AEROSPACE ELECTRICAL DIVISION

HIGH TEMPERATURE

ALKALI METAL RESISTANT INSULATION

USAF Contract AF33(615)1360

Project No. 8128
Task No. 8128-06

WESTINGHOUSE ELECTRIC CORPORATION

AEROSPACE ELECTRICAL DIVISION

LIMA, OHIO

HIGH TEMPERATURE ALKALI METAL RESISTANT INSULATION

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HIGH TEMPERATURE

ALKALI METAL RESISTANT INSULATION

2nd Quarterly Progress Report
Contract AF33(615)1360, Task No. 8128-06

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NOTICE

The work covered by this report was accomplished under Air Force Contract AF33(615)1360, but this report is being published and distributed prior to Air Force review. The publication of this report, therefore, does not constitute approval by the Air Force of the findings and conclusions contained herein. It is published for the exchange and stimulation of ideas.

FOREWORD

This 2nd Quarterly Report is submitted by the Aerospace Electrical Division, Westinghouse Electric Corporation, Lima, Ohio, on Air Force Contract AF33 (615)1360, Project No. 8128, Task No. 8128-06 High Temperature Alkali Metal Resistant Insulation. The contract is administered by the Air Force Aero-Propulsion Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Dayton, Ohio. Mr. Lester Schott is project engineer for APIP on this contract.

The work described in this report was done by personnel in the Materials Engineering and Research and Developments Groups at Westinghouse AED, Lima, Ohio.

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ABSTRACT

This report covers the progress during the second quarter on Air Force Contract AF33(615)1360.

Selected materials have been exposed to potassium vapor at 850°C. Materials have been selected from this group for a transformer test device. Preliminary transformers have been fabricated for electrical testing in potassium vapor. Several types of ceramic-to-metal seals have been obtained or fabricated for use as electrical terminal seals in potassium exposure capsules.

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I. INTRODUCTION

This report covers the second quarter from July 1, 1964 to October 1, 1964 on Air Force Contract AF33(615)1360, High Temperature Alkali Metal Insulation.

The program was initiated to investigate the effect of 600-850 C potassium vapor on selected materials in an electrical test device. The test device is a transformer designed to operate in potassium vapor at 600 C. Various voltages to 1000 VAC and frequencies to 3200 cps are to be applied to the primary windings. Fifty amperes at thirty two volts will be the output of the secondary winding. The transformer is to be operated at these electrical test conditions for 500 hours. Examination of the materials after the test period will be done to determine the effect of the combined environmental test conditions.

II. SUMMARY OF WORK PERFORMED AND MAJOR RESULTS

1. Ceramic insulators and magnetic materials, insulated with plasma-arc sprayed, high-purity alumina, have been exposed for 500 hours at 850 C to potassium vapor.

2. A preliminary test transformer using 50 turns of No. 22 AWG nickel-clad silver wire and 5 turns of No. 6 AWG nickel-clad silver wire has been constructed for electrical testing in 600 C potassium vapor.

3. Electrical resistivity measurements, both a-c and d-c, have been made on several ceramic insulating materials at temperatures up to 850 C.

4. A fluoride eutectic mixture of calcium fluoride-barium fluoride melting at 1022 C has been formed. Electrical conductivity measurements have been conducted on the material at elevated temperatures.

5. Columbium-clad, dispersion-strengthened copper conductors have been dip-coated with a high-purity ceramic, Alite A-610 (99.0% Al_2O_3-1% MgO) dispersed in a polyvinyl alcohol water mixture. This coating was followed by a coating of the fluoride eutectic mixture applied in the same manner

6. Four ceramic-to-metal seals, using an active-metal braze of titanium, columbium and nickel composition to join columbium-1% zirconium tubing to Lucalox, have been fabricated. A number of attempts to join metallized ceramic bodies to molybdenum metal pieces were unsuccessful.

7. Columbium-1% zirconium tubing has been brazed to Type 316 stainless steel tubing using Nicrobraz 130. This may permit the use of a stainless steel transformer test capsule instead of a columbium capsule.

8. Pressure sintered ceramic-to-metal bonds have been made and tested for shear strength.

9. Hiperco 27, magnetic core material, has been exposed to potassium vapor at 600 C for 500 hours. The material was brittle after exposure and could be shattered by a sharp blow. Magnetic properties were determined on the Hiperco 27. Core loss was slightly lower after exposure but more electrical energy input was required for the same degree of magnetization. Cubex (double oriented silicon iron) and Armco Ingot iron are still being exposed to potassium vapor at 600 C.

10. Transformer electrical testing procedures have been planned and several loading transformers are being constructed.

III. EXPERIMENTAL WORK

A. Potassium Vapor Exposure Tests

1. Results of 850 C Potassium Vapor Corrosion Tests

The materials, exposed to 850 C potassium vapor for 500 hours, were taken from the exposure test capsules. Residual potassium was neutralized by reacting it with isopropanol in an argon atmosphere. The samples were weighed after drying and weight loss or gain noted. Table I shows the changes resulting from potassium vapor exposure. Table II indicates elements picked up by the potassium during exposure. These results were obtained from emission spectrographic analysis of the isopropanol reacted with potassium. The results of these tests show several materials have possibilities in potassium vapor. The Alite A-610 ceramic (99.0% Al_2O_3-1% MgO) was chosen as a ceramic body for future electrical testing in potassium vapor

B. Preliminary Test Transformers

1. Description of Transformer Fabrication

a) Test Transformer - Plasma-Arc Sprayed Insulation

The primary winding of one test transformer was made by winding 50 turns of a No. 22 AWG (0.0254" diameter) nickel-clad silver on a coil form of Alite A-610 ceramic This coil form had a right hand screw thread machined to

TABLE I. Test Results - 500 Hour Exposure To Potassium Vapor - 850 C (Sheet 1 of 2)

Sample Ident.	Designation	Initial Wt. gm.	Final Wt. gm.	Difference	Initial Appearance	Final Appearance
1	Linde A (99.9% Al_2O_3) Plasma-arc sprayed on Hiperco 27	0.1485	0.1466	0.0019	dull blk. square	discolored coating removed
2	Strontium Fluoride	0.1632	--	--	clear glass chip	sample appears to have disintegrated dissolved
3	Calcium Fluoride	0.6577	0.5546	0.1031	clear glass	charred black, small silver deposit
4	Boron Nitride (Pyrolytic grade)	0.7592	0.7528	0.0064	white rectangle	darkened to dark grey one end, rest light grey coating, rest chipping
5	Triangle RR (99.7% Al_2O_3)	0.7524	0.6644	0.0880	bone white triangle	greyed, outer coating appears to have been removed
6	Yttrium Oxide (100%) (Plasma-arc sprayed on Hiperco 27)	0.2409	0.2321	0.0088	dull black one side porous grey on other (rectangle)	discolored both sides coating removed
7	Yttrium Oxide (100%) (Plasma-arc sprayed on Hiperco 27)	0.2794	0.2728	0.0066	dull black one side porous grey on other (rectangle)	both sides - silver colored coating removed

TABLE I. Test Results - 500 Hour Exposure To Potassium Vapor - 850 C (Sheet 2 of 2)

Sample Ident.	Designation	Initial Wt gm.	Final Wt. gm.	Difference	Initial Appearance	Final Appearance
8	Calcium Oxide	0.5518	0.5301	0.0217	clouded glass piece	piece covered with white coating like talc. some small chips
9	Barium Fluoride	1.4205	0.8328	0.5877	clouded round glass rod chipped in sealing	blackened with white film covering outside
10	Sylvania, Tungsten cased alumina core	3.3565 (expose capsule corroded through)			silver case white core - disintegrated into many pieces rectangle	
11	Alite A-610	1.7346	1 7344	0.0003	(tube leaked) after 250 hrs.	intact although yellowed

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TABLE II. Semi-Quantitative Potassium Analysis - Eleven Corrosion Tests
850 C Potassium Vapor - 500 Hr. Exposure

Sample Identification	Element Wt. %														
	Ca	Fe	Al	Ag	Cu	Ba	Sr	Y	Cr	Ni	Mg	Ti	Na	Rb	Cs
*MSA Potassium	0.006	0.004	-	-	-	-	-	-	-	-	-	-	0.02	0.02	0.02
Potassium Blank (in S/S capsule)	-	<0.01	-	-	-	0.01	-	-	-	-	-	-	0.02	0.02	0.02
Isopropanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
#1 Sample	-	0.03	0.04	0.002	-	0.01	-	-	-	-	-	-	0.02	0.02	0.02
#2 Sample	-	<0.01	-	-	-	0.01	0.02	-	-	-	-	-	0.02	0.02	0.02
#3 Sample	0.06	<0.01	-	0.002	-	0.01	-	-	-	-	-	-	0.02	0.02	0.02
#4 Sample	-	<0.01	-	-	-	0.01	-	-	-	-	-	-	0.02	0.02	0 02
#5 Sample	2	0.6	0.8	0.004	0.018	0.08	-	-	-	-	-	-	0.02	0.02	0.02
#6 Sample	-	<0.01	0.002	-	-	0.01	-	0.01	-	-	-	-	0.02	0.02	0.02
#7 Sample	-	<0.01	0.006	-	-	0.01	-	0.4		-	-	-	0.02	0.02	0.02
#8 Sample	0.1	<0.01	-	-	-	0.01	-	-	-	-	-	-	0.02	0.02	0.02
#9 Sample	-	<0.01	-	0.004	0.01	0.2	0.04	-	-	-	-	-	0.02	0.02	0.02

NOTE: Samples #10 & #11 gave no residue - leaked during test. Recorded on basis of potassium.
Where no figures are given quantities 0.001% or 10 PPM were present.

*MSA potassium used as blank control, empty stainless steel capsule used to contain potassium.

accommodate the No. 22 wire. The conductor was plasma-arc sprayed with Alite A-610 powder as it was being wound in the screw thread of the ceramic coil form. This plasma-arc spray of A-610 acted like a potting compound and sealed the conductor in the coil grooves.

The secondary winding was fabricated from 5 turns of No. 6 AWG nickel-clad silver conductor. This coil was plasma-sprayed with nickel aluminide followed by an insulating coating of 99.99% alumina approximately 0.001" thick. This secondary coil was slipped over the primary coil. Laminations of Hiperco 27 in an EI configuration were used as the magnetic core material. Interlaminar insulation was plasma-arc sprayed Linde A (99.99% Alumina) applied as described in the First Quarterly Report on this contract.

b) Concentric Ceramic Coil Transformer

The other transformer consists of a series of ceramic coil forms previously described in the first Quarterly Figure 1 shows an assembled and disassembled view of the ceramic forms. The primary coil is made up of ten coil forms designed to slip over each other. The wire size for the primary is No. 22 AWG nickel-clad silver. The secondary coil consists of a single ceramic coil form wound with No. 6 AWG

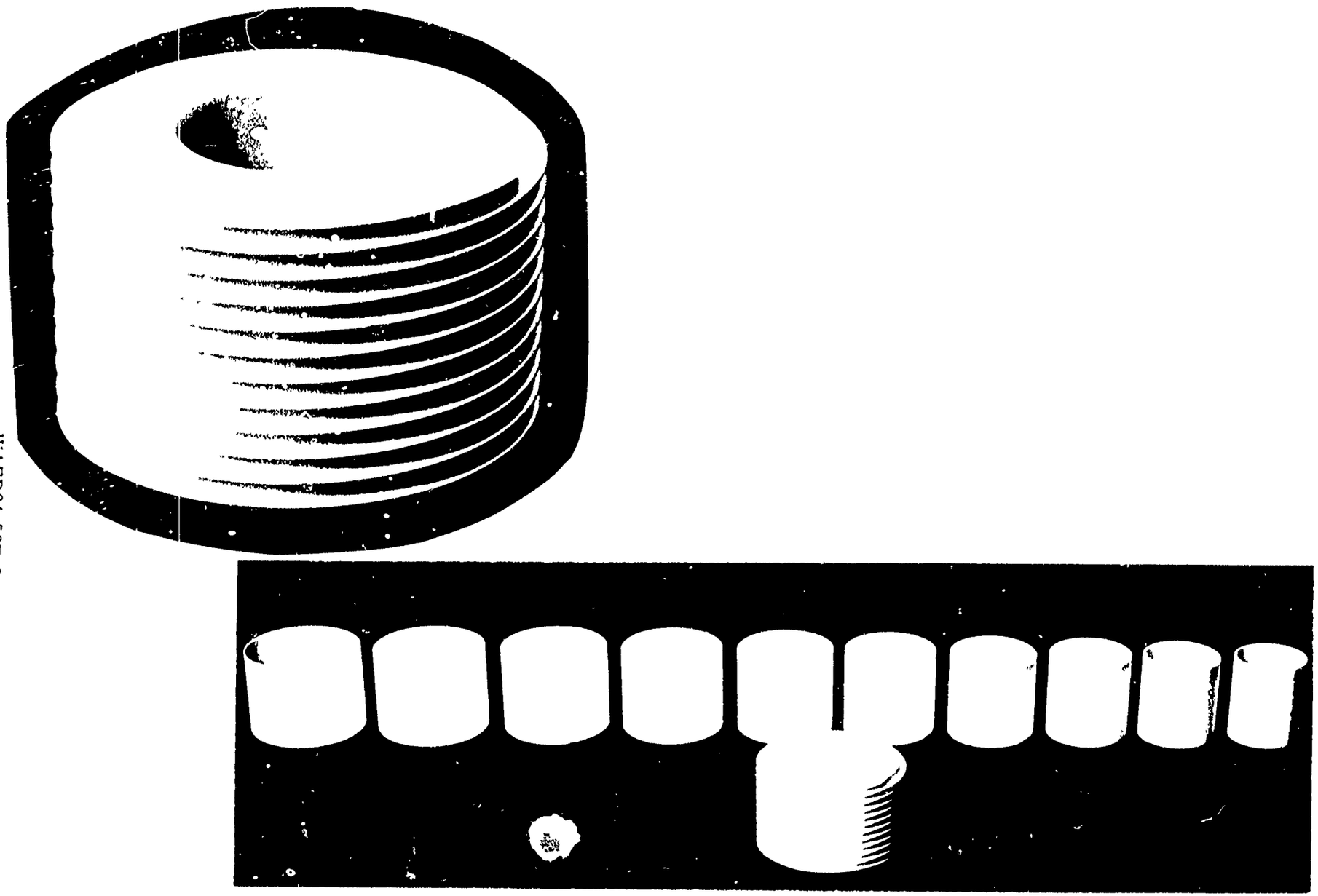

FIGURE 1. Assembled and Disassembled View of Concentric Ceramic Coil Forms of Test Transformer

rickel-clad silver wire. Hiperco 27, 8-mil laminations with alumina (99.99%) interlaminar insulation have been fabricated into an EI configuration for this transformer core.

C. D-C Electrical Resistivity Measurements

1. Sample Preparation (Lucalox)

Samples of commercially available Lucalox disks approximately 0.5 inches in diameter and 0.080 inches thick were lapped with silicon carbide abrasives to a thickness of 0.010 inches. Final polishing was done on hard wood laps using diamond abrasives. The samples were then washed thoroughly in a series of organic solvent and deionized water in an ultrasonic , agitated bath.

2. Application Electrodes

A special fixture was made which permitted a precision silk screen electrode configuration to be applied to the samples. Platinum paste (squeegee type #7724) was forced through a photo-resist pattern imprinted on a stainless steel 325 mesh screen. After the screen application of the platinum paste, the samples were dried and then fired to 2000 F. The firing operation burned off the organic binders in the platinum paste and formed an adherent and electrically continuous metallized layer.

On one surface of each sample, the platinum electrode pattern consisted of an inner electrode and a concentric guard ring elec-

trode (see Table III) All electrode dimensions were in accordance with ASTM D257-61 (Electrical Resistance of Insulating Materials) The other surface of each sample was completely metallized.

3. Measurements and Fixturing

The fixture described in the First Quarterly Report was satisfactorily modified to eliminate shunt resistance effects caused by the spacer insulators. Resistance measurements were made in a mullite tube furnace with tank argon flowing through the tube The furnace was heated with Globar heating elements Sample temperatures were determined with a chromel-alumel thermocouple located approximately 1/4 inch from the test specimen

To date, one series of measurements has been made with Lucalox test samples.

A Freed Megohmmeter was used for these tests The sensitivity of this instrument was found to be inadequate for high resistivity specimens such as aluminum oxide (Lucalox). It was necessary to raise this test temperature considerably above room temperature to obtain a readable sample resistance More sensitive instrumentation will be used on future tests

Resistance measurements were recorded at two temperatures (565 C and 850 C). The effectiveness of the guard circuit is

TABLE III. Resistivity Data For Lucalox Test Specimens

	565 C	850 C
Sample & Electrode Dimensions		
Measured Thickness	2.54×10^{-2} cm	same
Electrode Dia/Area	0.700 cm/0.385 cm^2	same
Gap Width	2.5×10^{-2} cm	same
Measured Volume Resistance @ 500 V DC		
Without Guard Electrode	1.5×10^{9} ohms	3×10^{7} ohms
With Guard Electrode	4×10^{9} ohms	5×10^{7} ohms
Calculated Volume Resistivity		
Without Guard Electrode	2.27×10^{10} ohm-cm	4.55×10^{8} ohm-cm
With Guard Electrode	6×10^{10} ohm-cm	7.55×10^{8} ohm-cm
Calculated Surface Resistivity	5.2×10^{10} ohms	Intermittent Short

illustrated by the differences in resistance values shown in Table III. Volume resistance was determined at each temperature using the 2 and 3 terminal methods. At 565 C, the volume resistivity is about 2-1/2 times higher. When the three terminal method is used at 850 C, the difference is less pronounced. This could be due to volatilization of surface condition species at the higher test temperature. The calculated surface resistivity is also shown in Table III. All calculations were made using ASTM D257-61 procedures.

During the course of these measurements, it became evident that additional refinements in the test fixture would be necessary when external connections were changed to make two and three terminal resistance measurements. Movement of the lead wires apparently caused the spring loaded contact rods to shift on the surface of the test specimens. This resulted in intermittent short circuits. It was decided to postpone further testing until the necessary modifications are made in fixturing.

D. Electrical Conductivity of Eutectic Fluorides

1. Sample Preparation

A eutectic mixture of BaF_2 and Ca F_2V (38° 10 CaF_2-62% BaF_2, Sylvania Crystal Grade) was prepared by mixing the raw materials with water in a Waring blender for 15 minutes. The mix was dried

at 120 C for 1 - 2 hours and then cooled in a dessicator.

Samples were fused by two methods 1) Vacuum melting and 2) Under an argon cover gas. In both instances the dried powder was melted in an inductively-heated, high-purity, graphite crucible. The temperature at which melting occurred was approximately 2100 F. As soon as the mix became molten, the RF power was turned off and the crucible was allowed to cool to room temperature.

The fused "eutectic" did not adhere to the crucible. A small button was formed (greyish white). The vacuum-melted specimen was ground flat on both surfaces for electrical measurements.

2. Conductivity Measurements

The a-c conductivity of the vacuum-melted specimen was determined using the stainless steel fixture previously described for d-c resistivity measurements. A-C tests were undertaken when d-c tests indicated a d-c voltage was being produced at high temperature No electrodes were applied to this specimen. The effective area under the top, spring-loaded, contact probe was used for conductivity calculations. The thickness of the specimen was measured to the nearest 0.001 inches with a micrometer. All tests were conducted in a mullite tube furnace with tank argon flowing through the tube.

Resistance measurements were made using a Hewlett-Packard (model 202) low-frequency generator (@ 1Kc), a Boonton a-c voltmeter (type 67) and a precision resistor (26.9K ohms). The voltage across the unknown at a given temperature was determined by substracting the voltage drop across the 26.9K ohm resistor from the generator voltage (10 volts). The unknown resistance was then calculated using Ohms law.

Resistance measurements were made over the temperature range from 250 C to 850 C. The measured conductivity vs. temperature is shown in Figure 2. There is a sharp knee in the curve at about 550 C. This knee apparently corresponds to a transition from extrinsic to intrinsic conductivity. In the low temperature region ($<$ 550 C) the conductivity has a smaller activation energy and the concentration of lattice vacancies and other imperfections is independent of temperature. The conductivity of the sample below 550 C is due primarily to the presence of impurities.

Selected data from a study by R. W. Ure (1) on pure CaF_2 and doped crystals of CaF_2 is also plotted in Figure 2. It is evident from these curves that a small quantity of NaF increases the conductivity. Pure CaF_2 has about the same activation energy as the eutectic sample in its intrinsic temperature range The conductivity of pure CaF_2 is almost an order of magnitude less than the eutectic sample.

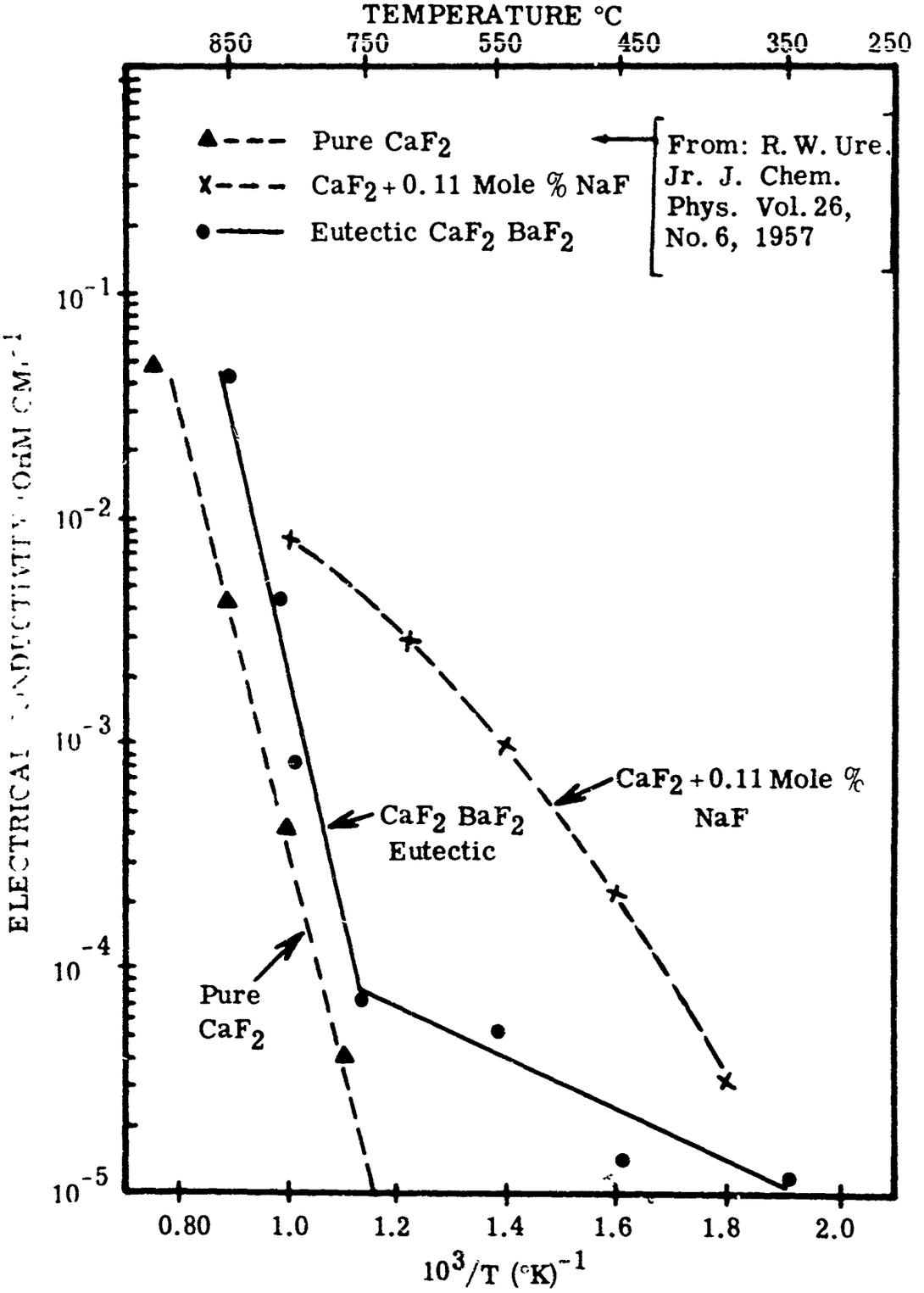

FIGURE 2. Electrical Conductivity of Eutectic BaF_2 CaF_2 Measured at 1000 cps in Argon

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Although these results are preliminary, they indicate that the electrical insulating characteristic of the CaF_2-BaF_2 eutectic above 500 C would be borderline for some applications Some improvement can be expected by preparing higher purity samples In addition, if fluoride eutectic materials are potassium vapor resistant, they can be used as interlaminar insulation or in composite insulation systems as a secondary bonding phase or potassium vapor barrier layer.

