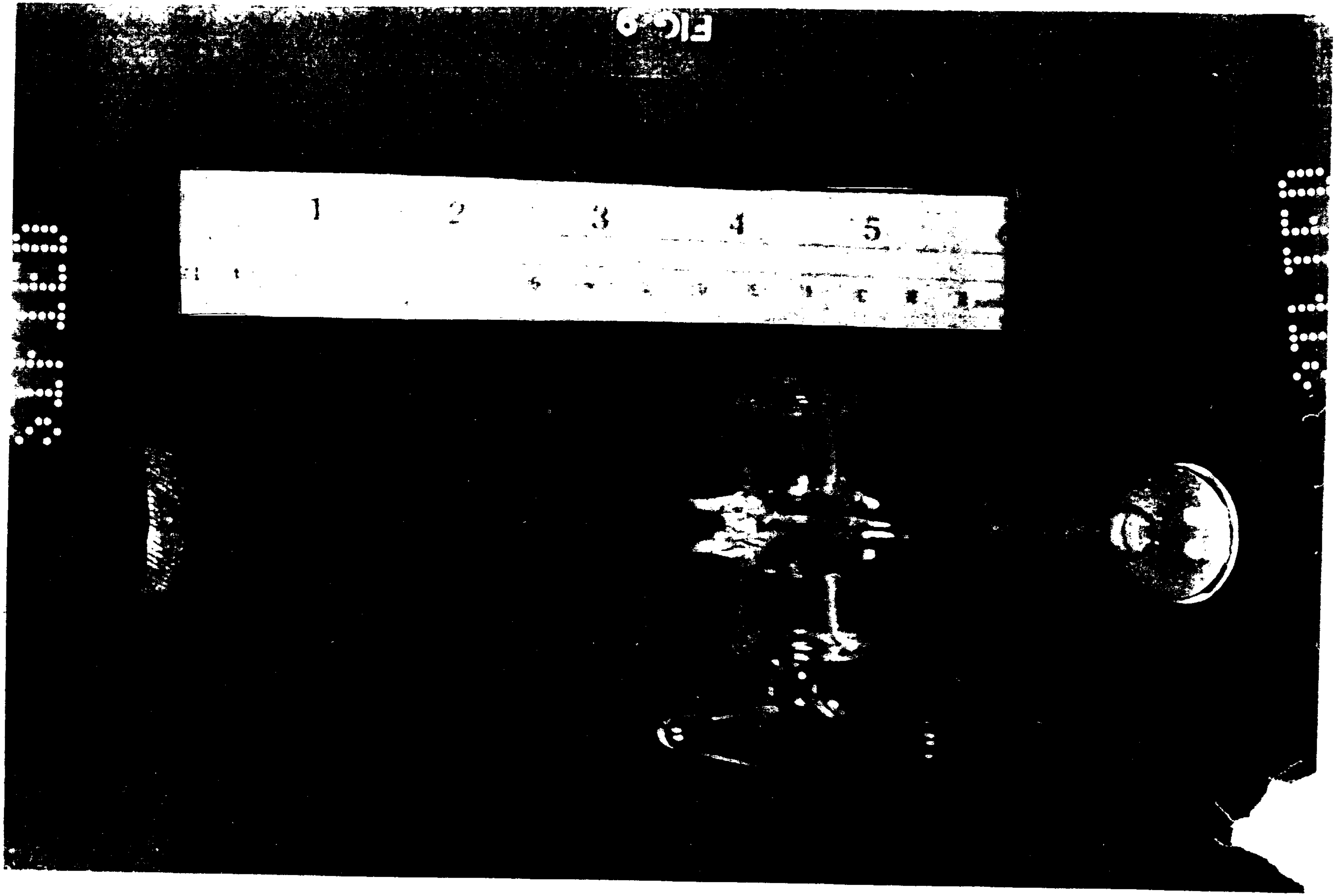

FIG 9

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FIG. 10