F.

E. Application of Insulation Conductor

1. Dip Coating Conductors

A 70% columbium-clad, dispersion-strengthened copper conductor was dip-coated with Alite A-610 ceramic dispersed in a polyvinyl alcohol solution. The ceramic had previously been reduced to 0. 3 micron particle size by ball milling in the high-alumina ball mill described in the First Quarterly Report. After the ceramic coating was dry, a second coating of calcium fluoride-barium fluoride eutectic was applied by the procedure described for the ceramic material. This eutectic melts at 1022 C and was used to form a glassy-phase binder for the ceramic. Examination of the coating under a microscope ($\sim$200 power) showed very little if any cracking due to thermal mismatch. This method of applying insulation to a conductor, winding the conductor into the desired configuration, then raising the temperature to 1022 C seems

G.

to have promise so more experimental work will be done in this area.

F. Welding in Vacuum - Inert Gas Glove Box

1. Purity of Atmosphere - Effect on Welding Columbium-1% Zirconium

A Westinghouse oxygen analyzer has been installed on the glove box and is being used to monitor the oxygen level of the argon atmosphere. When columbium-1% zirconium and other capsules are being loaded with potassium this oxygen level becomes quite critical. Welds made on columbium-1% zirconium in an atmosphere containing $\sim$500 PPM oxygen were very brittle and could be easily broken. The final welding of the columbium electrical test capsule was done in an argon atmosphere with a purity $<$ 1 PPM as determined by the oxygen analyzer. The weld was ductile and helium, leak tight.

G. Ceramic-To-Metal Seals

1. Molybdenum Manganese Titanium Metallized Seals - Palladium Cobalt Braze Joint

Attempts to join a high-purity ceramic body (Alite A-610) metallized with molybdenum - manganese and molybdenum - manganese - titanium were not successful. Table I V gives the metallizing and brazing conditions that were used with varying results The main difficulty in this approach seems to be the great affinity of the brazing alloy for the metallized surface.

TABLE IV. Ceramic-to-Metal Sealing Attempts With Molybdenum - Manganese Metallizing * (Sheet 1 of 3)

Assembly No.	Type Metallizing	Metallizing Temp. (F)	Braze Material	Braze Temp. (F)	Remarks
1	Mo Mn	2525	Palco	2355	Leaker, cap on, sleeve slipped off
2	Mo Mn	2525	Palco	2355	2 sleeves slipped off
3 (1st coat)	Mo Mn	2525	Palco		Sleeve slipped off
(2nd coat)	Mo Mn	2750	Palco	2350	Cap leaker
4 (1st coat)	Mo Mn	2525	Palco		2 sleeves, 1 slipped off
(2nd coat)	Mo Mn	2750	Palco	2335	1 leaker
5 (1st coat)	Mo Mn	2525	Palco		2 sleeves
(2nd coat)	Mo Mn	2750	Palco	2310	Both slipped off
6	Mo Mn Ti	2525	Palco	2350	Cap leak tight, tube slips off, over-alloyed
7	Mo Mn Ti	2525	Palco	2350	Cap: 125 microns Hg leak tight, tube slips off
8	Mo Mn Ti	2525	Palco	2350	Cap stud broken, sleeve slipped off

* Work done at Alite Division of U S Stoneware, Orville, Ohio

TABLE IV. Ceramic-to-Metal Sealing Attempts With Molybdenum - Manganese Metallizing * (Sheet 2 of 3)

Assembly No.	Type Metallizing	Metallizing Temp. (F)	Braze Material	Braze Temp. (F)	Remarks
9	Mo Mn Ti	2525	Palco	2350	Braze appears to be fair, leak tight to 120 microns Hg, apparently leaks in sleeve bond
10	Mo Mn Ti	2525	Palco	2350	Braze fair, leak tight to 180 microns Hg, appears to leak in sleeve bond
11	Mo Mn Ti	2525	Palco	2350	Braze fair, leak tight to 300 microns Hg
12	Mo Mn Ti	2525	Palco	2350	Ni plated 0.002 to 0.003. Braze appears to be improved. Leak tight to 325 microns Hg

* Work done at Alite Division of U. S. Stoneware, Orville, Ohio

TABLE I V. Ceramic-to-Metal Sealing Attempts With Molybdenum - Manganese Metallizing * (Sheet 3 of 3)

Assembly No.	Type Metallizing	Metallizing Temp. (F)	Braze Material	Braze Temp. (F)	Remarks
13	Mo Mn Ti	2525	Palco	2350	Ni plate 0.005 to 0.006. Good braze. Very small leak on most sensitive scale of leak detector.

Conclusion: The metallizing-to-ceramic bond is improved but Palco solder appears to over-alloy with the metallizing. Generally, a fair mechanical seal is obtained but complete vacuum integrity is not attained.

* Work done at Alite Division of U. S. Stoneware, Orville, Ohio

2. Active Metal Braze Ceramic-to-Metal Seals

Two seals using the active-metal brazing technique are shown in Figure 3. These seals are part of the electrical test capsule used for conducting electrical tests in potassium vapor at 850 C. The seal is comprised of a columbium-1% zirconium tube joined by an active-metal brazing alloy. The seal was checked and found to be helium leak tight.

H. Electrical Testing in Potassium Vapor at 850 C

1. Electrical Test Capsules

a) Small Test Capsules

One of the electrical test capsules for small size samples of ceramic or ceramic-insulated conductors shown in Figure 3 has been loaded with high-purity potassium and is being tested at 600-850 C.

b) Transformer Test Capsule

The sealing of the ceramic (Lucalox) to columbium-1% zirconium has been done with active-metal brazing alloy. The columbium-1% zirconium tube has been joined to stainless steel pipe using Nicrobraz 130 nickel-base brazing alloy manufactured by Wall-Colmonoy Corporation. The joint between the columbium-1% zirconium and type 316 stainless steel has been helium leak tested and found to be tight. The brazing alloy used to join the columbium-1%

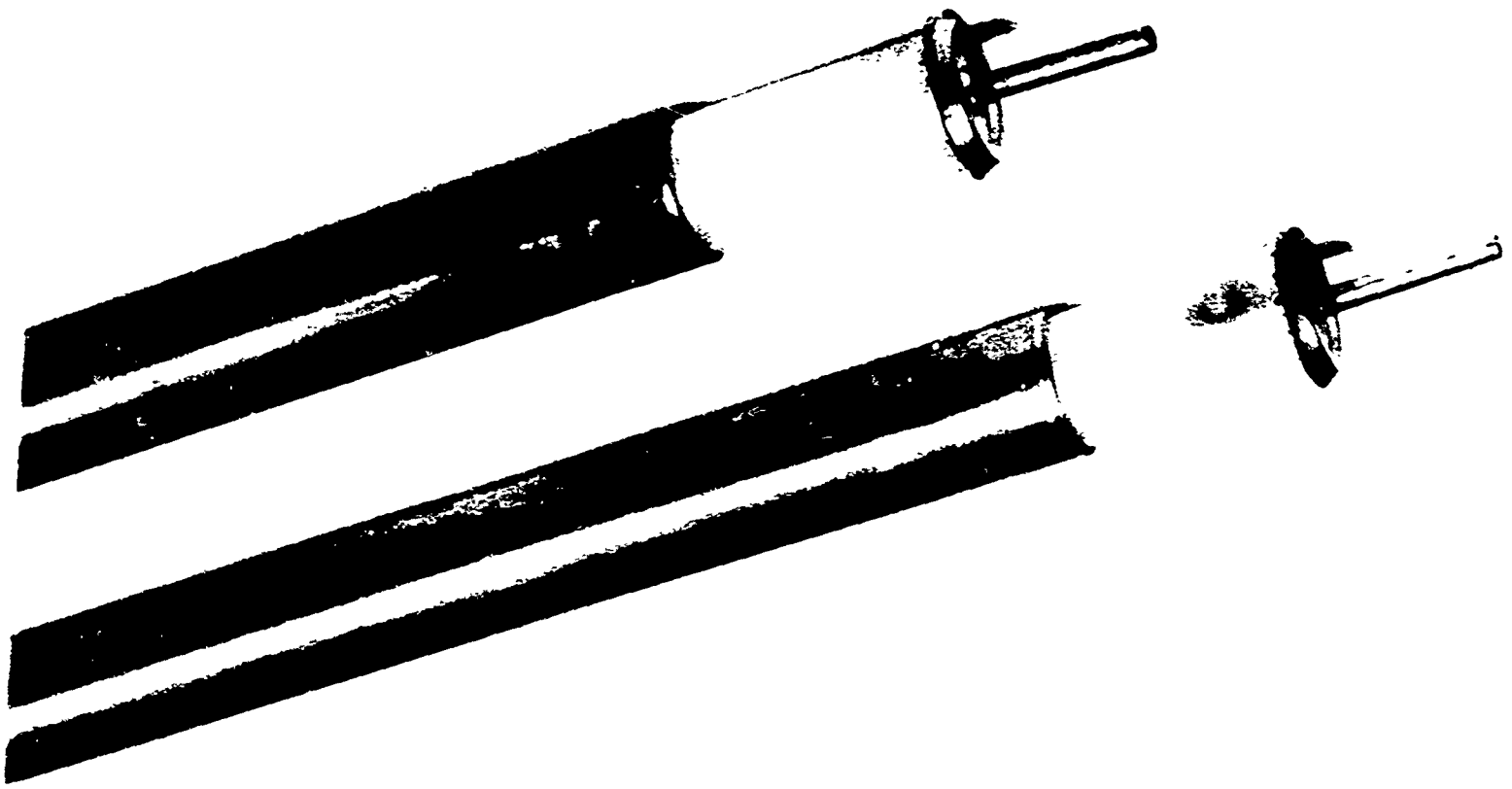

FIGURE 3. Electrical Test Capsules - Ceramic-to-Metal Seals

zirconium to ceramic has also been successfully used to join stainless steel and columbium-1% zirconium. The terminal seal using Nicrobraz 130 to join columbium and stainless steel was then joined by TIG welding to a cylindrical pipe 6" I. D. x 6" in length. The test transformer previously described in this report using plasma-arc sprayed insulation was put in the capsule and connected to the terminal seal using one side of the primary to the capsule ground as an electrical connection. The other end of the primary winding will be connected to the terminal seal. A load resistor of 0.018" Nichrome resistance wire has been wound on an Alite A-610 ceramic coil form. The value of this resistor is 0.8 ohms, 100 watt. This will be used for a secondary load inside the test capsule. This preliminary transformer was chosen as a test device to electrically test materials in potassium vapor before proceeding to the more elaborate test transformers.

I. Pressure Sintered Ceramic - Metal Composites and Hermetic Seals

Another approach to the problem of developing hermetic potassium resistant electrical terminal seals is hot pressing and sintering ceramic-to-metal compacts.

Hot pressing was applied to stacked compacts of metals, metal-alumina mixtures, and alumina which had low initial densities. The result was

a composite pellet which had strong bonds across the various interfaces.

1. Materials Used in Composites

The powders used in this investigation were as follows:

Powder	Purity	Particle Size	Source
Molybdenum		-150 +325 mesh	Plasmadyne
Tungsten	>99.9%	3-5 microns	Engineered Materials
Alumina	>99.9% Metallurgical Grade Linde A	0.3 microns	Union Carbide

2. Pressing Procedure

The sequence of operations in producing metal-to-ceramic seals is illustrated in Figure 4. The cold compacting operation was conducted at room temperature in a 0.365 inch diameter steel die Pressures were held for one minute. The amount of each powder charged into the die was calculated to be sufficient to yield a compact of 100% density (after hot pressing) having a thickness of approximately 0.125 inch. The metal plus alumina mixtures were made by stirring the ingredients in a polyethylene beaker followed by five minutes in a food blender. The alumina powder was mixed with a water solution of 2.5% soluble starch which acted as a binder. After cold compacting, the drying operation for the alumina pellet consisted of heating in air for one hour at 130 C Presintering (before hot pressing) consisted of heating the alumina

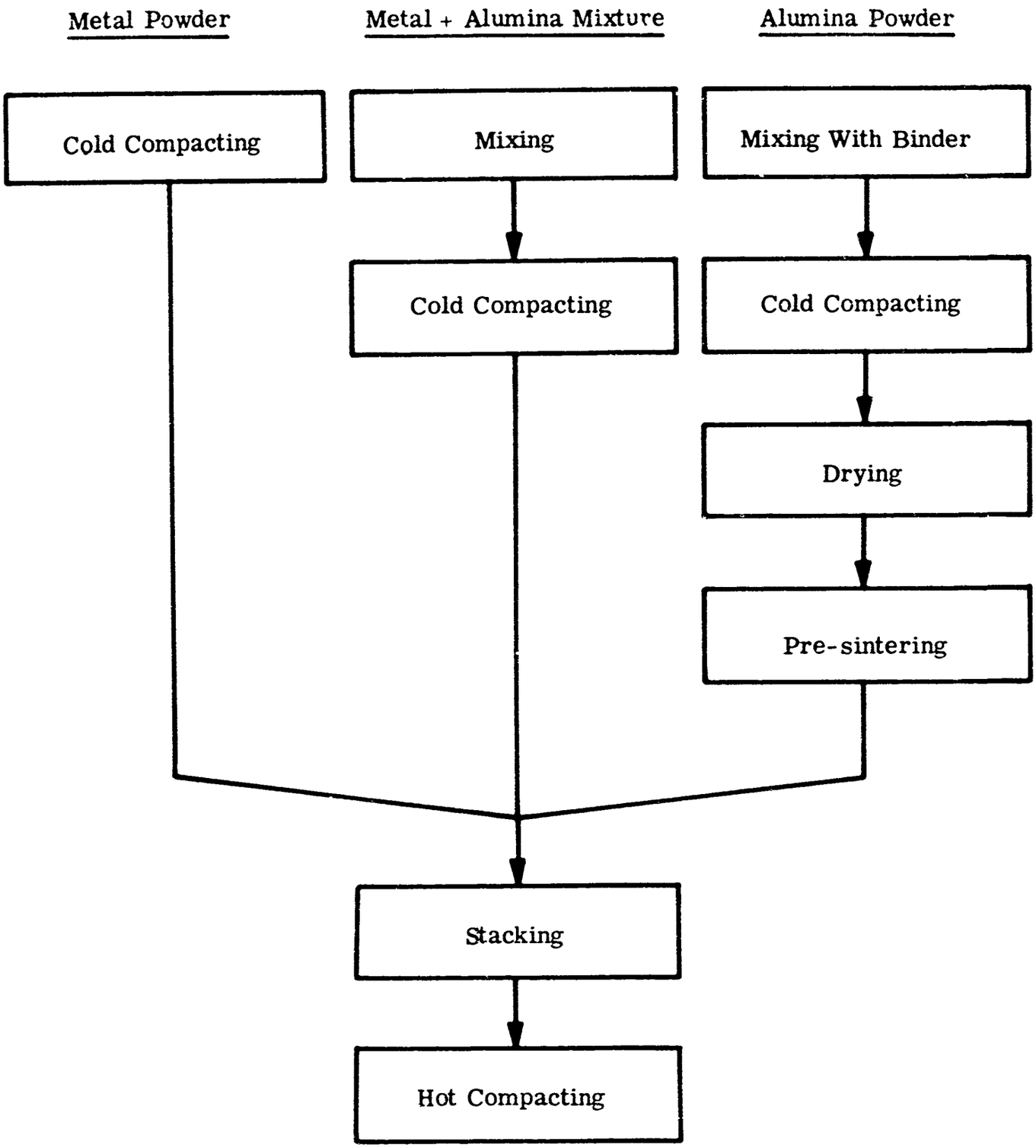

FIGURE 4. Production of Metal-to-Ceramic Seals by Hot Pressing

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for 6 minutes at 1093 - 1410 C. The compact densities obtained with different pressures are presented in Figure 5 Sufficient data were taken for the molybdenum and molybdenum + alumina mixture to draw curves. The density of the cold compacts remained substantially below 10^% even at high pressures All of the compacts could be handled satisfactorily without breakage including those of the lowest density. Thus the compact density of the various materials appeared to be adjustable over a rather wide range without penalty, if required to achieve optimum conditions for subsequent hot compacting.

The hot pressing operation was conducted on the cylindrical compacts stacked end to end using a 0. 375 inch diameter graphite die shown in Figure 6. An insulating alumina tube surrounded the graphite die and reduced oxidation, Figure 7. The remaining space inside the tube was filled with alumina powder to reduce heat loss and oxidation. Induction heating was applied to the die assembly shown in Figure 8. Argon gas flowed theoretica- or at least close to 100%, since little or no evidence of porosity was found during metallographic examination. This was true of the tungsten to alumina seals as well, except that in both the three layer and five layer seals Table V, the alumina layer contained cracks running both roughly parallel and perpend cular to the inter face which were believed to result from differences in coefficient

FIGURE 5. Density of Compacts Made at Room Temperature as a Function of Compacting Pressure

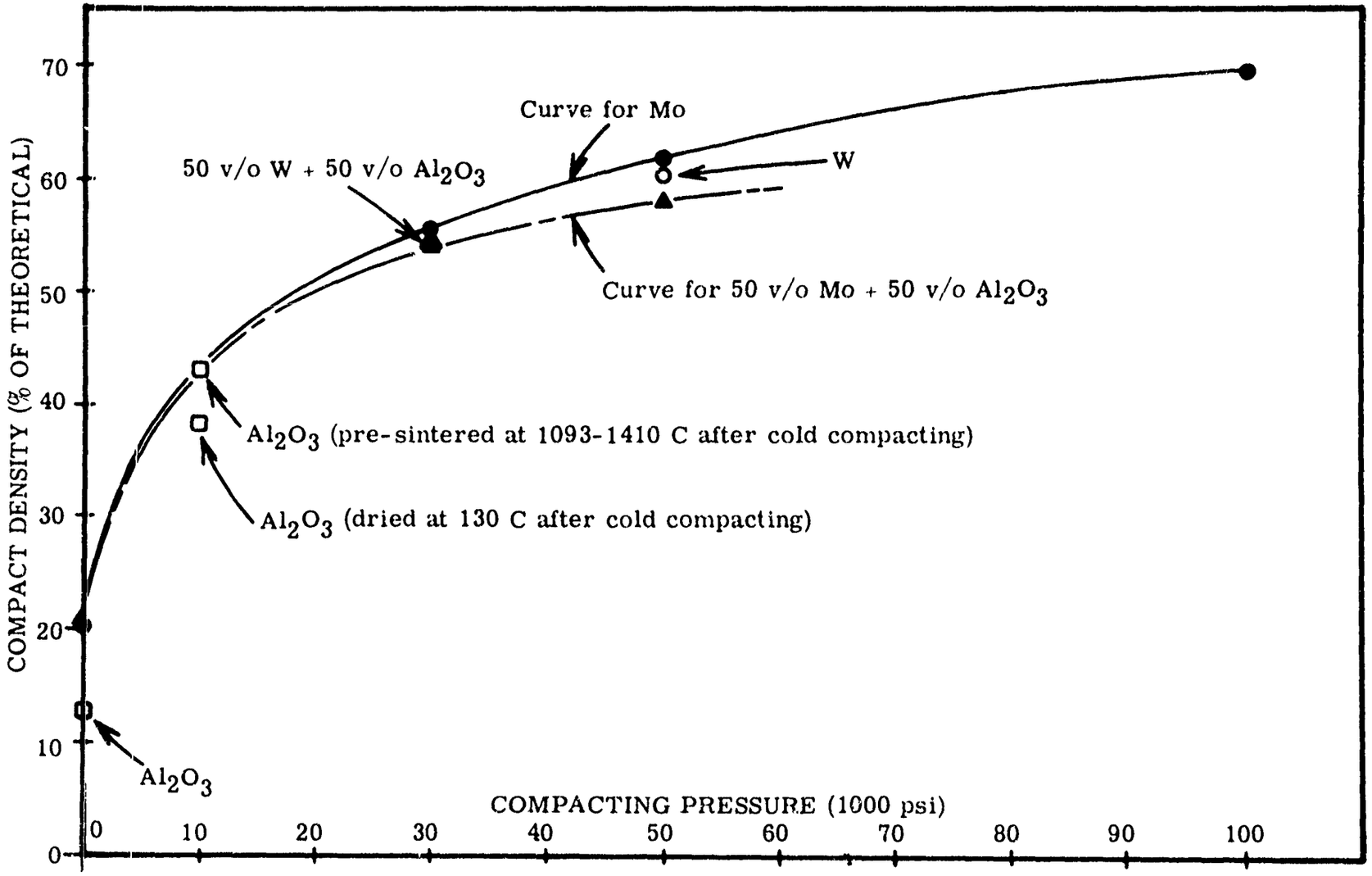


FIGURE 5. Density of Compacts Made at Room Temperature as a Function of Compacting Pressure

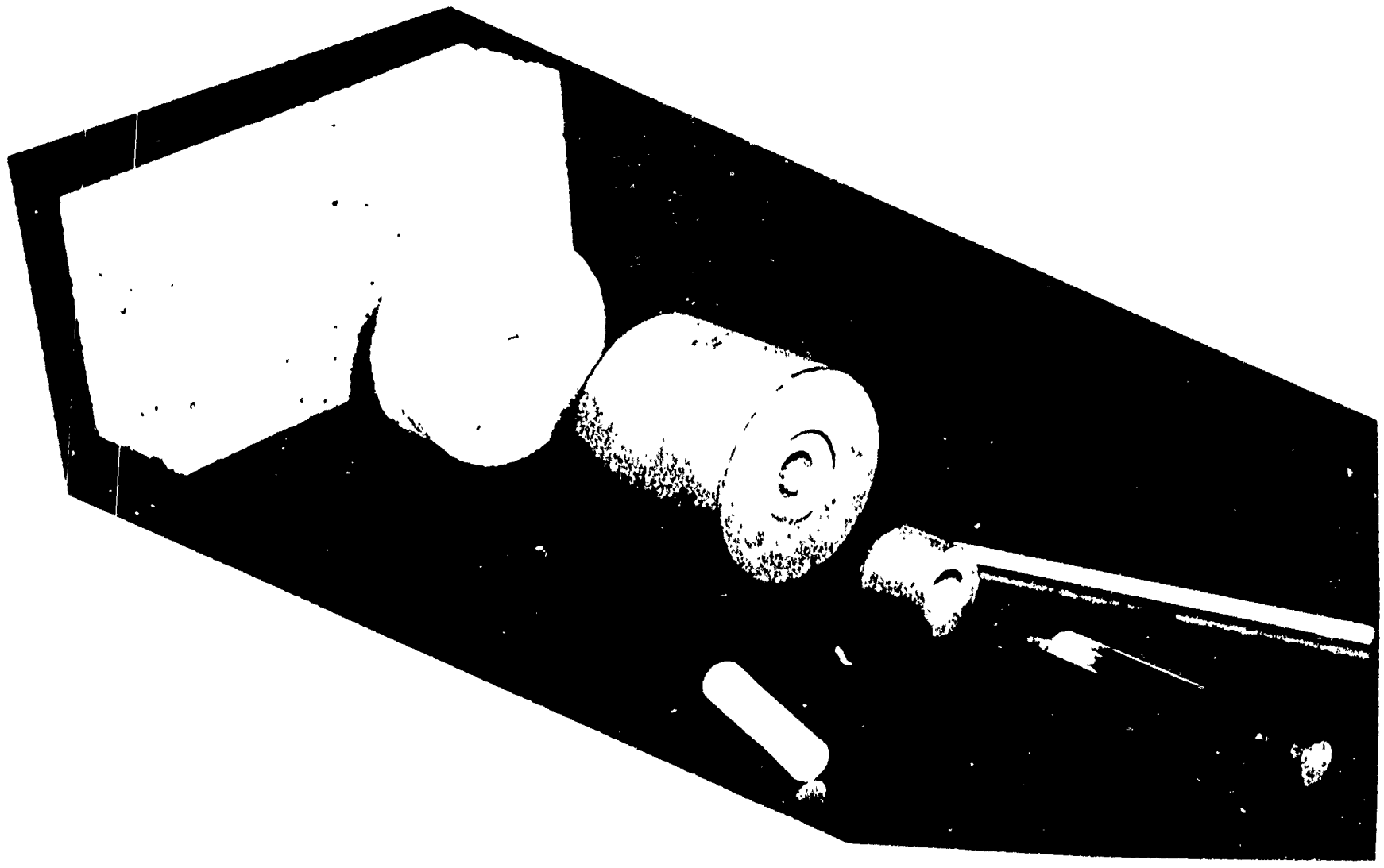


FIGURE 6. Exploded View of Graphite Die and Refractory Parts

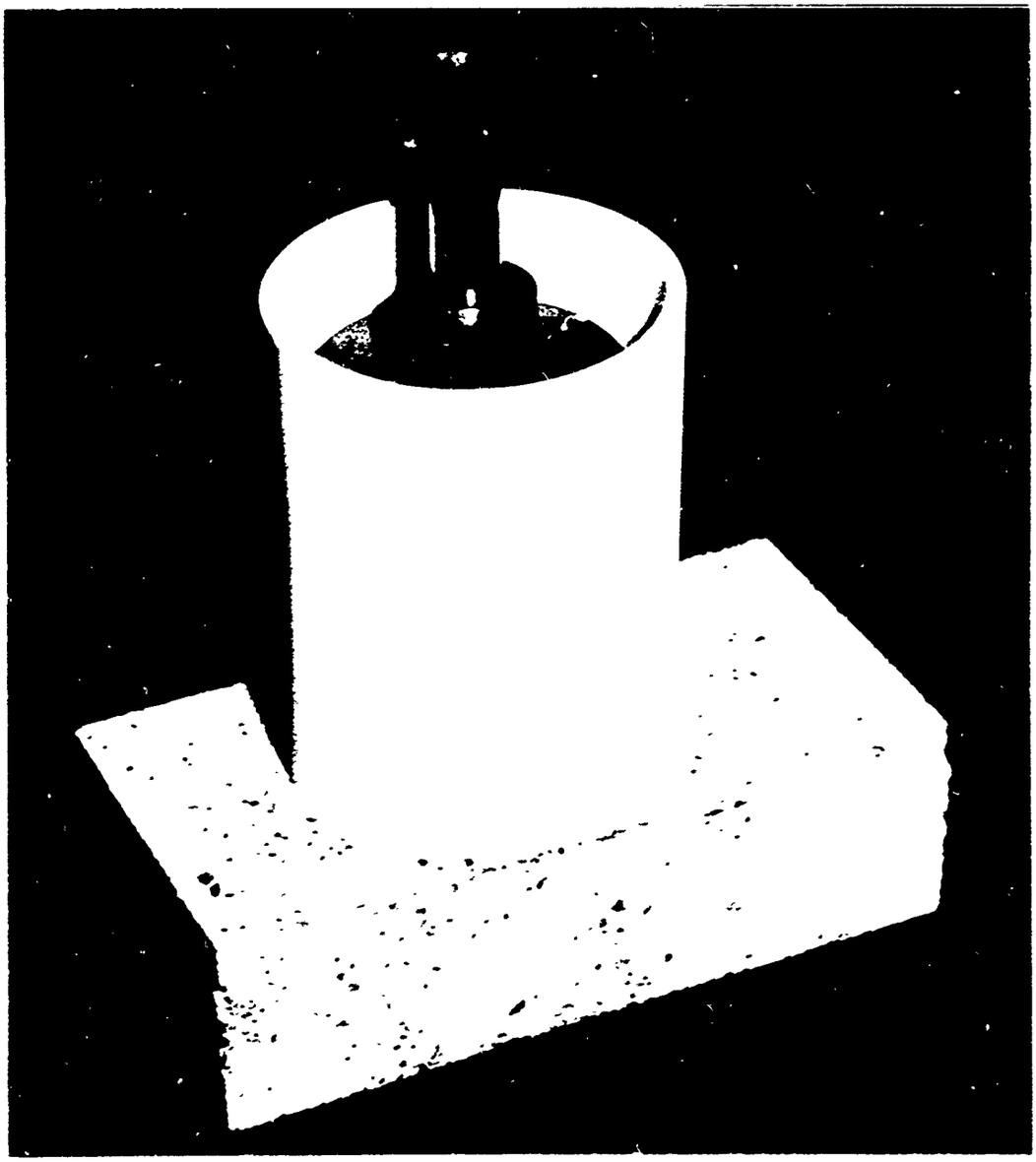


FIGURE 7. Graphite Hot Pressing Die and Alumina Protection Tube

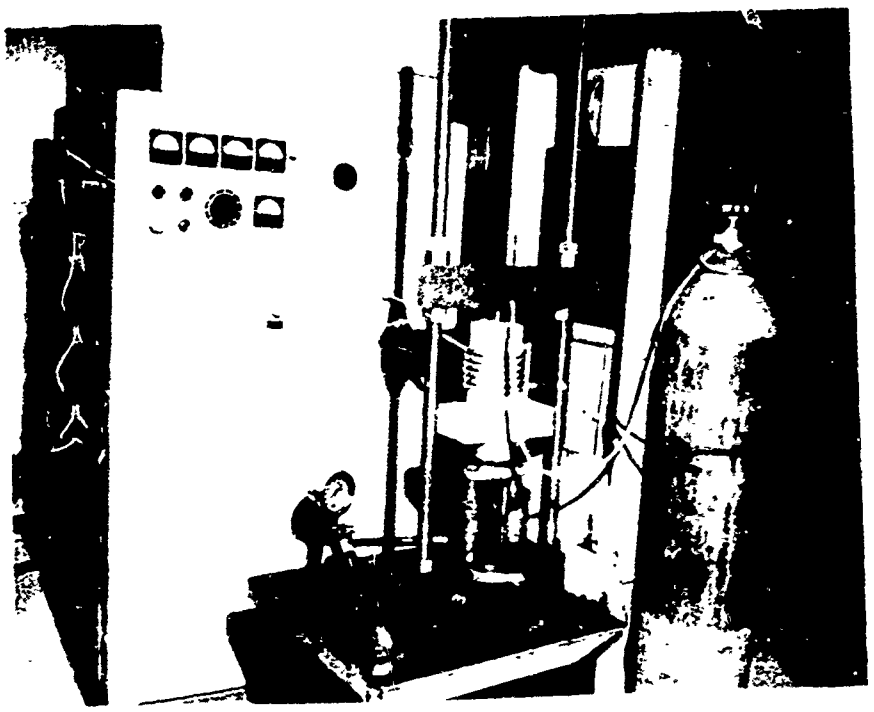


FIGURE 8. Complete Hot Pressing Assembly Including 20 KW RF Generator

TABLE V. Hot Compacted Metal-to-Ceramic Seals

Sample No.	No. of Layers	Materials Stacked					Hot Pressing Conditions		
		Metal	Mixture	Ceramic	Mixture	Metal	Temperature	Time Min.	Pressure psi
17	3	Mo (60.9%)*	Mo+Al_2O_3 (54.1%)*	Al_2O_3 (38.4%)*			1093-1438 C	45	5000
18	3	Mo (62.6%)*	Mo+Al_2O_3 (54.1%)*	Al_2O_3 (44.4%)*			1093-1604 C	47	5000
21	3	W (60.3%)*	W+Al_2O_3 (54.2%)*	Al_2O_3 (42.2%)*			1093-1654 C	76	5000
47	5	W (60.5%)*	W+Al_2O_3 (53.8%)*	Al_2O_3 (43.9%)*	W+Al_2O_3 (53.8%)*	W (60.5%)*	1093-1582 C	76	5000

* Density before hot compacting.

of thermal expansion of the tungsten and alumina. The absence of cracks in the molybdenum to alumina seals was believed to result from the slightly higher coefficient of expansion of molybdenum compared with that of tungsten, giving a better match for molybdenum with alumina.

A molybdenum to alumina seal, Sample #18 in Table V, was tested in tension by bonding the flat ends to the ends of two steel tensile grips using an epoxy cement, Armstrong #701. The tensile testing machine applied a load which was perpendicular to the various interfaces in the pellet at a head speed of 0.006 inch per minute. Failure at the epoxy bond between the molybdenum and the steel grip occurred at a load of 500 lbs. This corresponded to a tensile stress of 4,440 psi in the seal sample which did not appear to be affected by the test, since no damage was observed at either the molybdenum-molybdenum + alumina mixture interface nor the mixture-alumina interface.

The molybdenum to alumina seal, Sample #18, was next tested in three-point loading to determine the modulus at 3 CFH into the top of the assembly, while pressure was applied and maintained by a manually operated 30 ton hydraulic press. Temperature readings were taken with an optical pyrometer (and occasionally checked with a thermocouple) focused on the bottom of an alumina sight-tube (Figure 6 foreground) located in close proximity to the

sample being pressed. (A hole was drilled in the graphite die to accommodate the sight-tube after the photographs in Figures 6 and 7 were taken.)

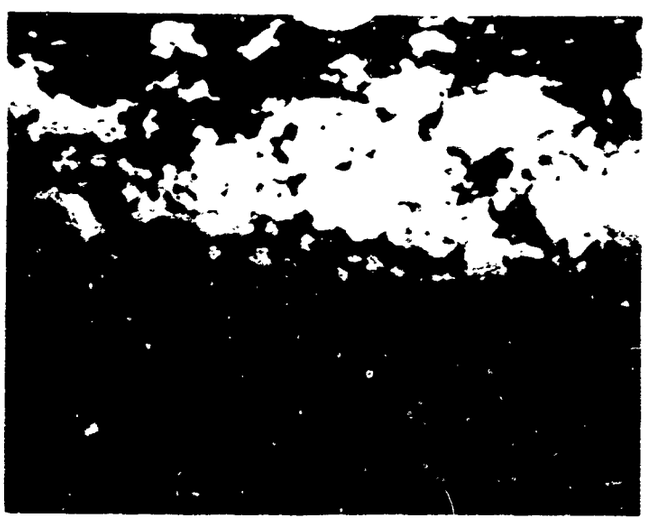
3. Experimental Results

As mentioned earlier, a pellet of the metal + alumina mixture was always inserted between the pure metal and alumina pellets to provide a transition zone which would facilitate bonding, reduce thermal stresses resulting from differences in coefficient of thermal expansion, and perhaps increase resistance to corrosion by potassium at the interface. The four samples of metal to ceramic joints made to date are described in Table V.

The molybdenum to alumina seals appeared to be of high quality in tests made so far. The photomicrographs in Figures 9 and 10 indicate excellent bonding occurred at the interfaces between the various components. No separation between layers was observed. On the contrary, frequent points of penetration of one material into another were seen. The density of the various components after hot pressing appeared to be 100% of rupture using a testing machine head speed of 0.006 inch per minute. However, the steel pin, 0.119 inch diameter, placed at a right angle to the axis of the cylindrical pellet on its top side started to deform at 1500 lb. load and when 1900 lb. load was reached, the slotted V-block fixture supporting the bottom side of the pellet was plastically deformed. Since the sample did not appear to be damaged in this test either, hardened

Unetched 1000X
Sample #17

FIGURE 9. Interface Between Al_2O_3 (top) and 50 v/o Mo + 50 v/o Al_2O_3 Mixture (bottom)



Unetched 1000X
Sample #17

FIGURE 10. Interface between 50 v/o Mo + 50 v/o Al_2O_3 Mixture (top) and Mo (bottom)

steel tools (R_c62-63) were obtained for another try. This time a ram having an edge radius of 0. 125 inch applied the load to the top of the pellet directly on the molybdenum-mixture interface where fracture occurred at 1410 lbs. corresponding to a modulus-of-rupture of 14, 500 psi. These results were additional evidence that the various materials in the hot pressed seal were strongly bonded at the interfaces. This modulus-of-rupture value of 14, 500 compares favorably with modulus-of-rupture values obtained on ceramic-to-metal seals using Mo-Mn metallizing (3).

J. Magnetic Materials

1. Potassium Exposure Tests

In Table VI, the data shows that, of the materials not exposed to potassium vapor, 0. 006" Cubex is the best magnetic material. The 0. 008" Hiperco 27, exposed to potassium vapor, using similar ring material as the unexposed rings, shows no significant change in magnetic properties. The Hiperco 27 rings that were exposed to potassium vapor were brittle when struck a sharp blow. Surface corrosion seemed negligible and microscopic examination proved inconclusive. Further investigation will be done.

In Table VII the data indicate that if a properly roughened surface such as unannealed Hiperco 27, is used for spraying Linde A, 99. 99% Al_2O_3 (1 micron particle size) that the insulation properties

TABLE VI. Magnetic Properties Before and After Potassium Vapor Exposure

Material	Insulation	Core Nos. *	B-80KL/in^2 ~ 12.4KG @ 400 cps P_c Watts/Lb.	B-80KL/in^2 ~ 12.4KG @ 400 cps P_a Volt-Amps/Lb.	D-C H Oersteds @ B-12.4 KG
0.006" Cubex	0.25 mil Mylar	2, 2A, 2C, 2D	7.75	15.6	3.6
0.008" Armco Ingot Iron	0.25 mil Mylar	3, 3A, 3C, 3D	22.2	27.9	4.33
0.008" Hiperco 27	0.25 mil Mylar	1, 1B, 1E, 1F	19.6	37	7.55
0.008" Hiperco 27 after K exposure	0.25 mil Mylar	1C, 1D	19.5	38.5	8.5

* 2, 1, and 3 original curves reported in first quarterly.

TABLE VII. Unannealed 0.008" Hiperco 27 Compared At 50 KL/in^2 ($\sim$ 7.75 KG), 400 cps

Insulation	Core Nos.	P_c Watts/Lb.
Linde A	4	51
0.25 mil Mylar	5	52

of Linde A are the same as Mylar. However, any iron oxide present is undesirable from the standpoint of attack by potassium vapor.

The 5% Al Fe alloy and the 3% Al - 1% Y, Fe alloy were annealed in air for one hour at 980 C to check oxidation effects. The 3% Al - 1% Y, Fe alloy was more brittle than the 5% Al, Fe alloy and also developed a thin tight adhering oxide. The 5% Al, Fe alloy oxidized more severely, and the oxide spalled off. Both alloys showed more ductility at 90° than at 0° to the rolling direction. Ingot #665 of the 3% Al - 1% Y, Fe alloy that had an intermediate anneal showed larger grain size than Ingot #664 of the same alloy. The intermediate anneal was necessary in order to be able to roll to gauge with-

out excessive cracking. The 5% Al, Fe alloy showed larger grain size than all of the 3% Al - 1% Y, Fe alloy. This is an indication of the grain refining properties of Y. The rings from these alloys have been annealed in both wet and dry hydrogen. The 5% Al, Fe alloy at 980 C and the 3% Al - 1% Y, Fe alloy at 1180 C.

The 3% Al - 1% Y, Fe alloy has developed a thin tight oxide in wet hydrogen but the 5% Al, Fe alloy did not. Further evaluation is underway.

In Table VIII the data on plasma-arc sprayed rings using Linde A is shown. Further evaluation of this coating has been deferred until examination of Hiperco 27, plasma-arc sprayed and exposed to potassium vapor, is made.

2. Magnetic Properties

In Figures 11 through 54, the additional magnetic test data obtained since the first quarterly report are shown. The important observations from these curves have been previously discussed in Tables VI, VII, and VIII. D-C magnetization data is reported as well as P_c, total core loss, and P_a, apparent core loss.

K. Electrical Testing Procedures - Test Transformers

1. Test Methods

The methods for testing the Test Transformer have been planned With the exception of 1000 volt input at 1000 and 3200 cps, all

TABLE VIII. Comparison Data on Various Interlaminar Insulated Materials At 80KL/in^2 ($\sim$12.4 KG), 400 cps

Material	Insulation	Core Nos.	P_c Watts/Lb.	P_a Volt-Amps/Lb.
0.008" Hiperco 27	Linde A	1A *	21.2	54
0.006" Cubex	Linde A	2B	3	20
0.008" Armco Ingot Iron	Linde A	3B	23.8	33

* Original curve on 1A reported in first quarterly.

CONT.

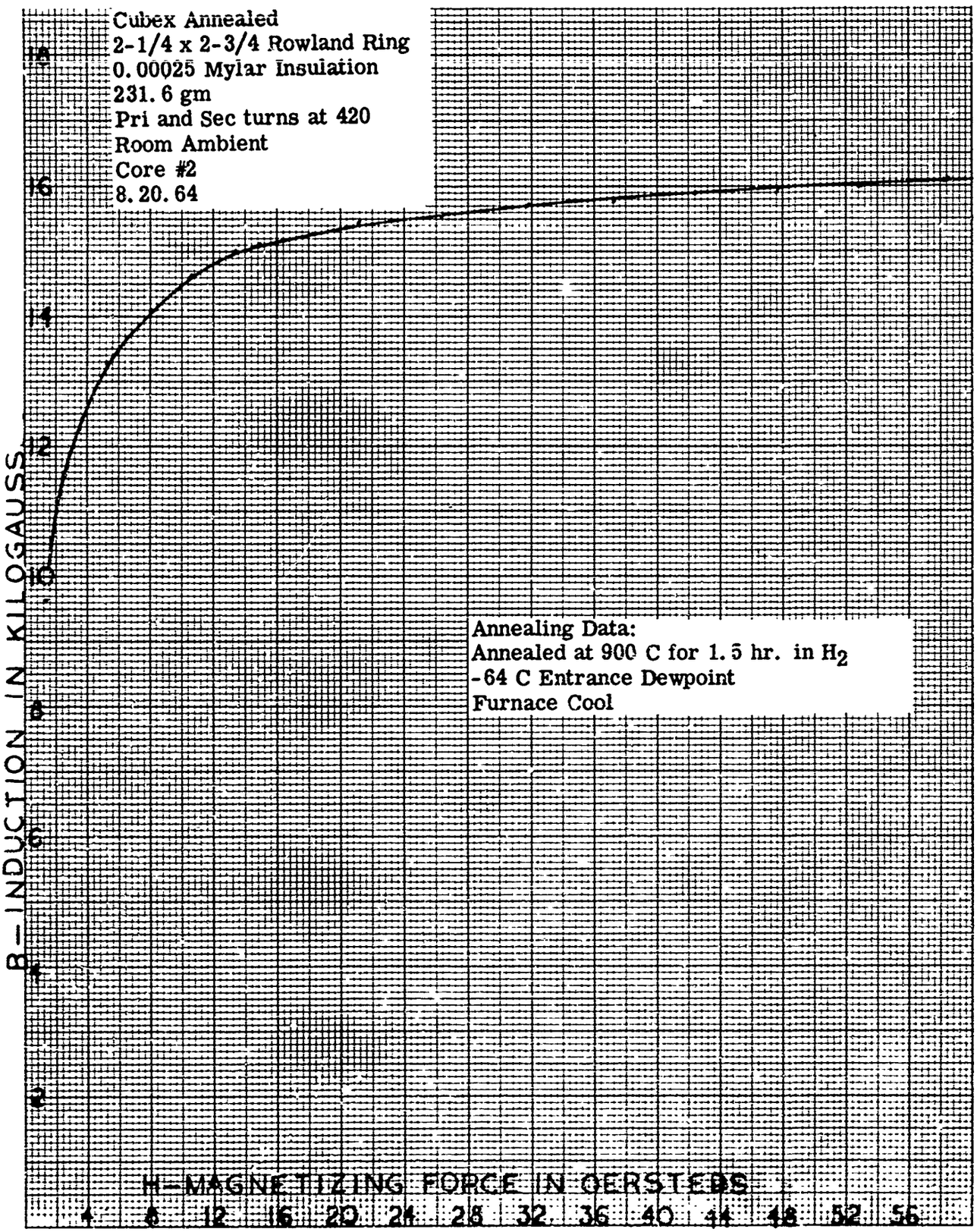


FIGURE 11. D. C. Magnetization of 0.006 Cubex Mylar Insulated

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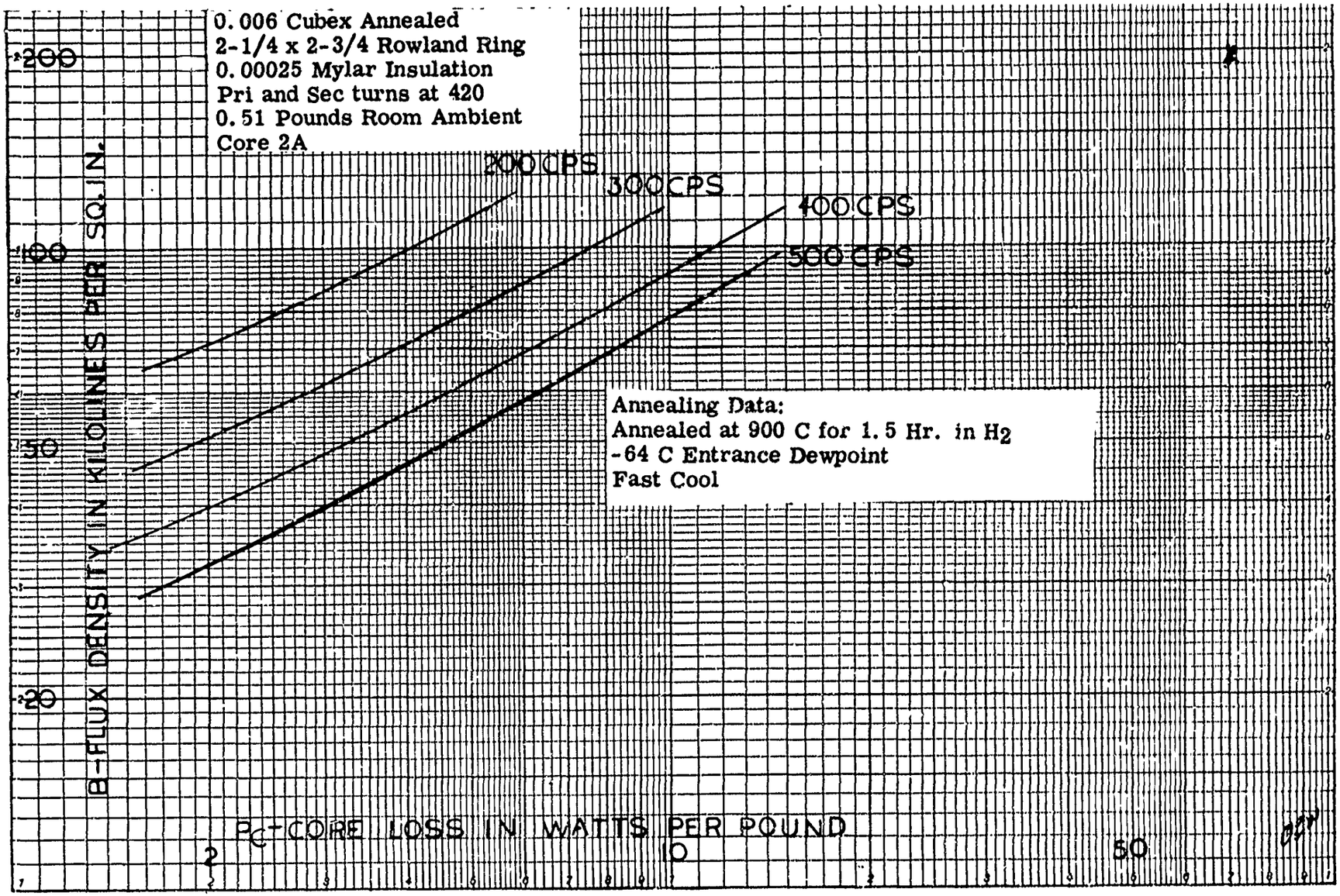