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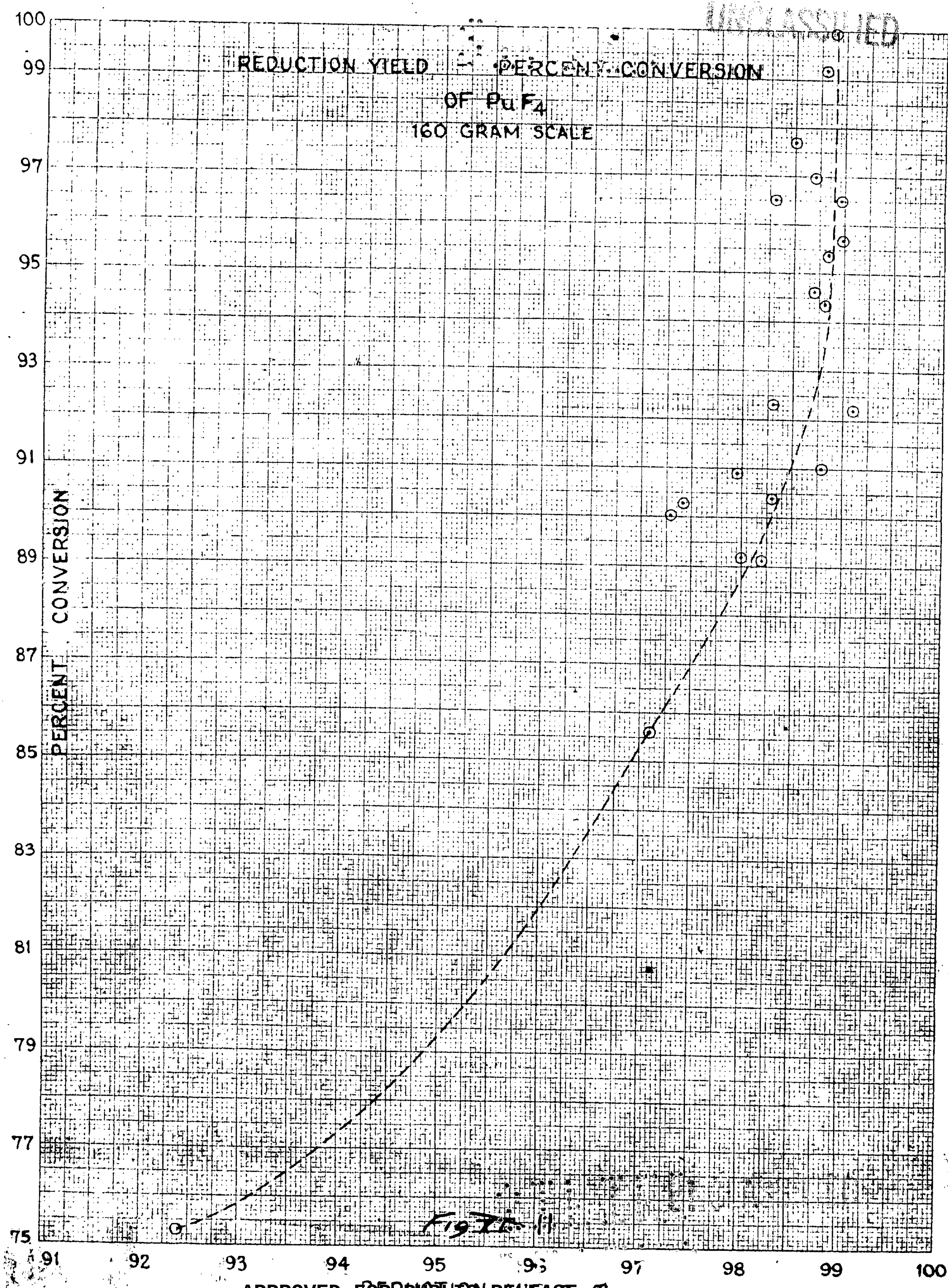