FIGURE 12. Core Loss of 0.006 Cubex Mylar Insulated

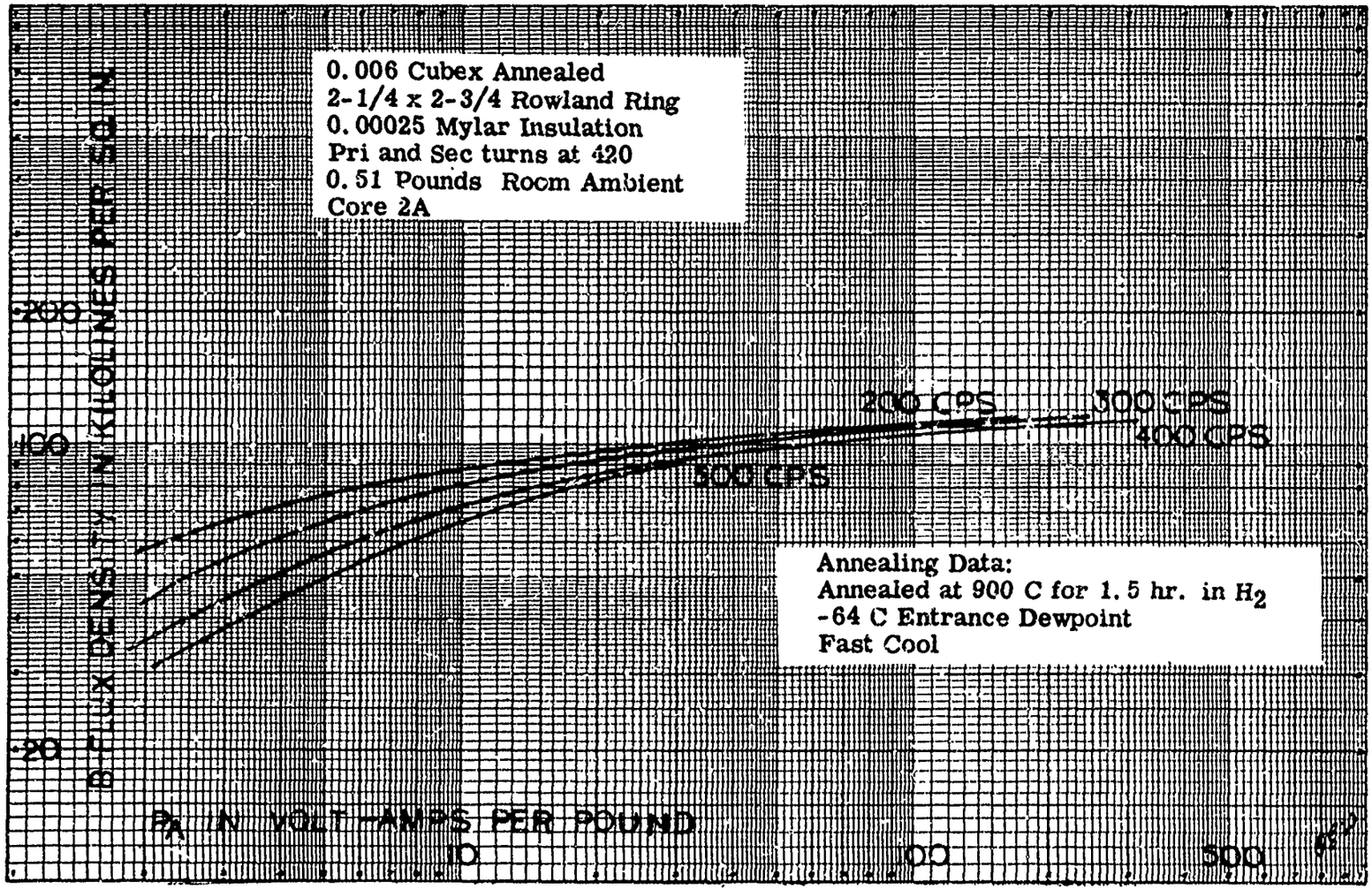

FIGURE 13. Apparent Core Loss of 0.006 Cubex Mylar Insulated

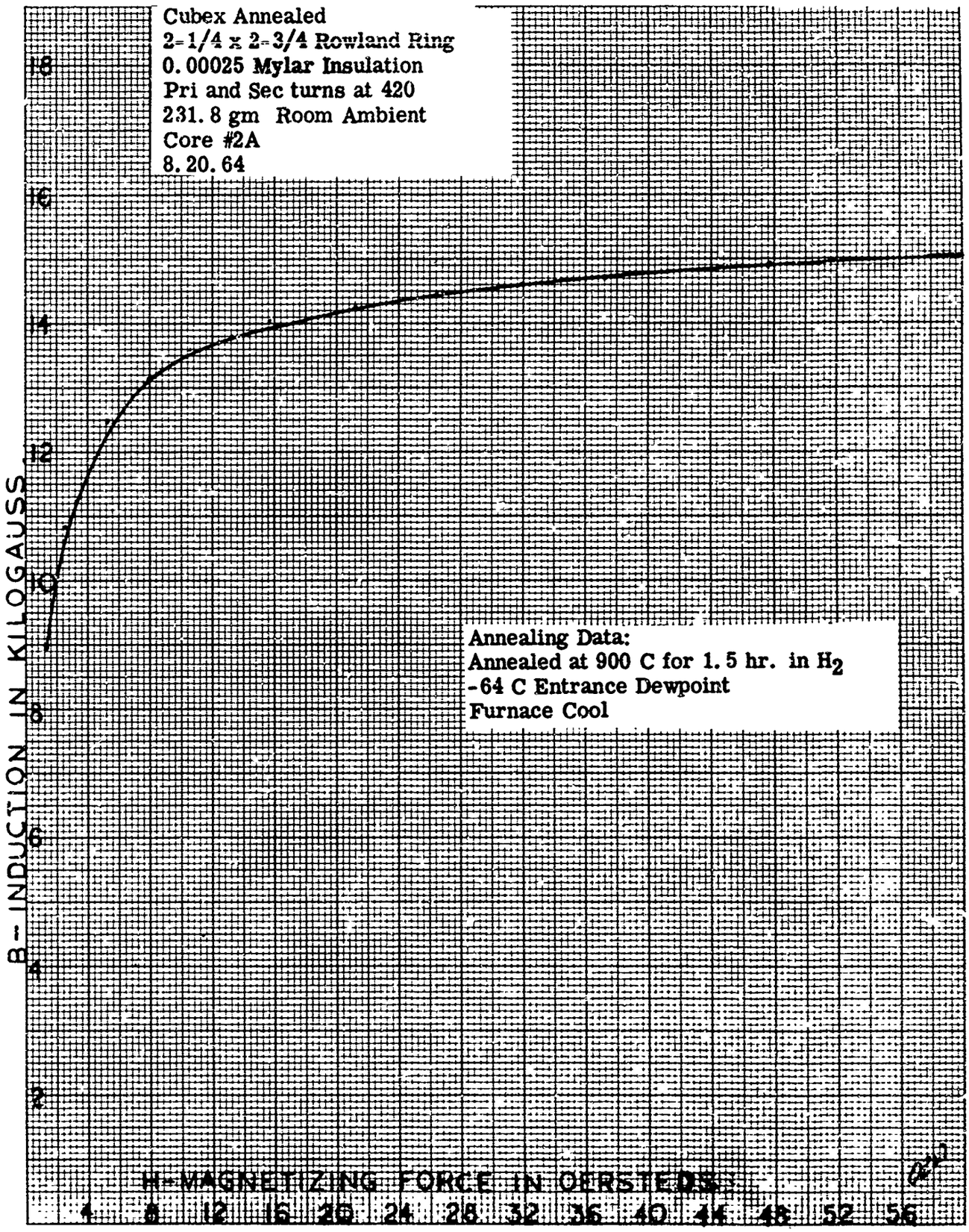

FIGURE 14. D-C Magnetization of 0.006 Cubex Mylar Insulated

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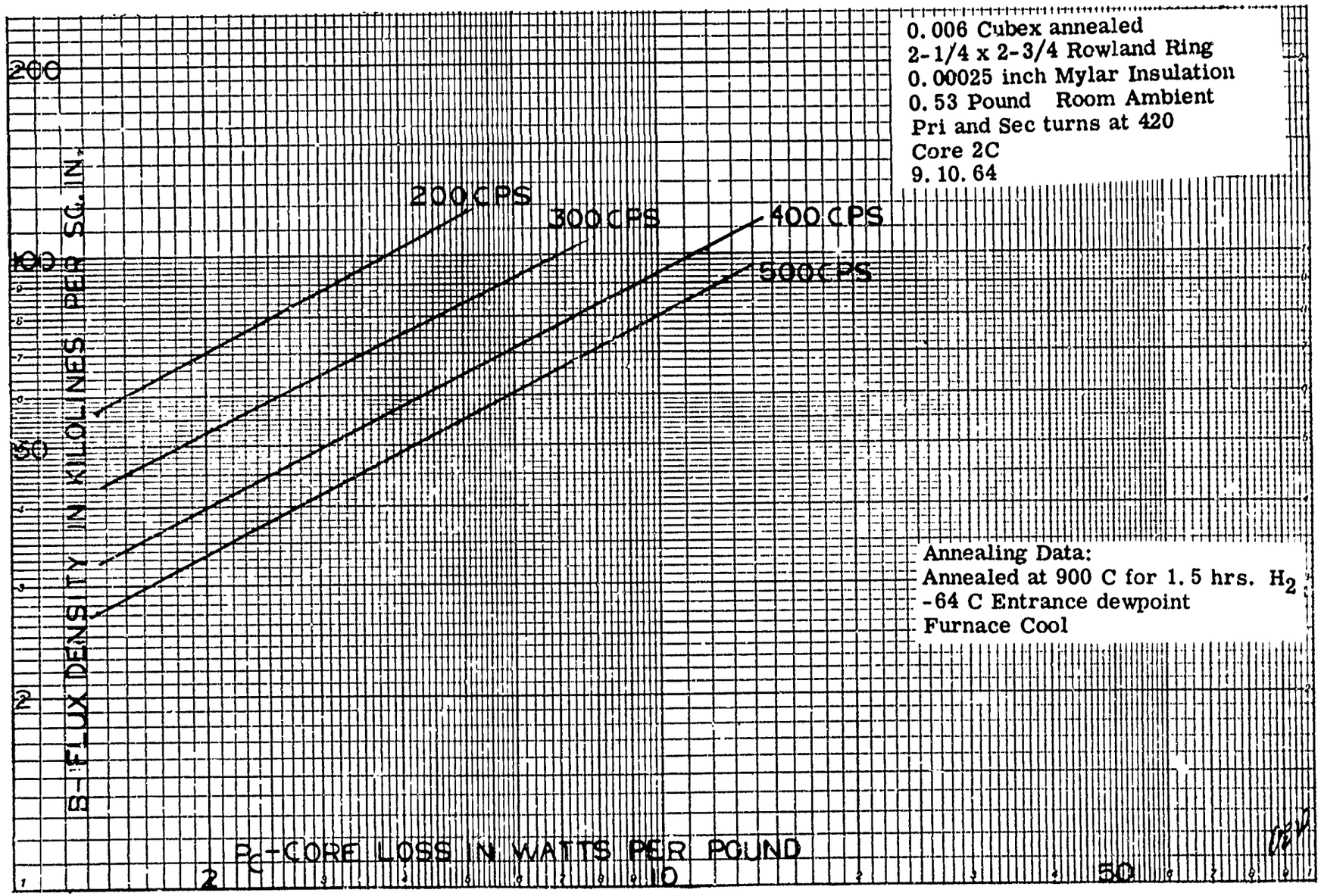

FIGURE 15. Core Loss of 0.006 Cubex Mylar Insulated

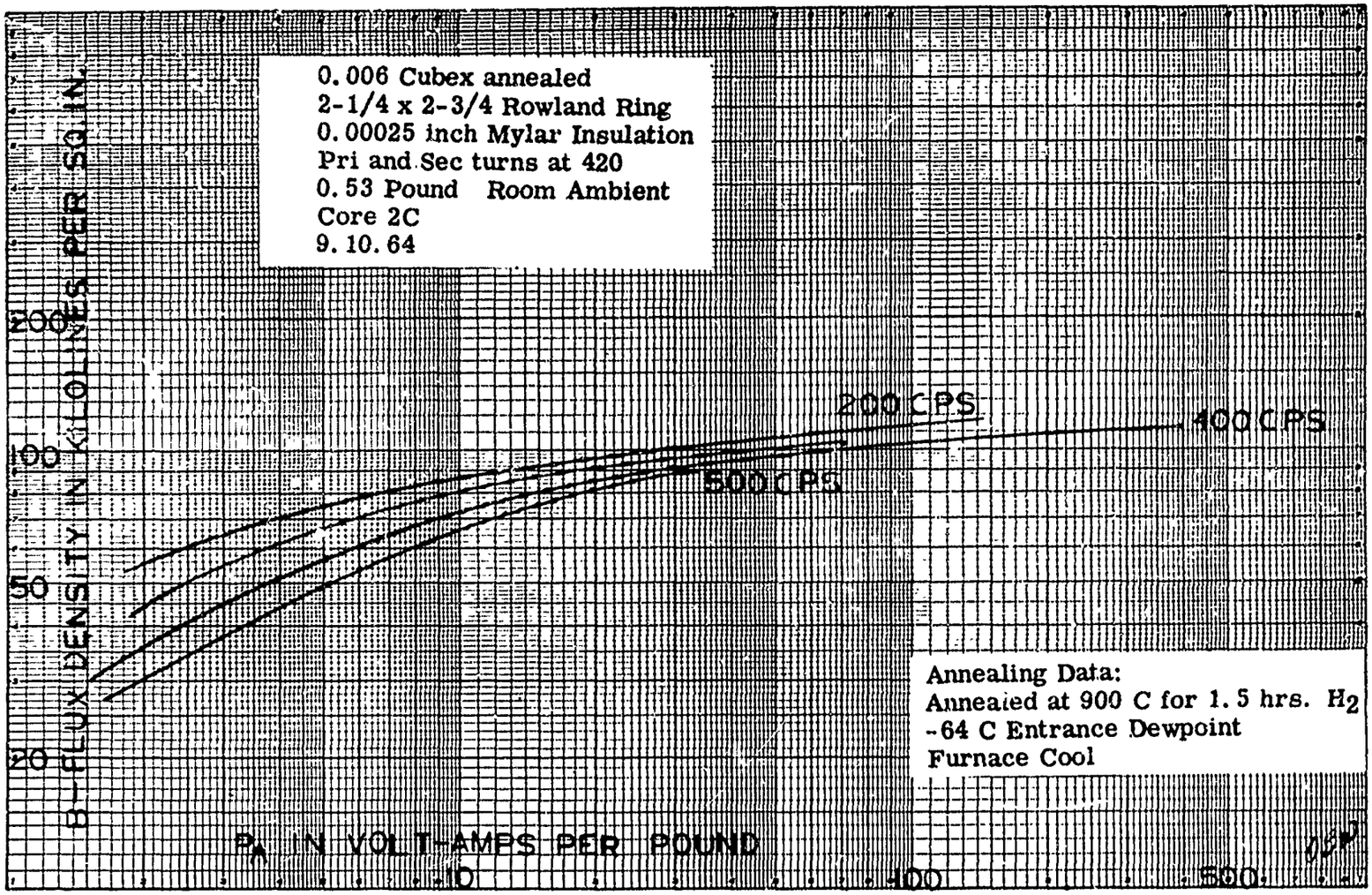

FIGURE 16. Apparent Core Loss of 0.006 Cubex Mylar Insulated

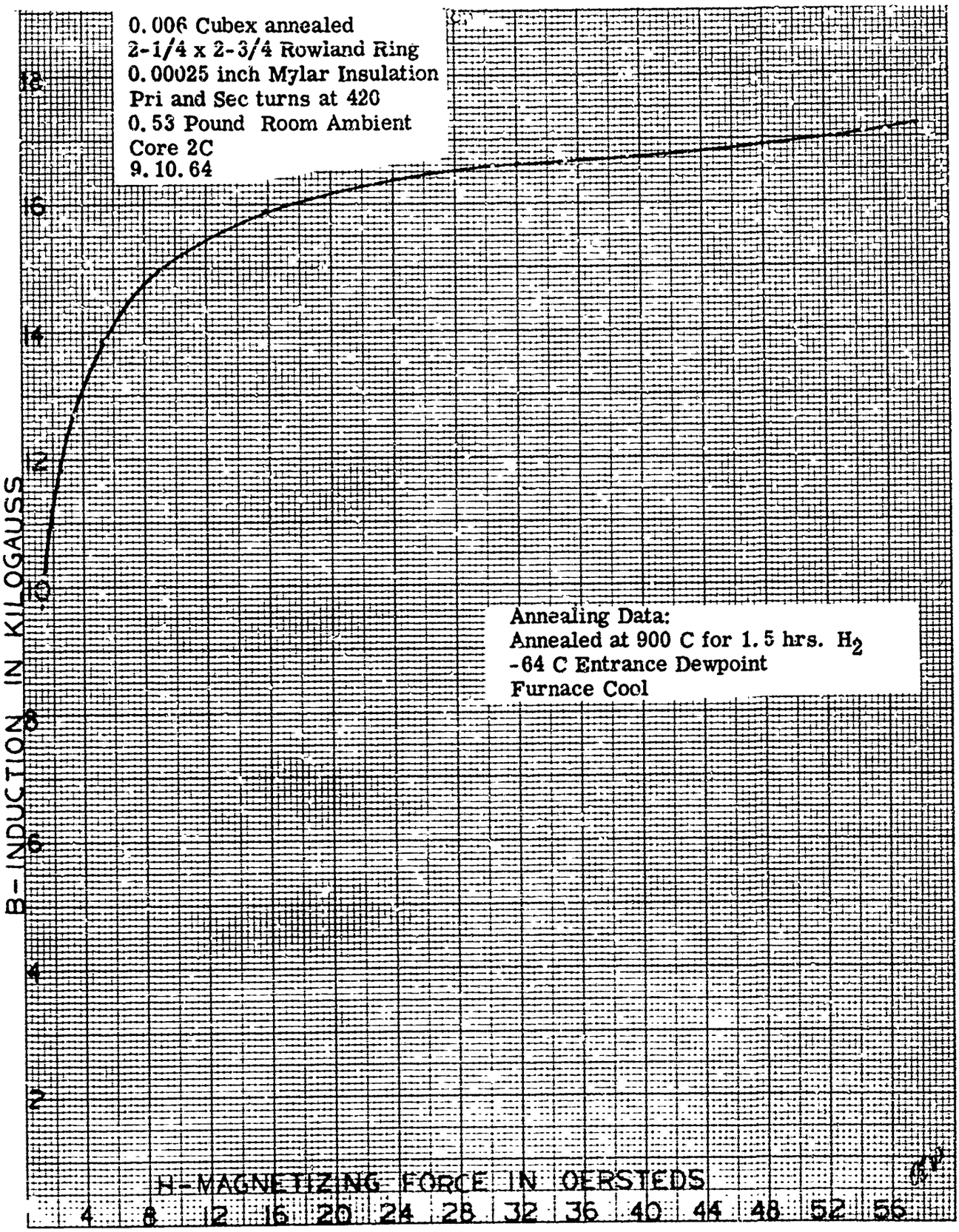

FIGURE 17. D-C Magnetization of 0.006 Cubex Mylar Insulated

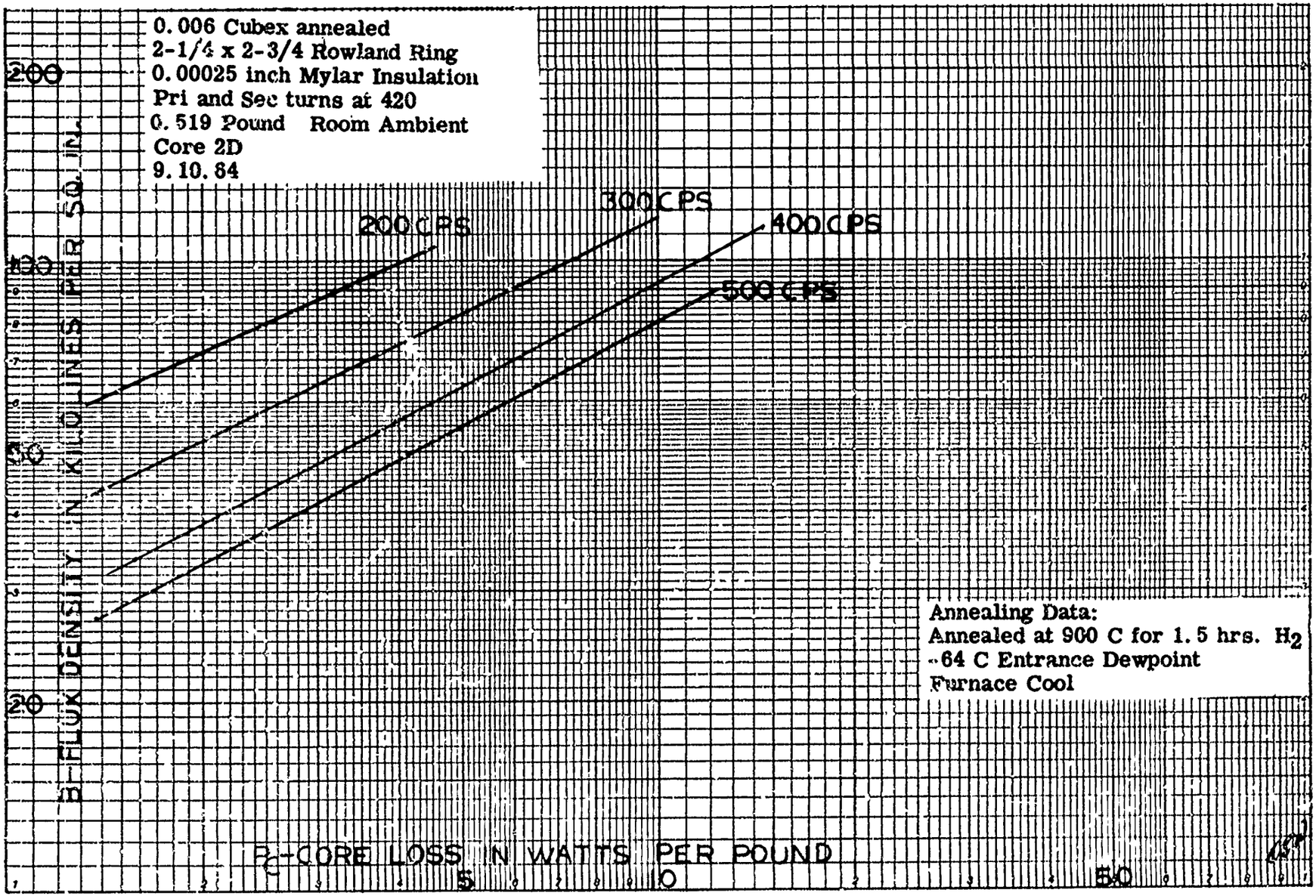

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FIGURE 18. Core Loss of 0.006 Cubex Mylar Insulated

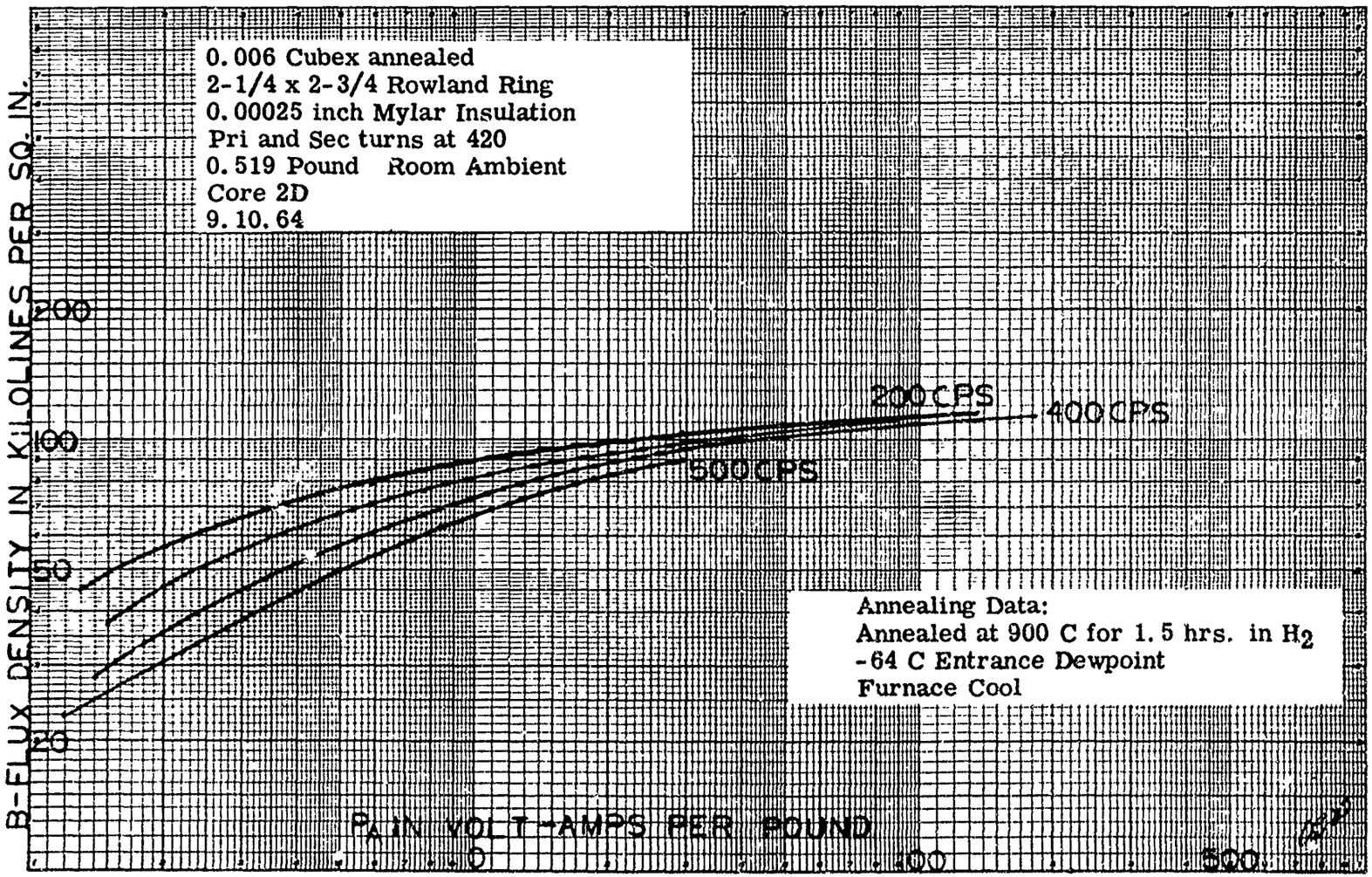

FIGURE 19. Apparent Core Loss of 0.006 Cubex Mylar Insulated

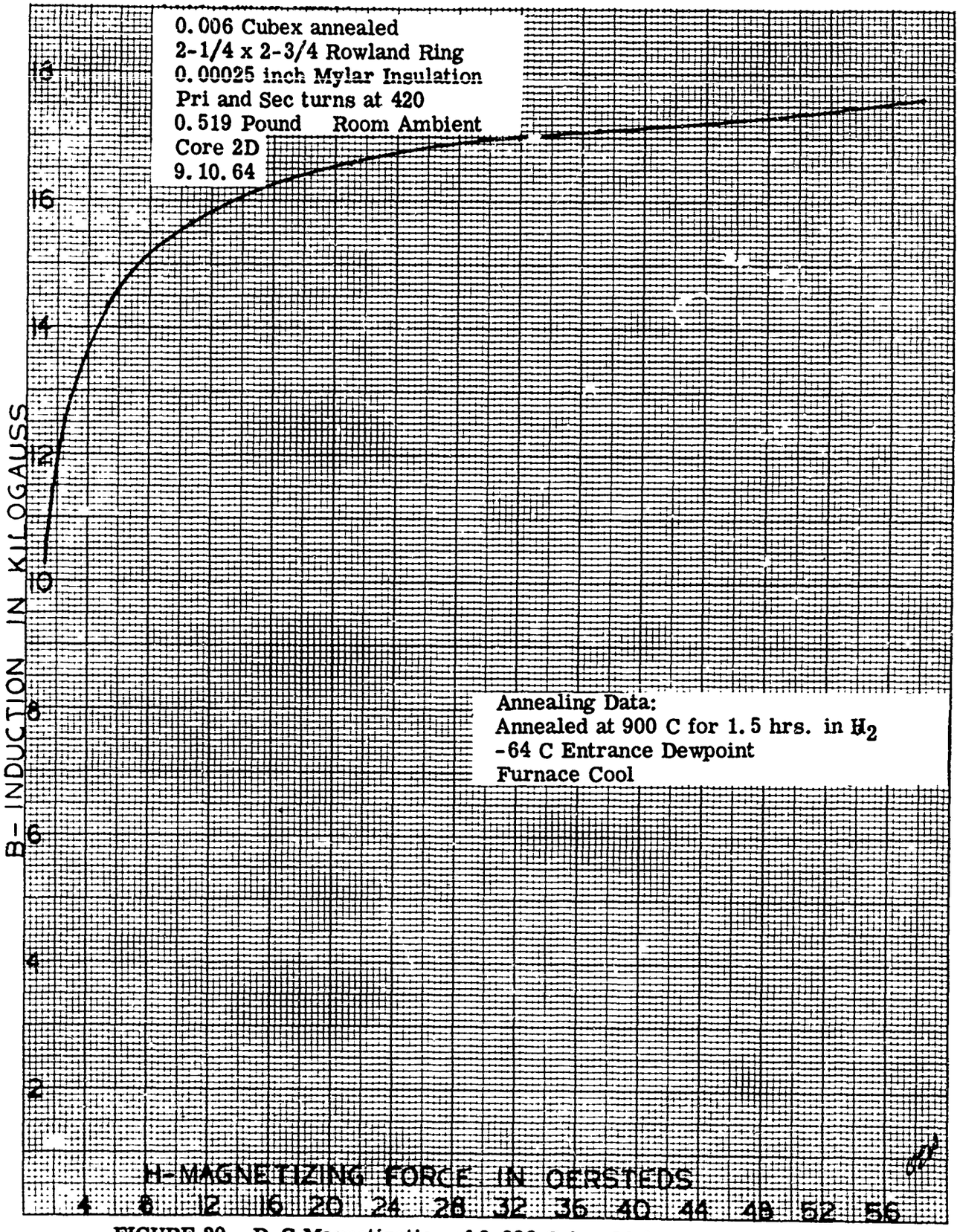

FIGURE 20. D-C Magnetization of 0.006 Cubex Mylar Insulated

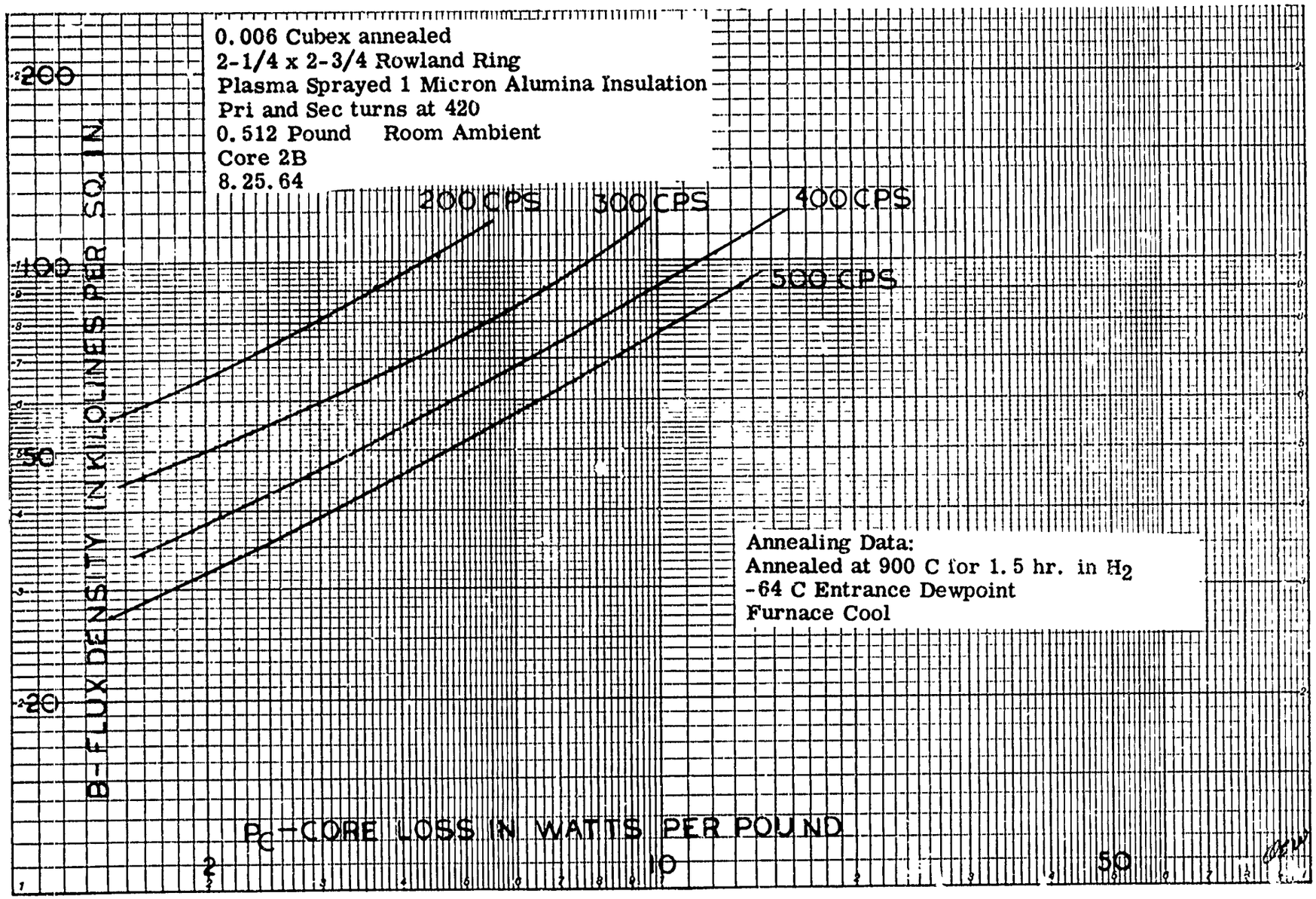

FIGURE 21. Core Loss of 0.006 Cub x Mylar Insulated

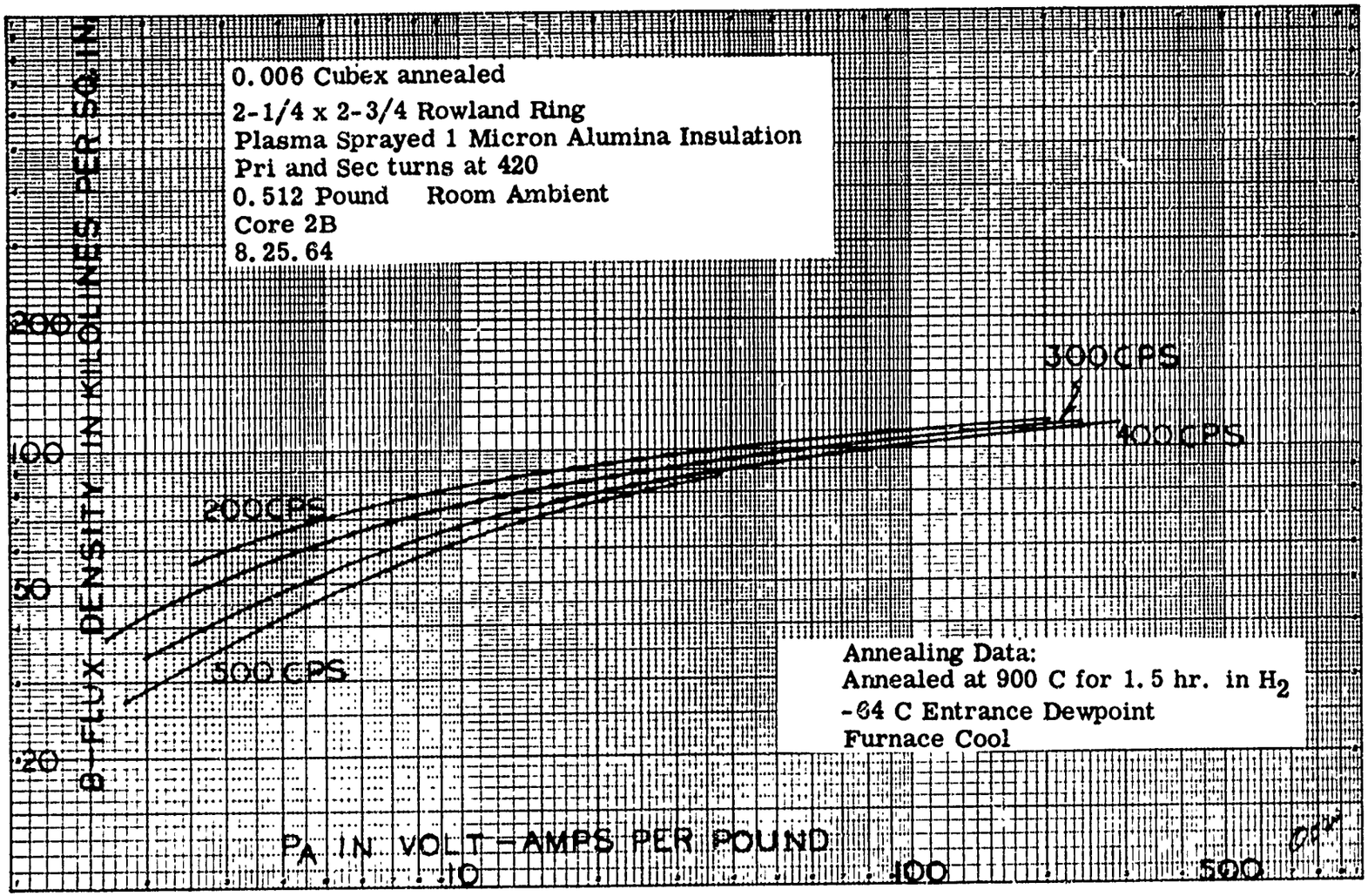

FIGURE 22. Apparent Core Loss of 0.006 Cubex Mylar Insulated

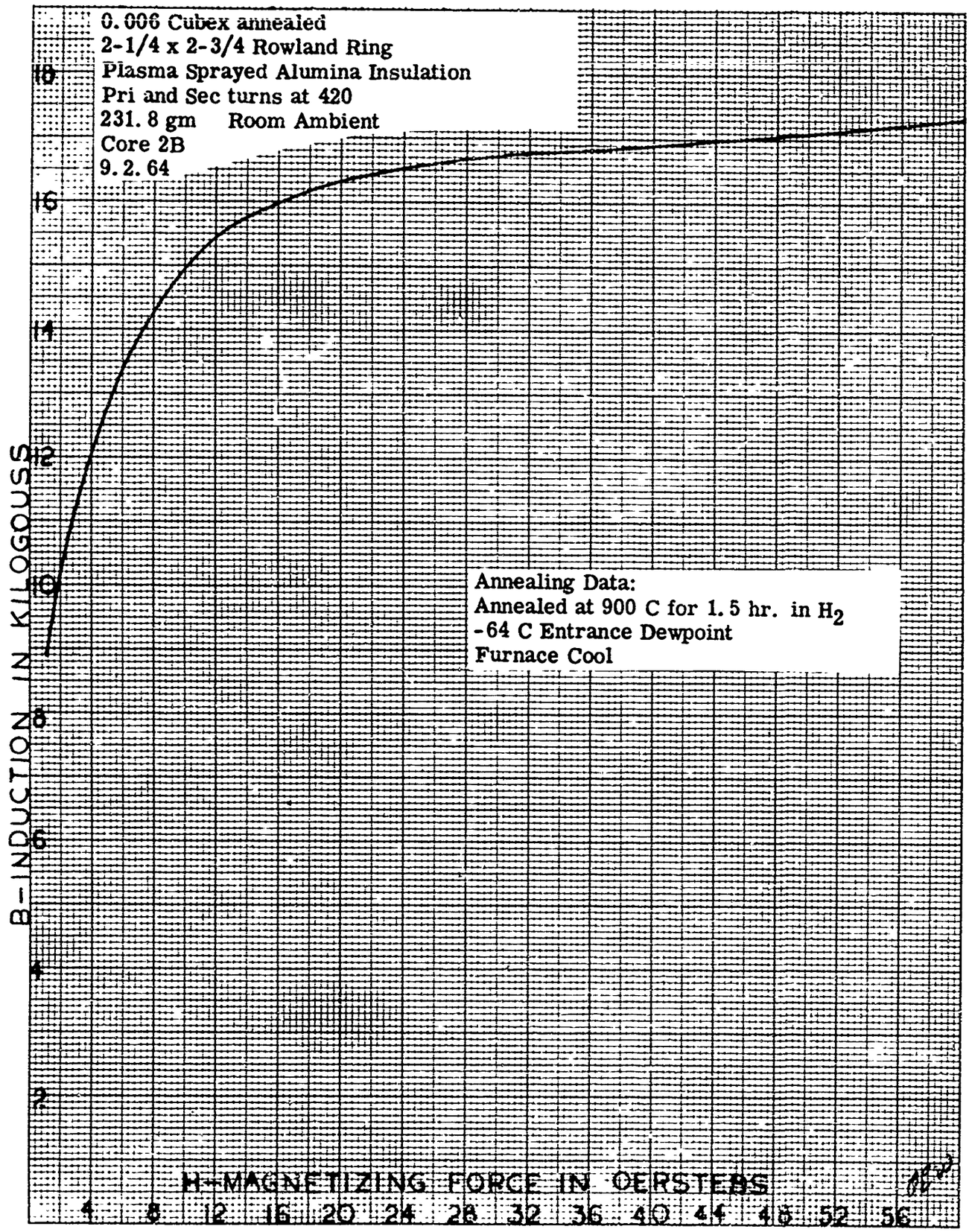

FIGURE 23. D-C Magnetization of 0.006 Cubex Al_2O_3 (99.99%) Insulated

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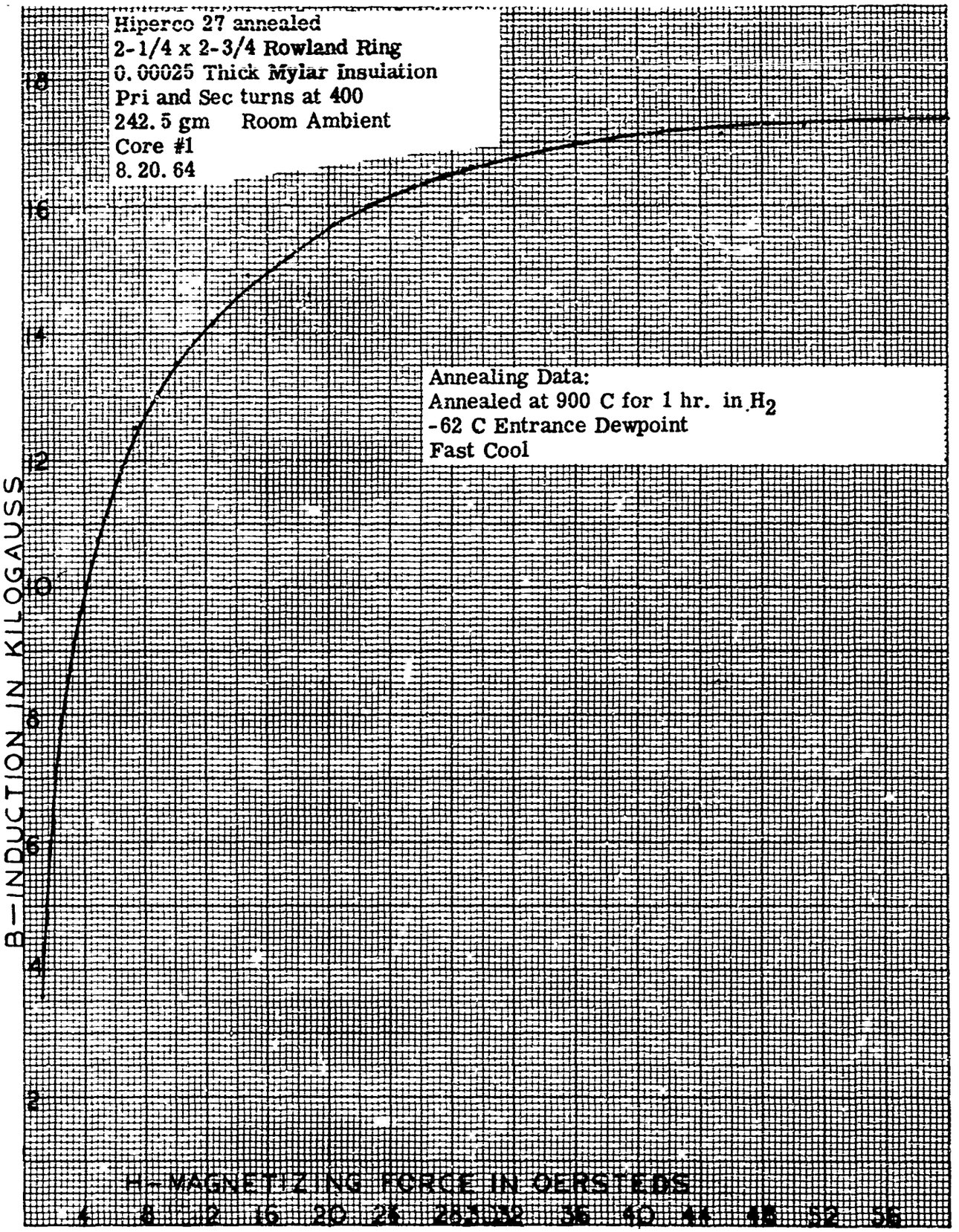

FIGURE 24. D-C Magnetization of 0.008 Hiperco 27 Mylar Insulated

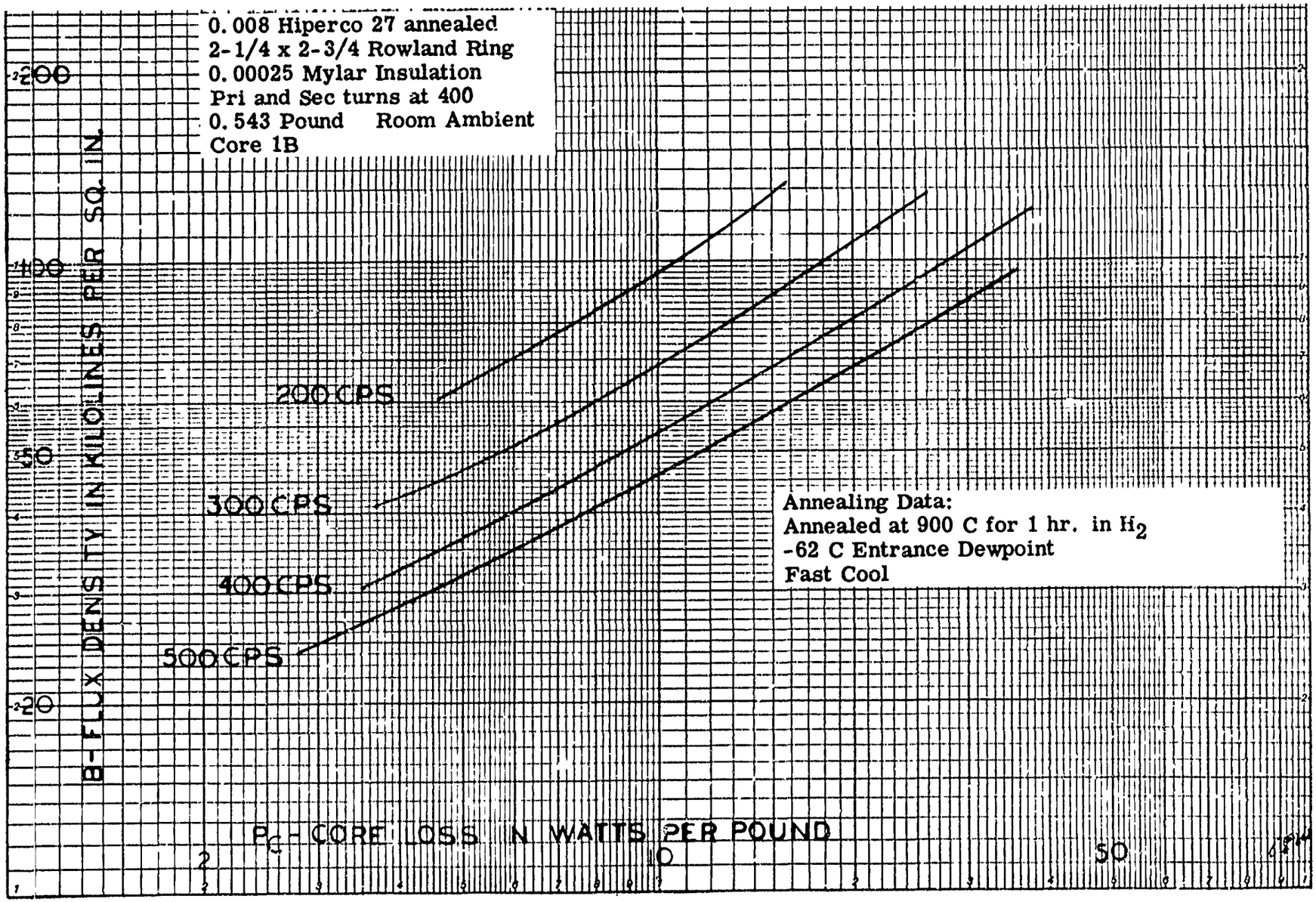

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FIGURE 25. Core Loss of 0.008 Hiperco 27 Mylar Insulated