Fig 11

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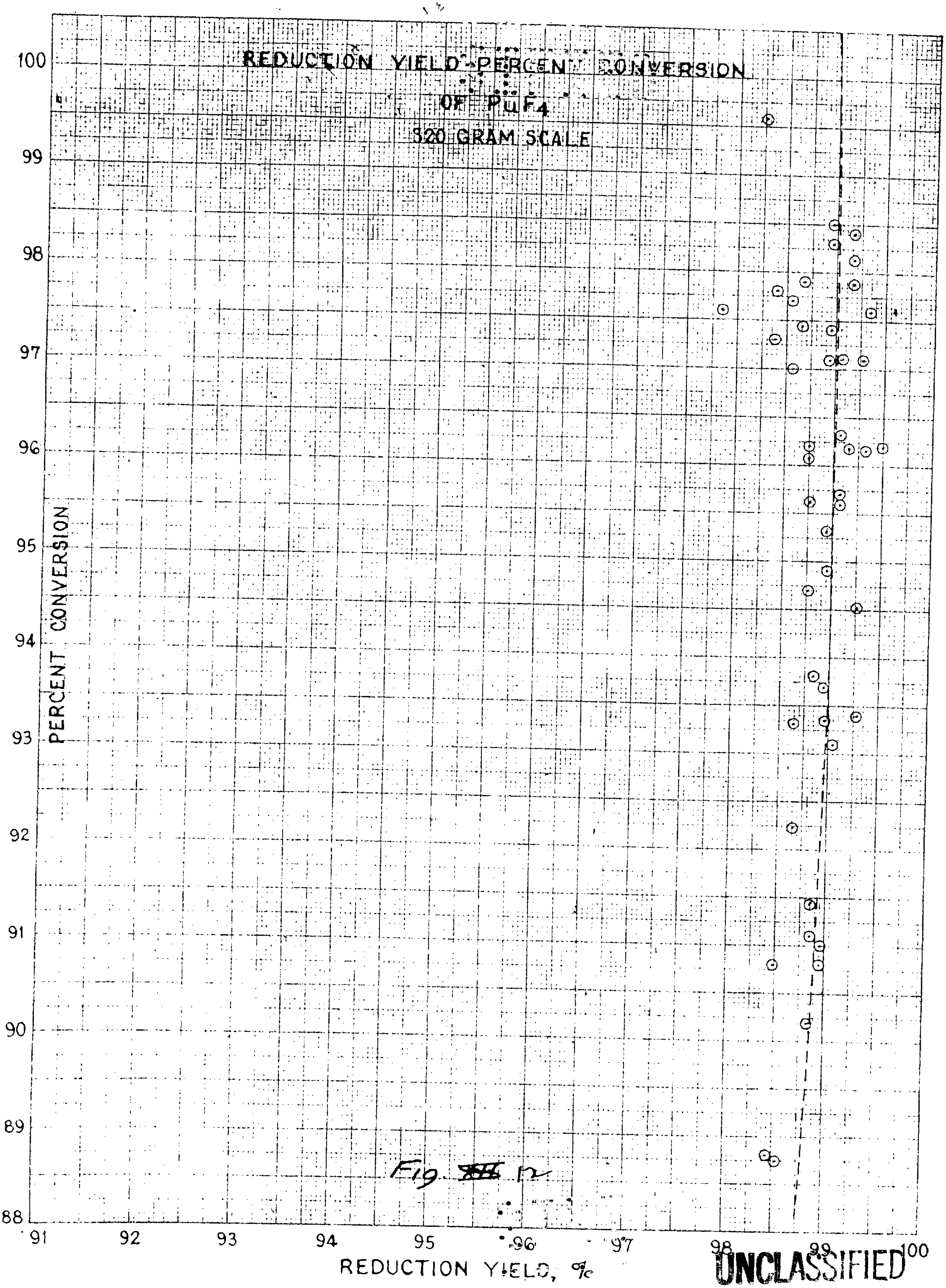