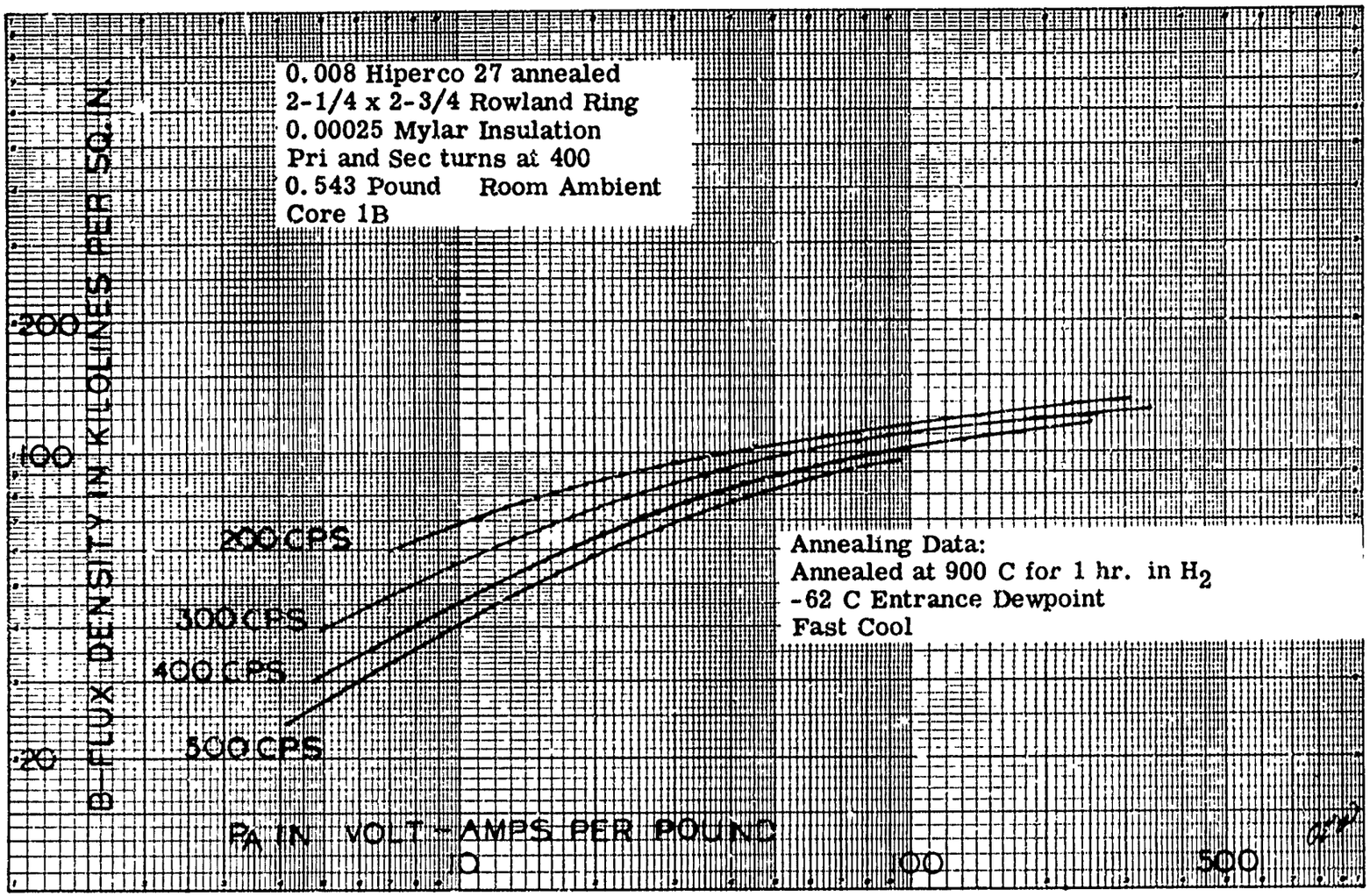

FIGURE 26. Apparent Core Loss of 0.008 Hiperco 27 Mylar Insulated

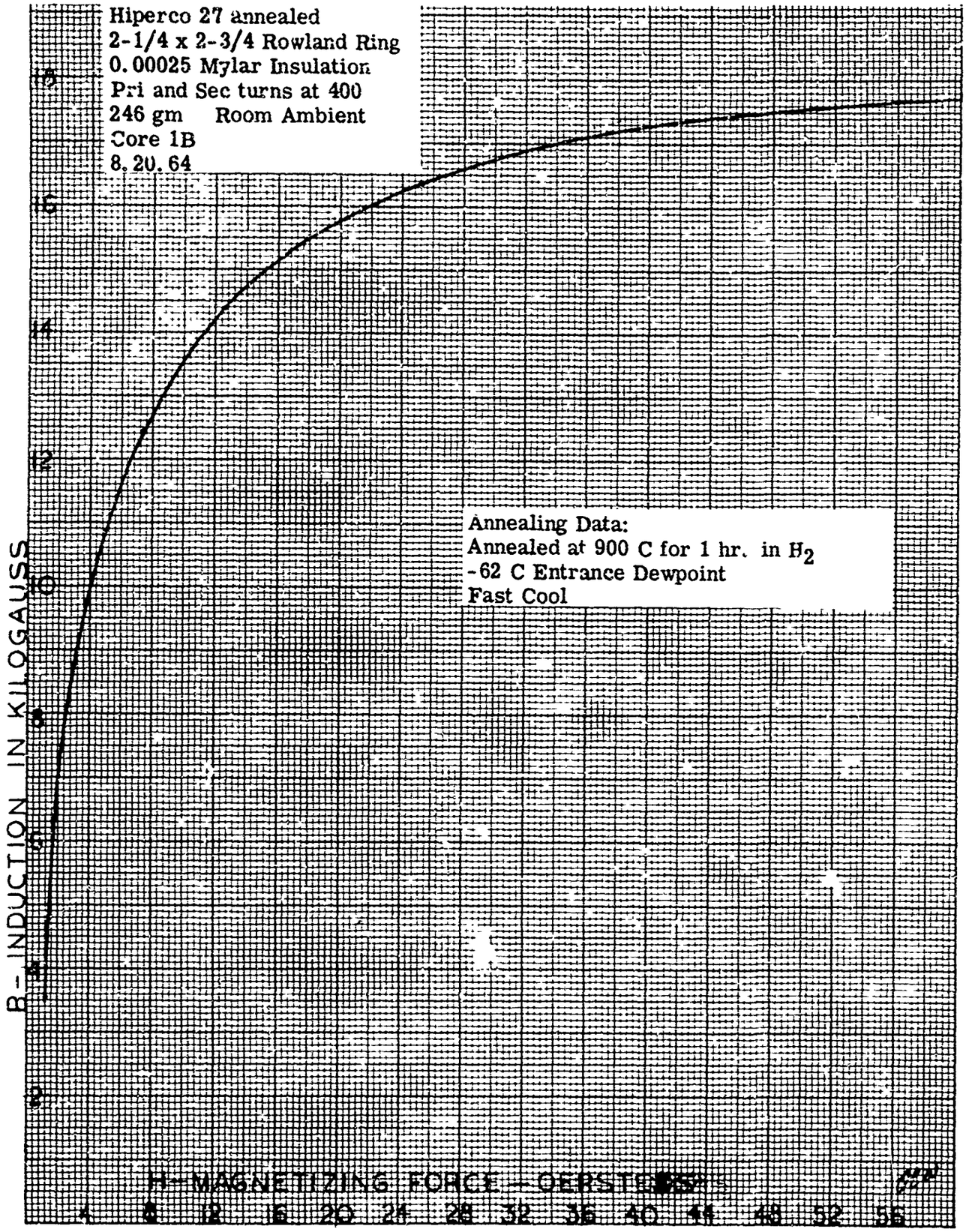

FIGURE 27. D-C Magnetization of 0.008 Hiperco 27 Mylar Insulated

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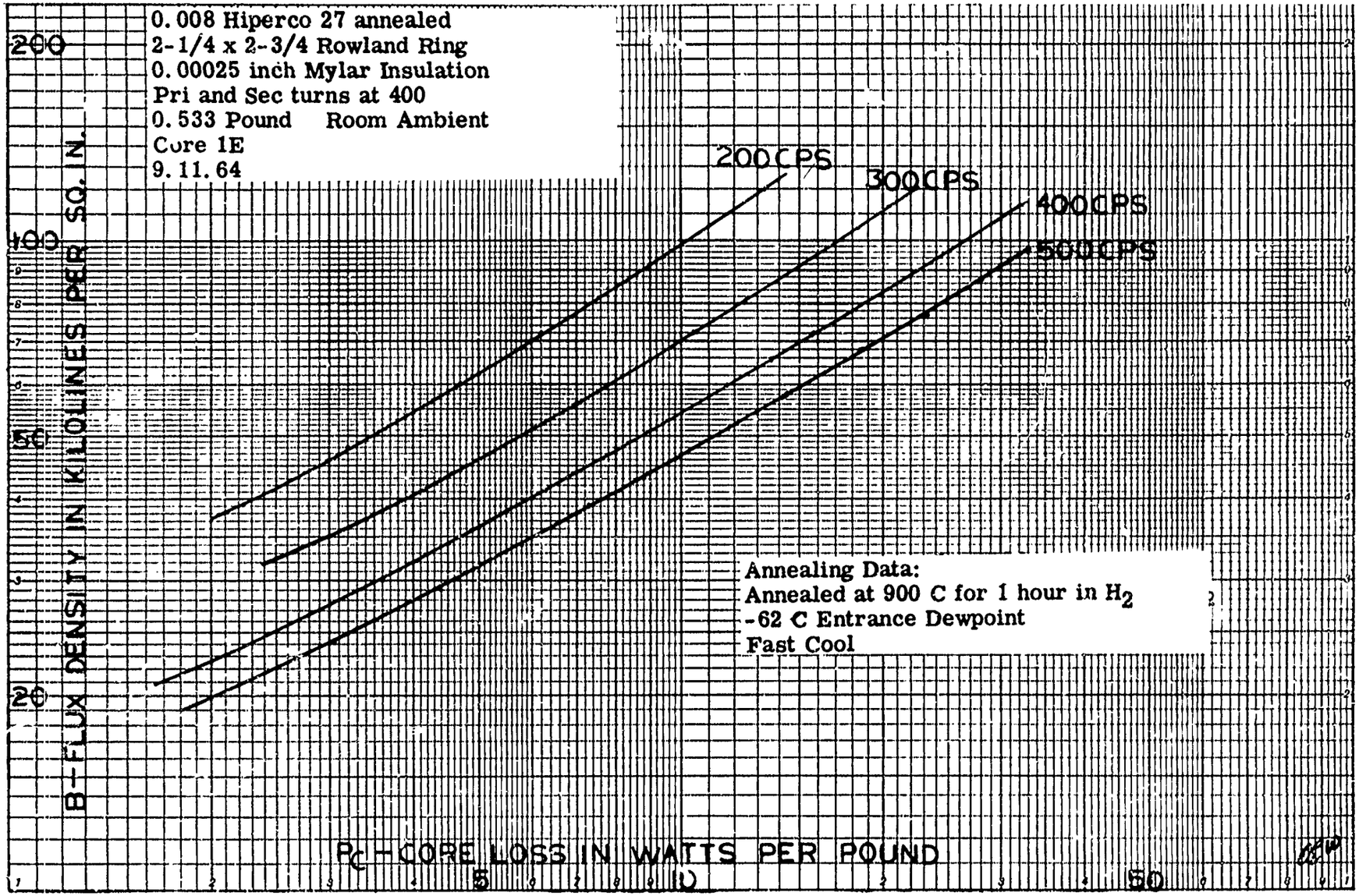

FIGURE 28. Core Loss of 0.008 Hiperco 27 Mylar Insulated

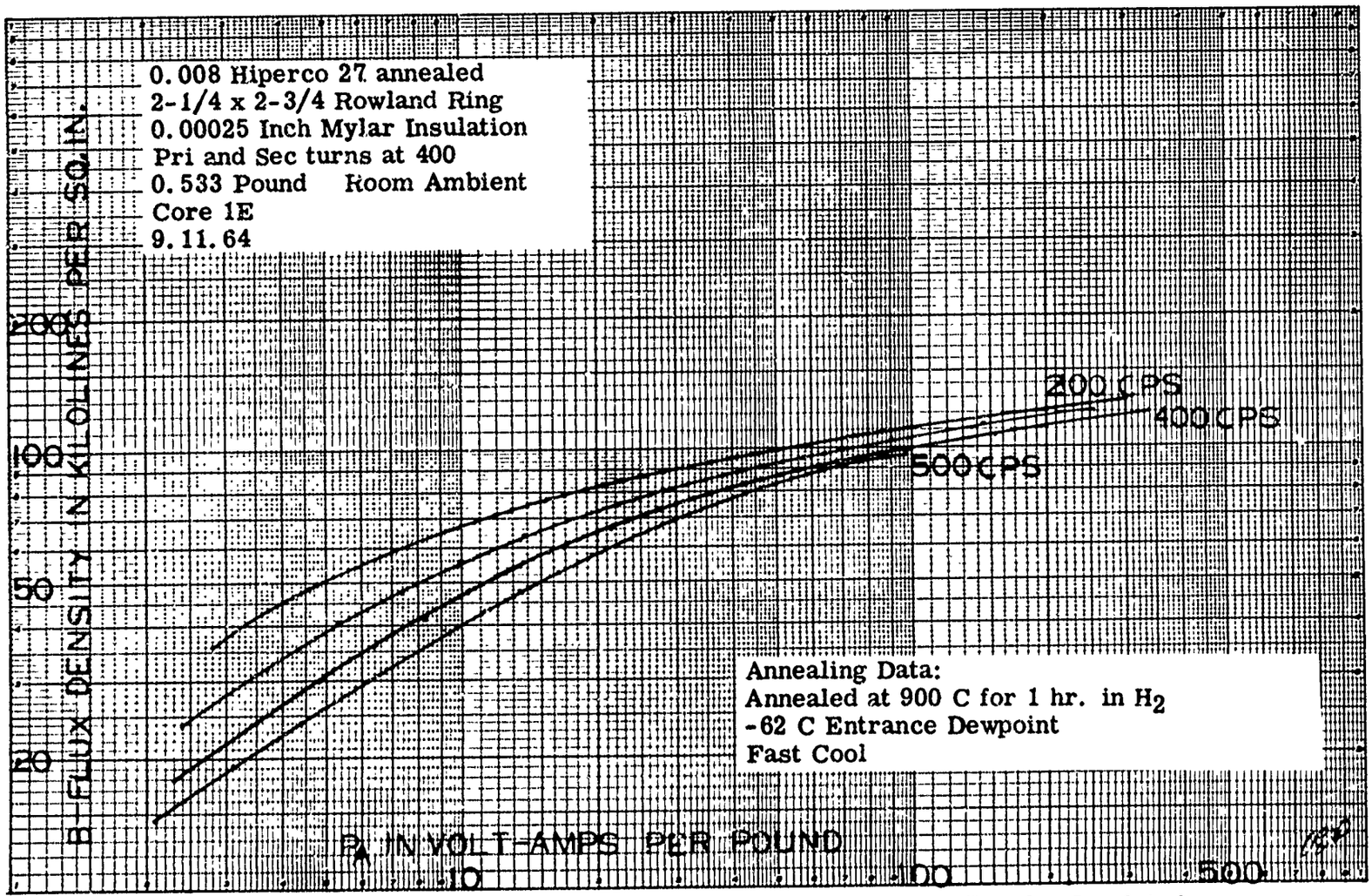

FIGURE 29. Apparent Core Loss of 0.008 Hiperco 27 Mylar Insulated

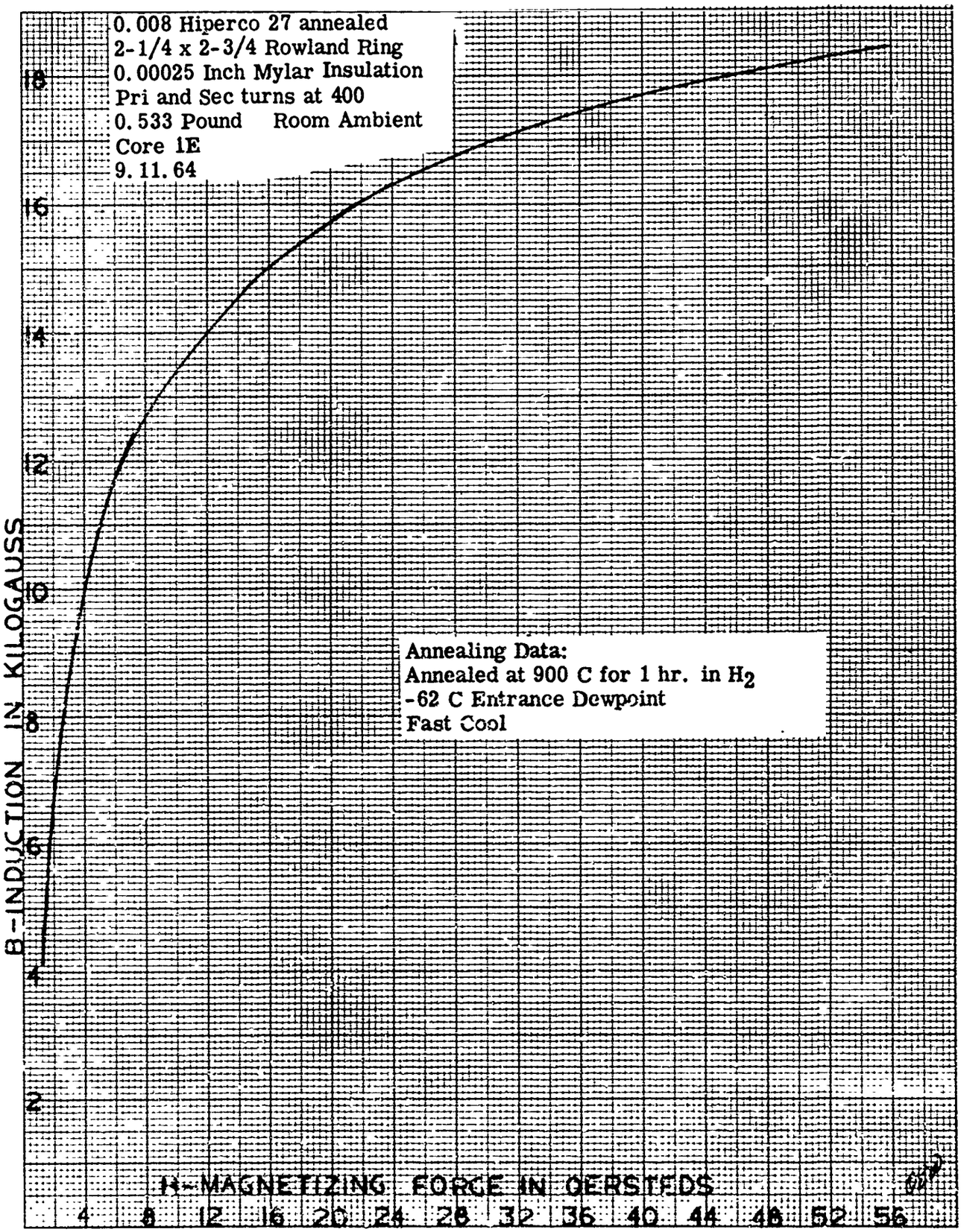

FIGURE 30. D-C Magnetization of 0.008 Hiperco 27 Mylar Insulated

FIGURE 31. Core Loss of 0.008 Hiperco 27 Mylar Insulated

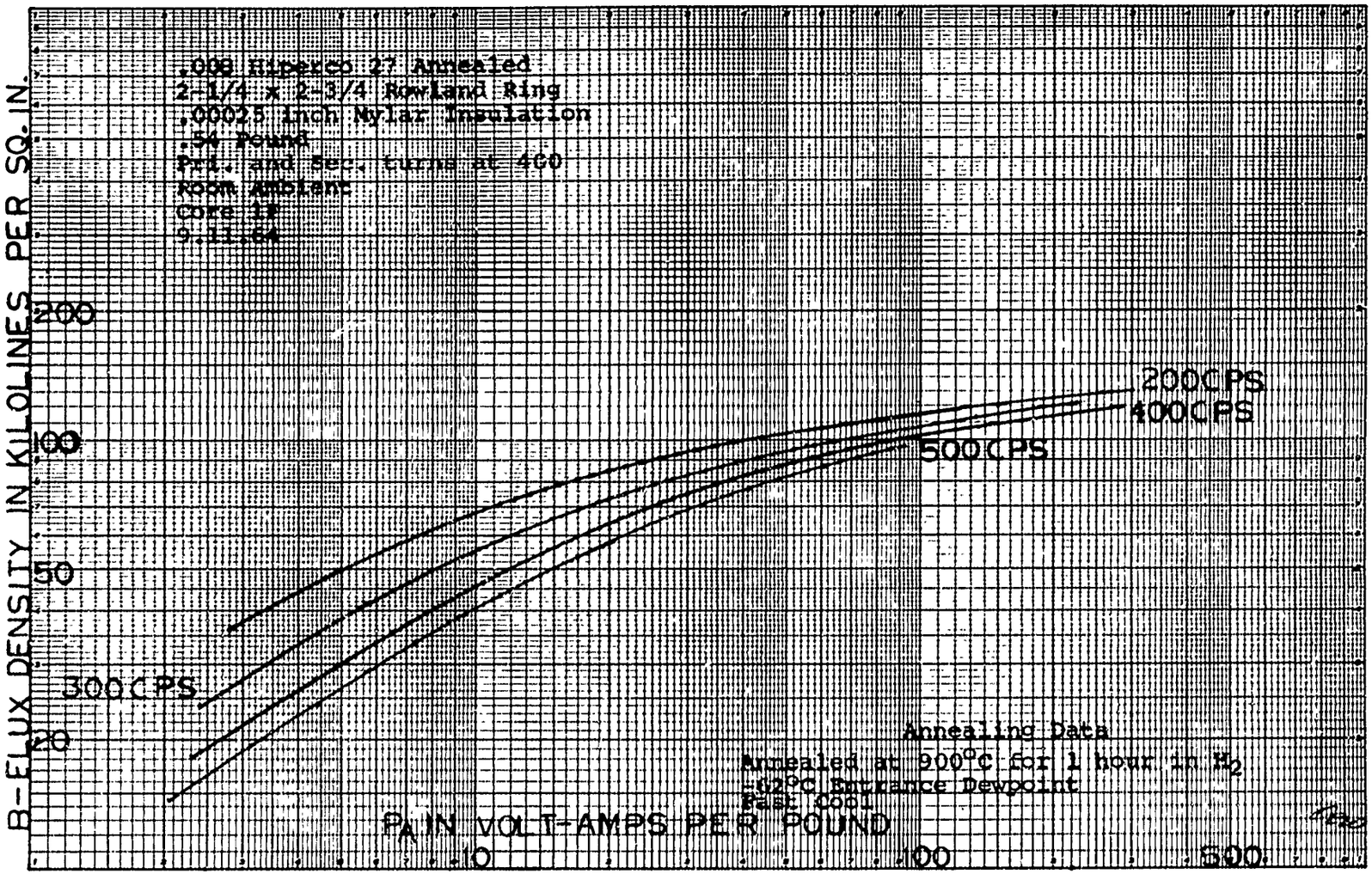

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FIGURE 32. Apparent Core Loss of 0.008 Hiperco 27 Mylar Insulated

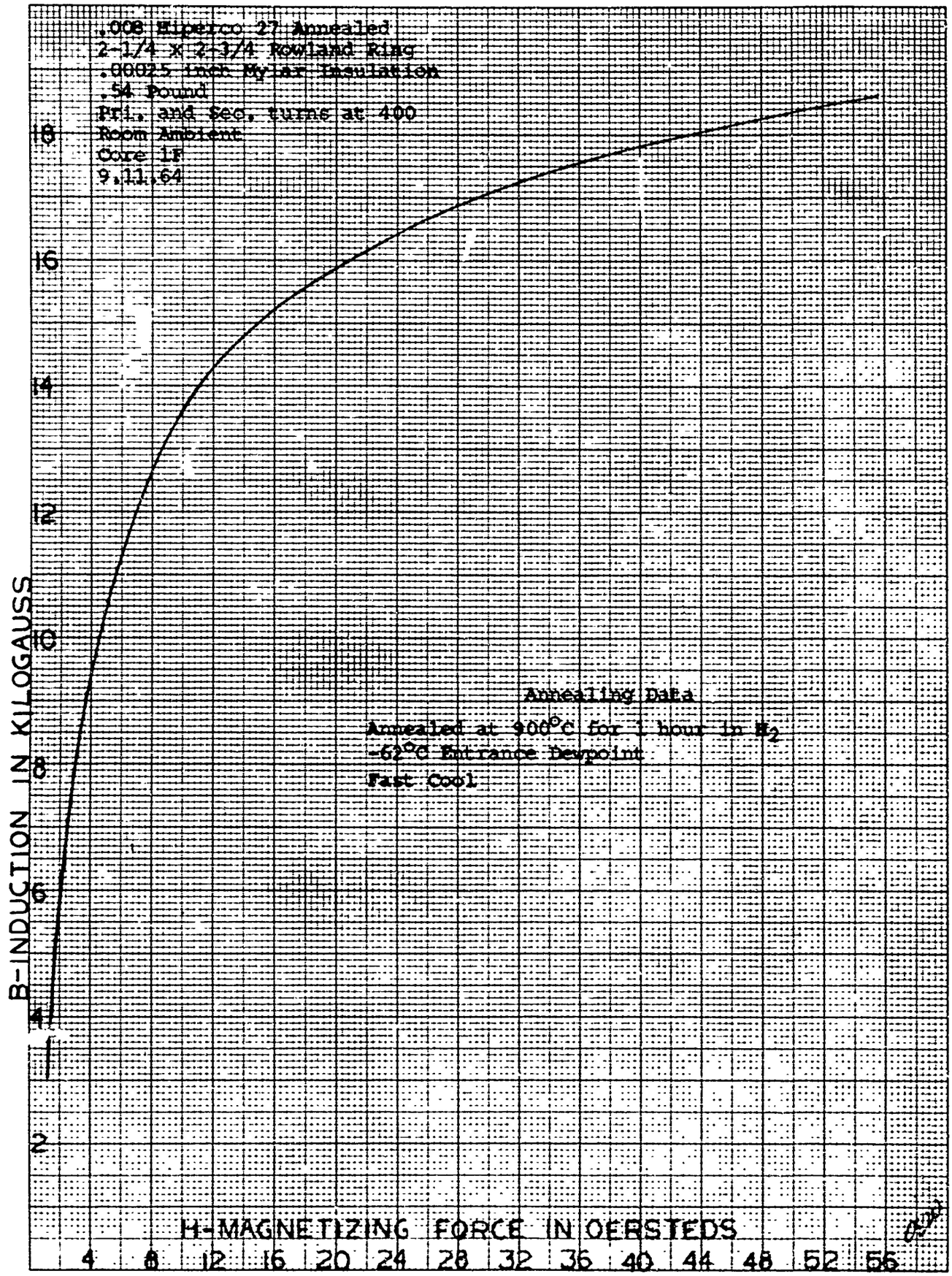

FIGURE 33. D-C Magnetization of 0.008 Hiperco 27 Mylar Insulated

WAED64.56E-63

FIGURE 34. Core Loss of 0.008 Hiperco 27 After Exposure to Potassium Mylar Insulated

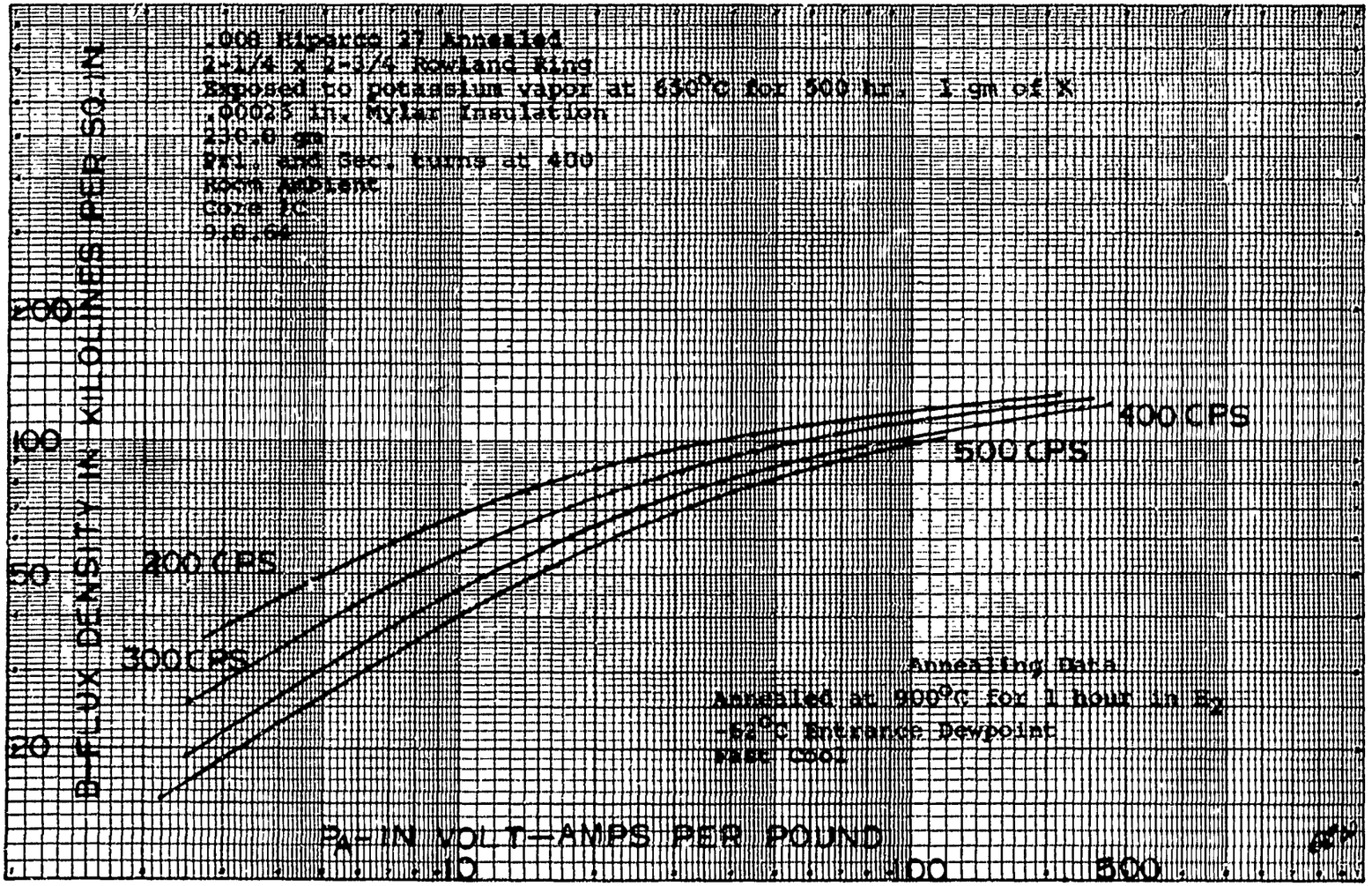

FIGURE 35. Apparent Core Loss of 0.008 Hiperco 27, After Exposure to Potassium, Mylar Insulated

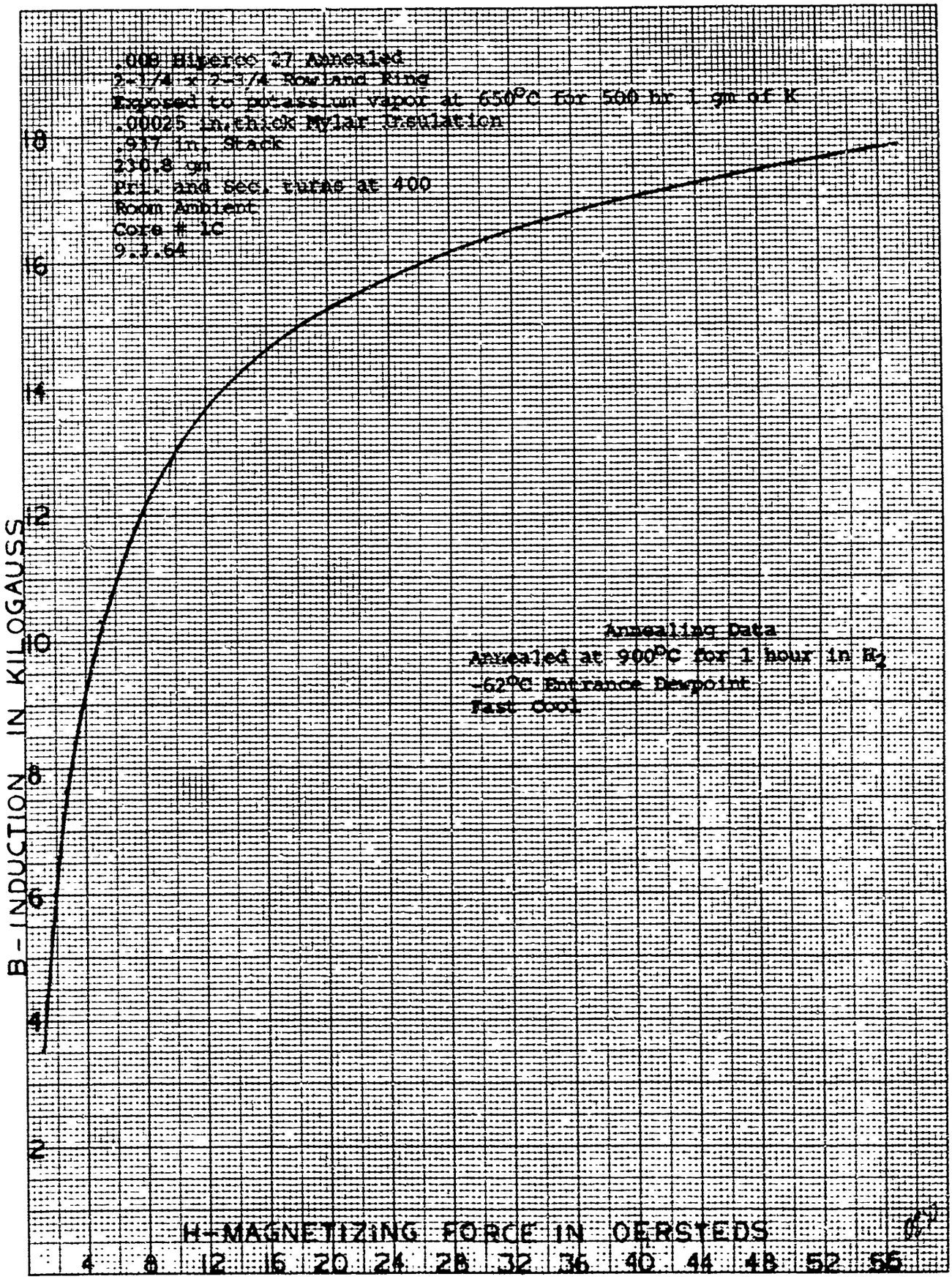

FIGURE 36. D-C Magnetization of 0.008 Hiperco 27, After Exposure to Potassium, Mylar Insulated

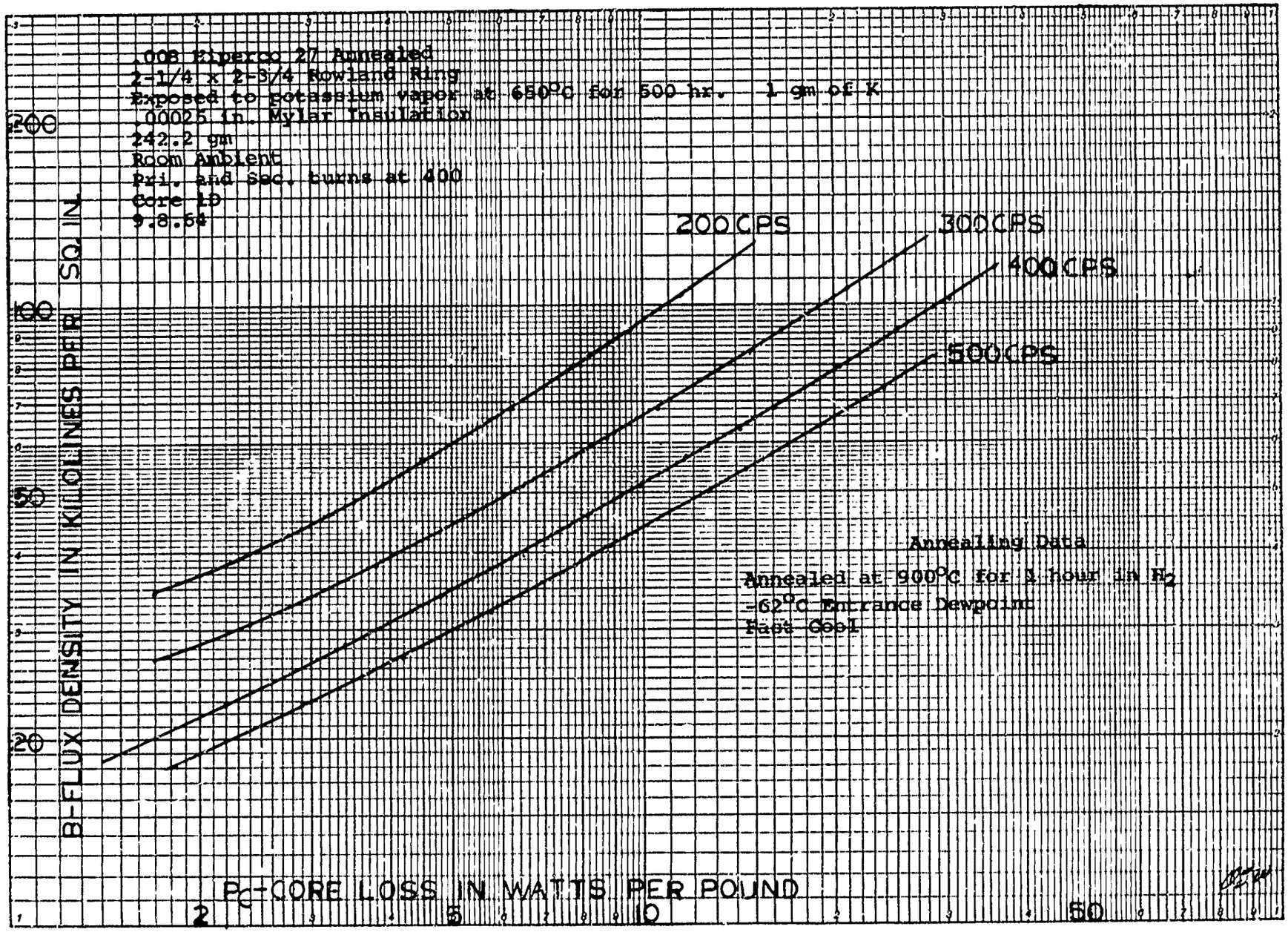

FIGURE 37. Core Loss of 0.008 Hiperco 27, After Exposure to Potassium, Mylar Insulated

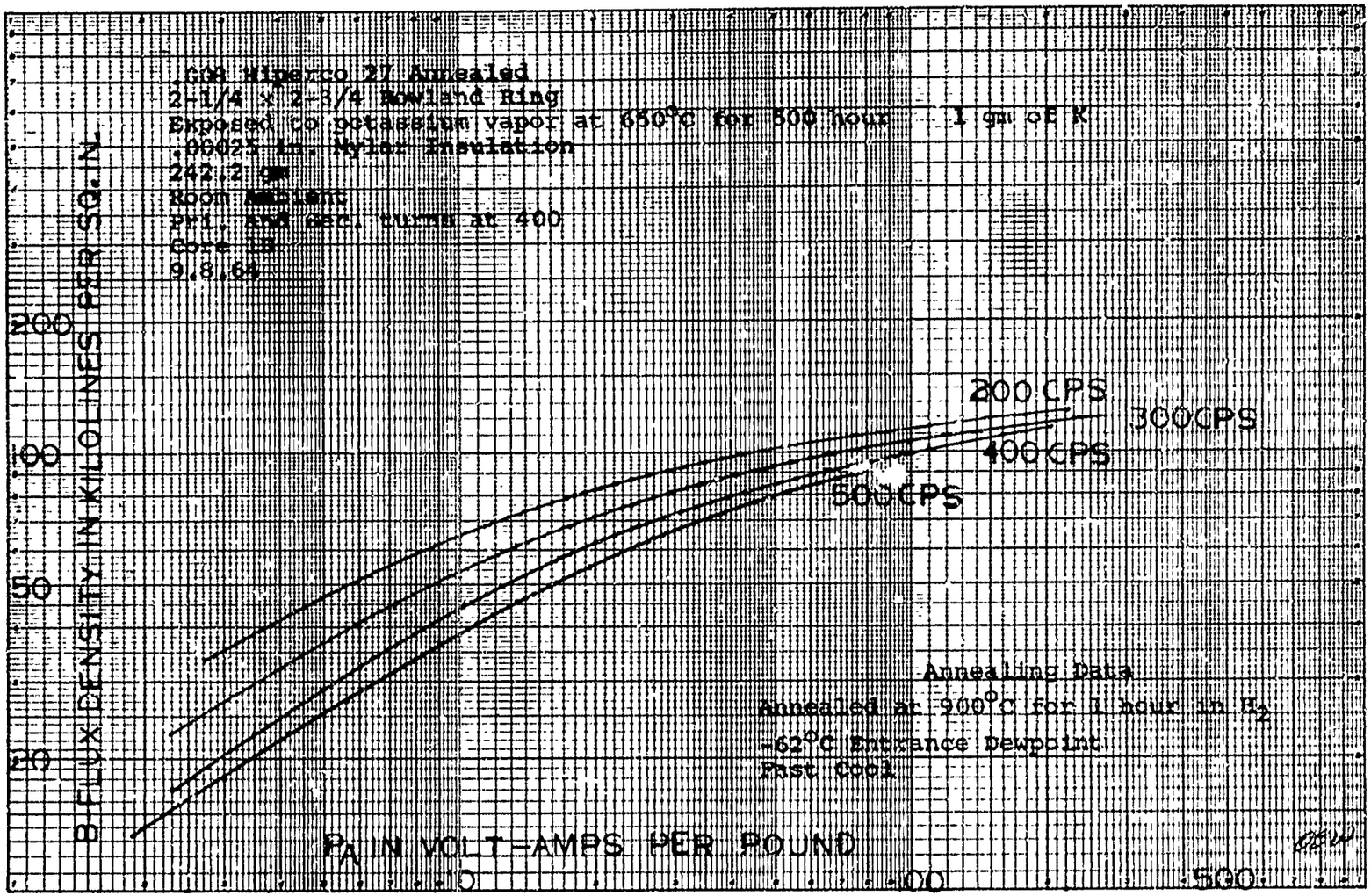

FIGURE 38. Apparent Core Loss of 0.008 Hiperco 27, After Exposure to Potassium, Mylar Insulated

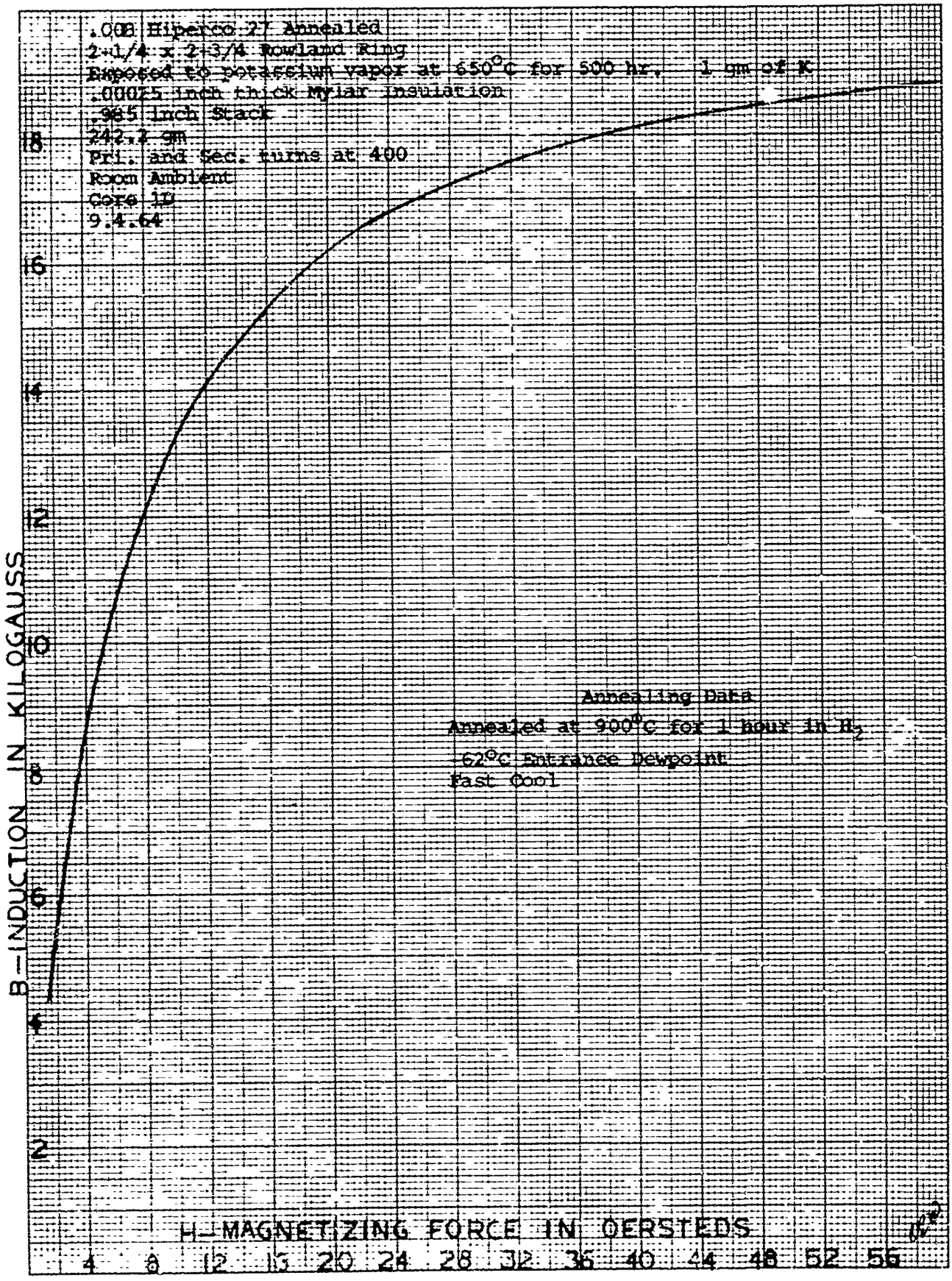

FIGURE 39. D-C Magnetization of 0.008 Hiperco 27, After Exposure to Potassium, Mylar Insulated