Fig. 12

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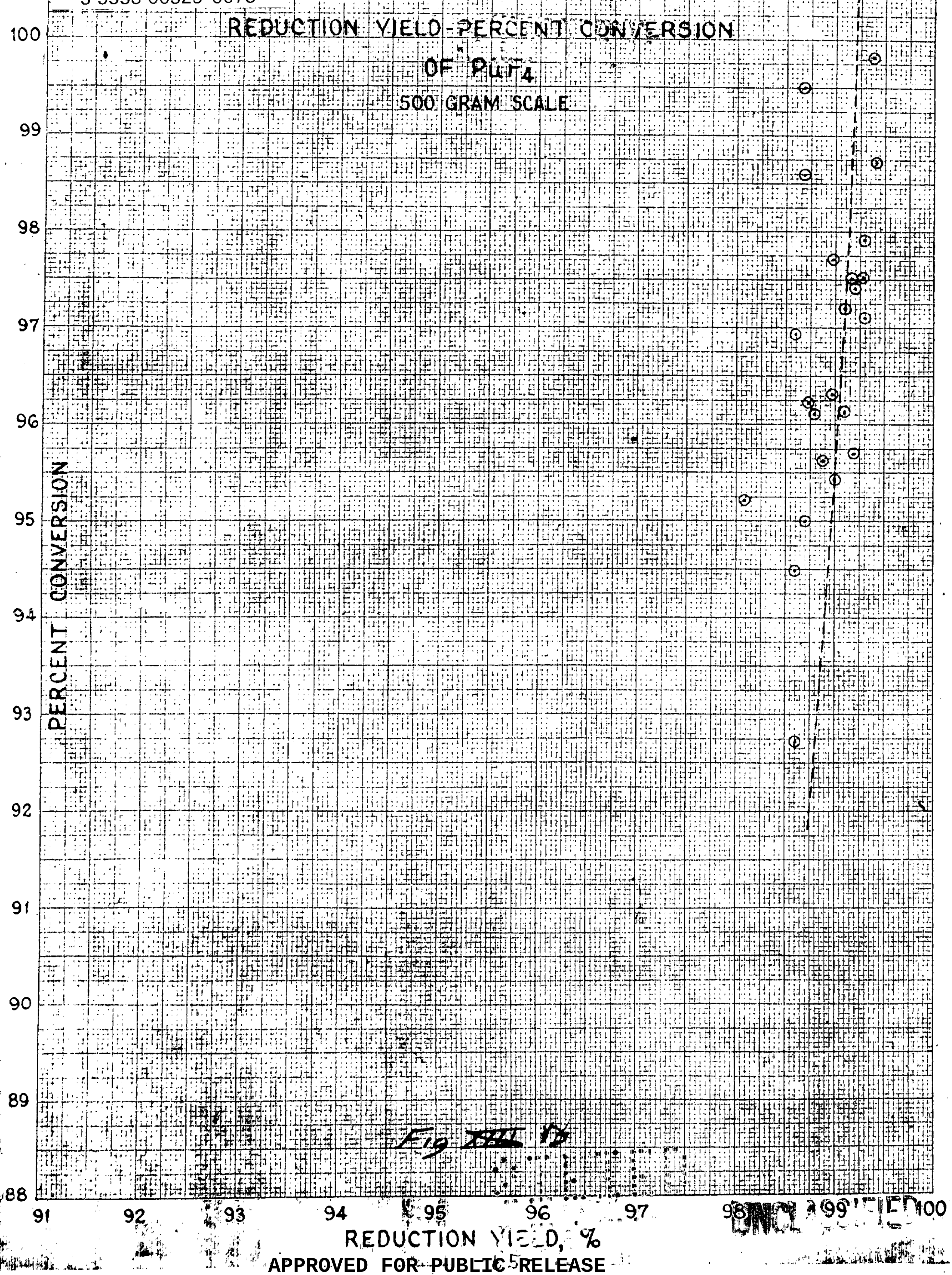

REDUCTION YIELD-PERCENT CONVERSION OF PuF_4

500 GRAM SCALE

Fig 13