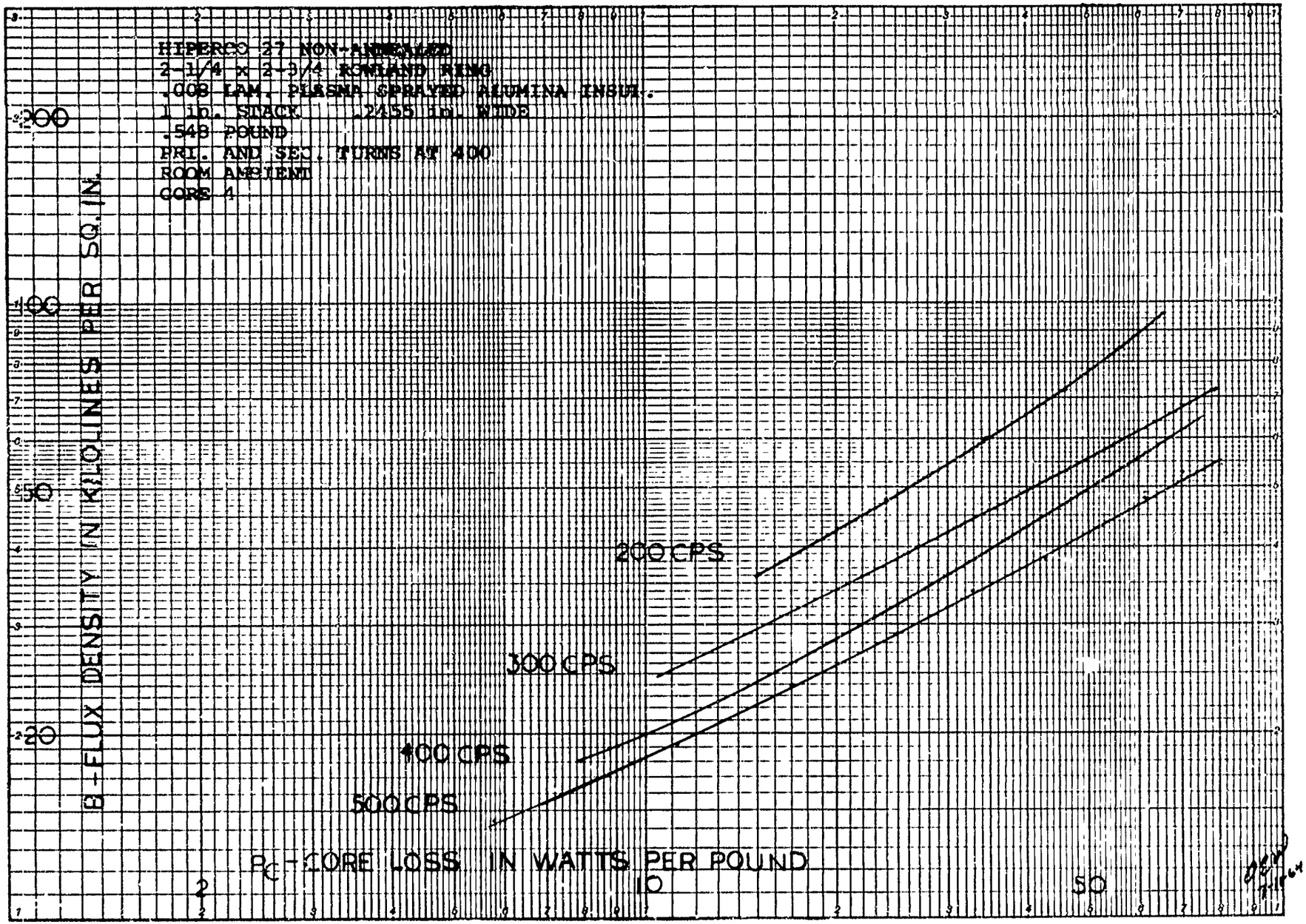

FIGURE 40. Core Loss of 0.008 Hiperco 27, Not Annealed, Al_2O_3 (99.99%) Insulated

FIGURE 41. Core Loss of 0.008 Hiperco 27, Not Annealed, Mylar Insulated

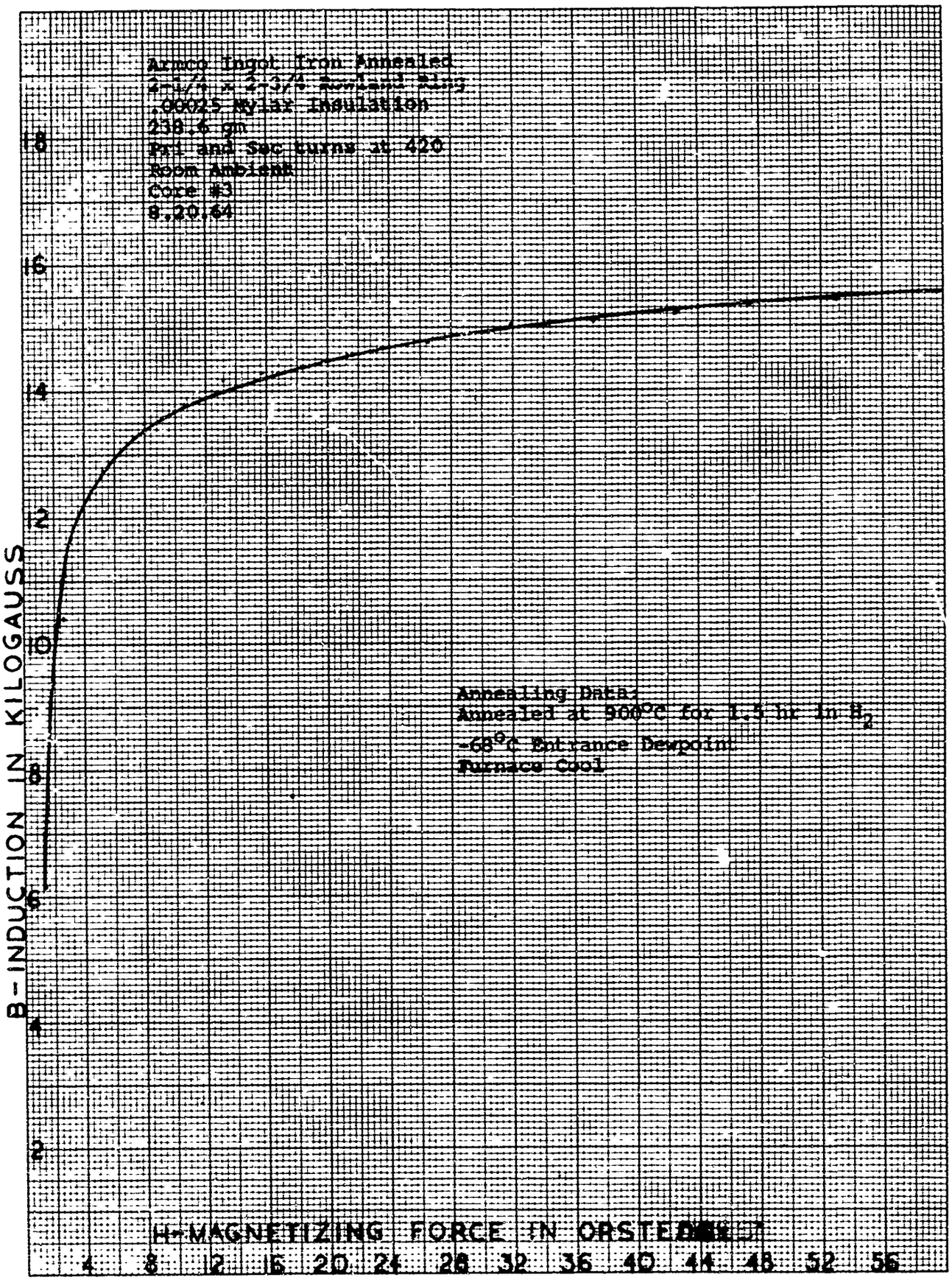

FIGURE 42. D-C Magnetization of 0.008 Armco Ingot Iron Mylar Insulated

FIGURE 43. Core Loss of 0.008 Armco Ingot Iron Mylar Insulated

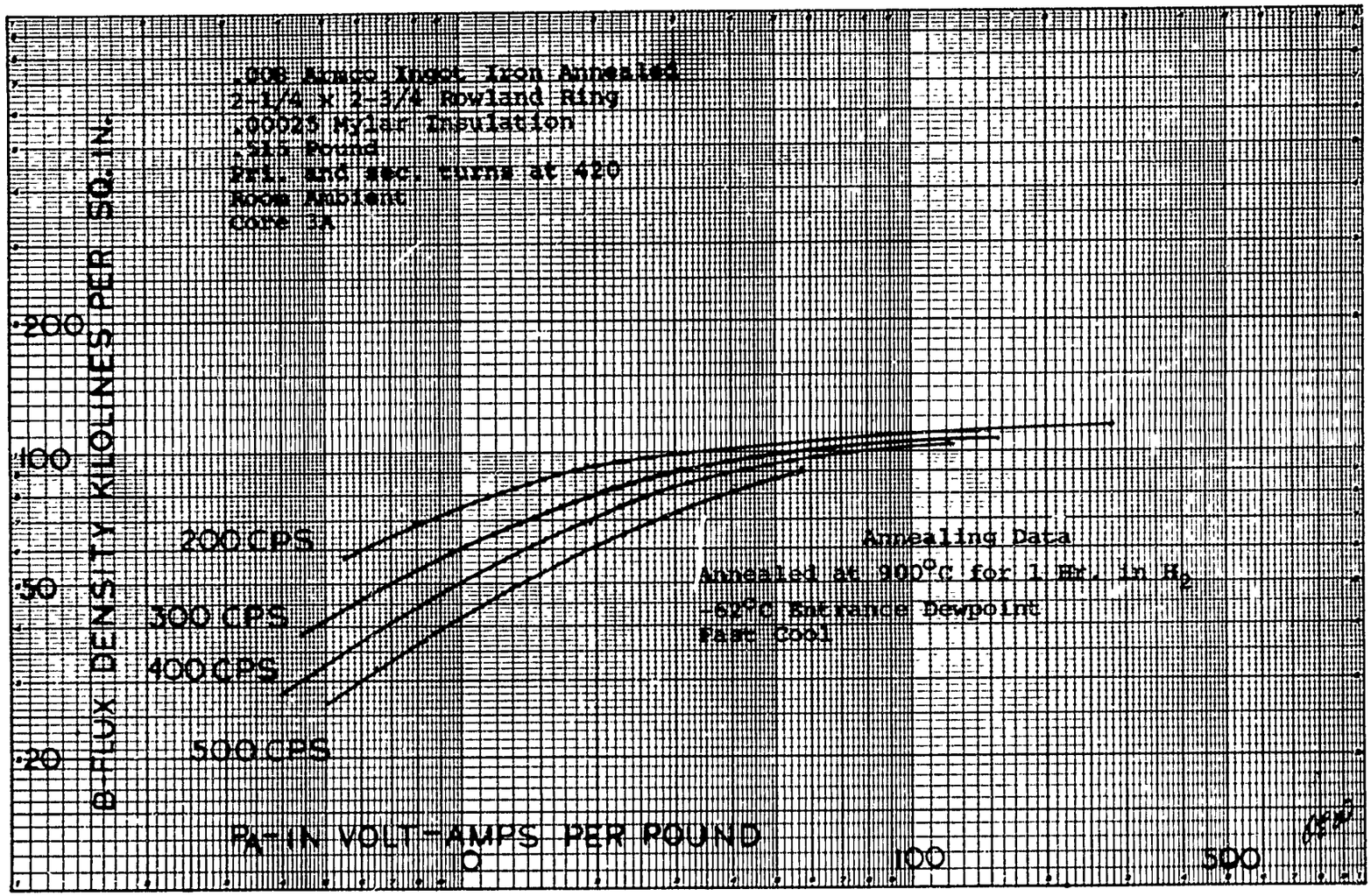

FIGURE 44. Apparent Core Loss of 0.008 Armco Ingot Iron Mylar Insulated

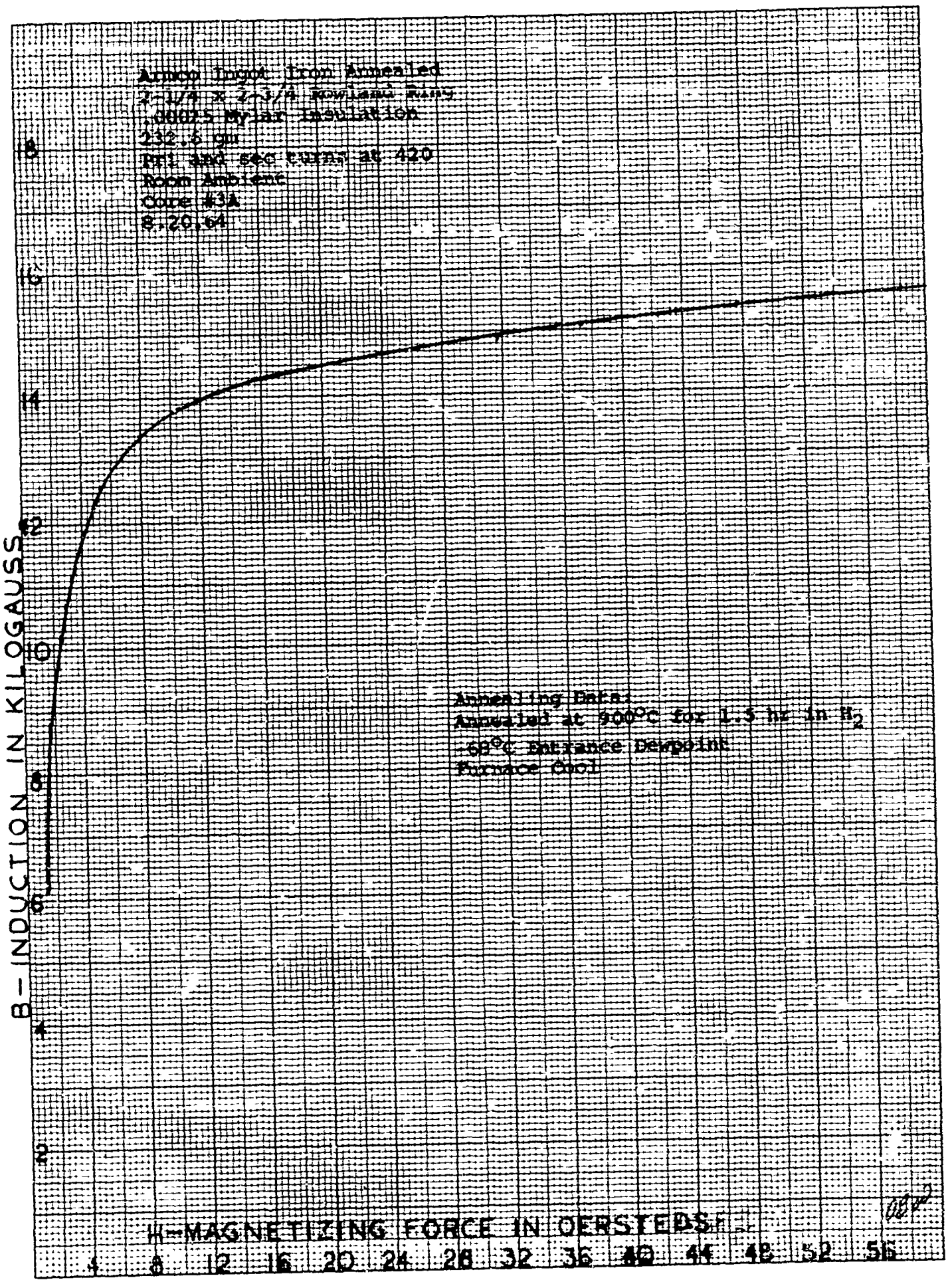

FIGURE 45. D-C Magnetization of 0.008 Armco Ingot Iron Mylar Insulated

FIGURE 46. Core Loss of 0.008 Armco Ingot Iron Mylar Insulated

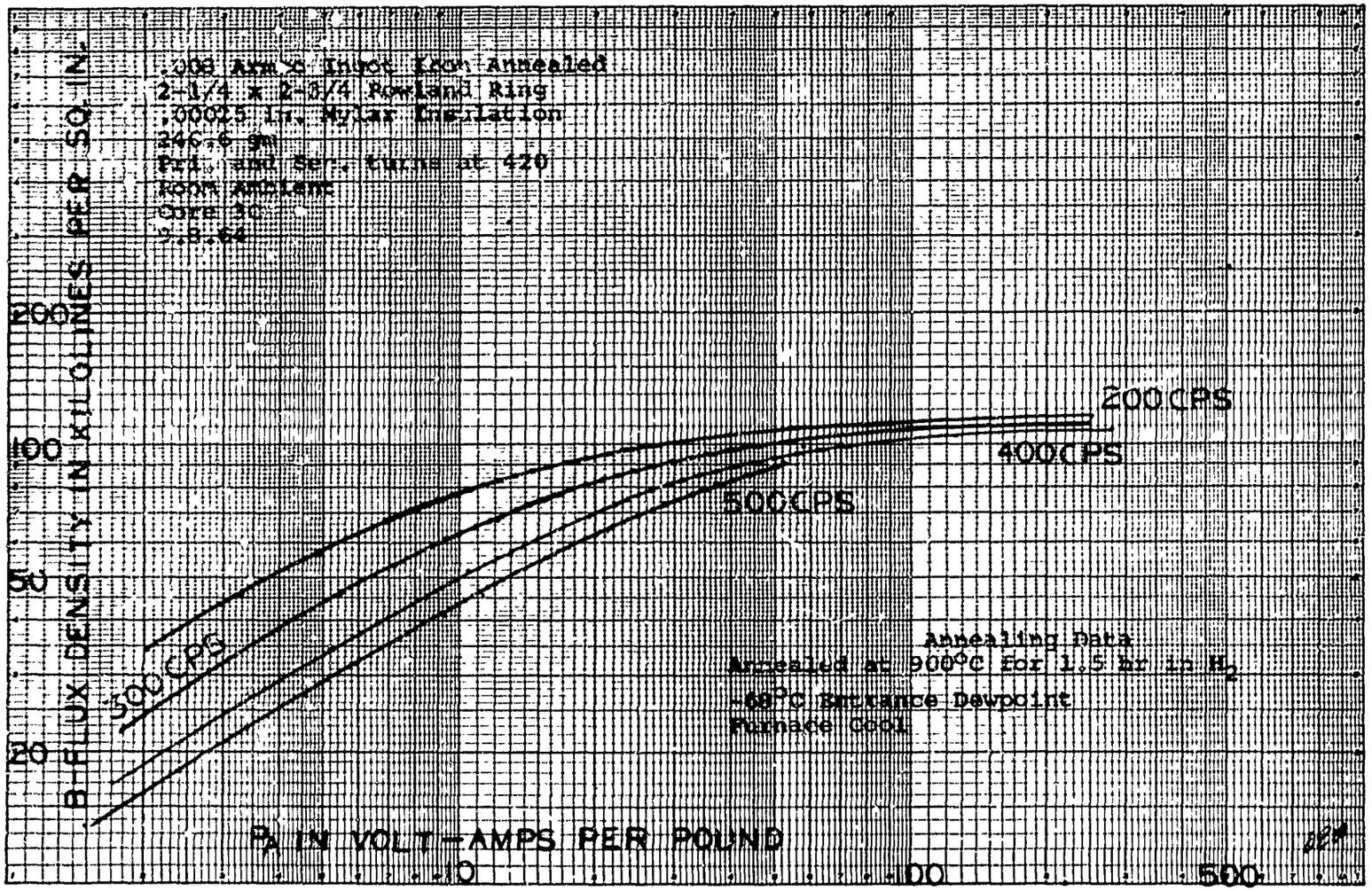

FIGURE 47. Apparent Core Loss of 0.008 Armco Ingot Iron Mylar Insulated

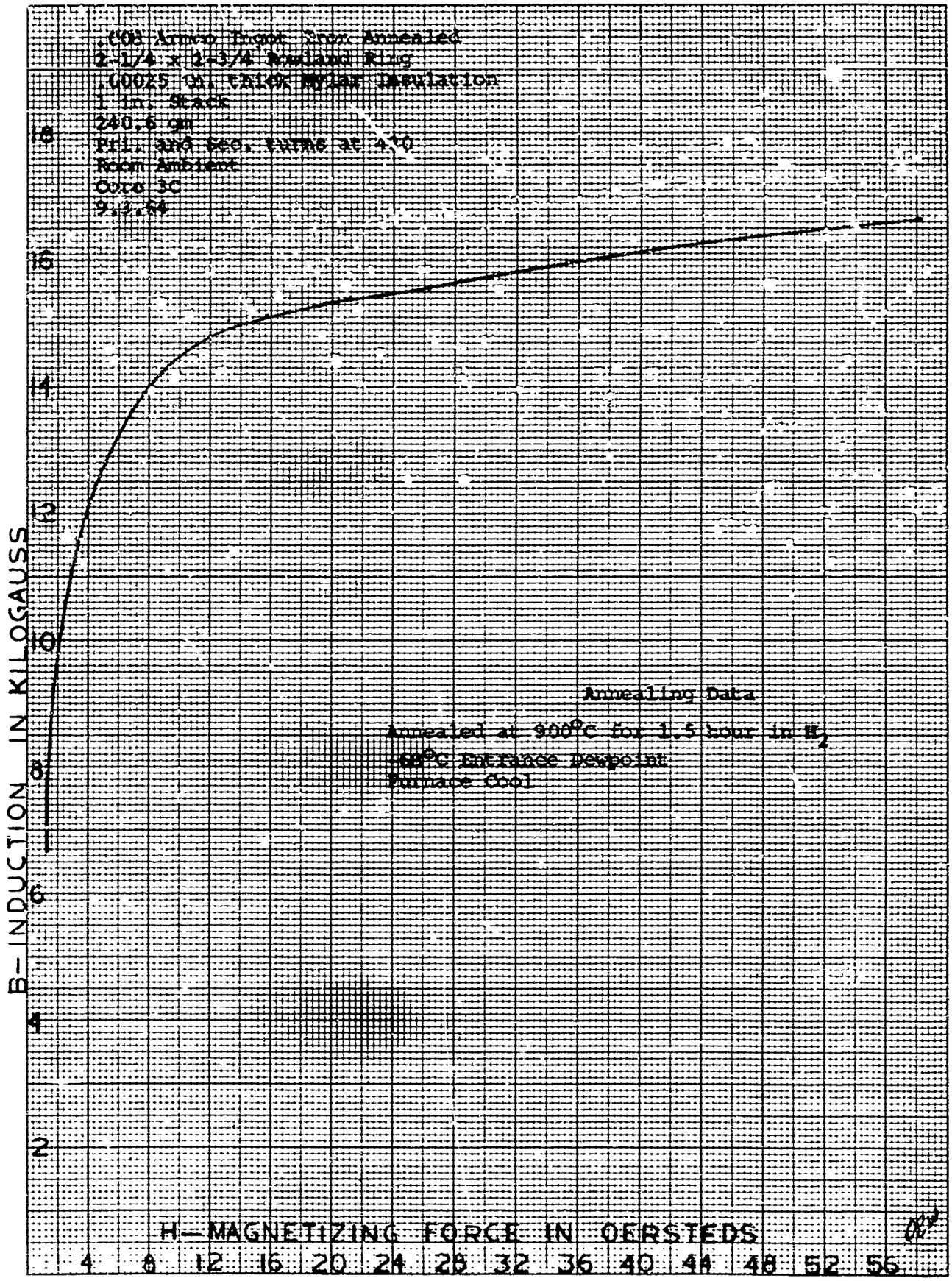

FIGURE 48. D-C Magnetization of 0.008 Armco Ingot Iron Mylar Insulated

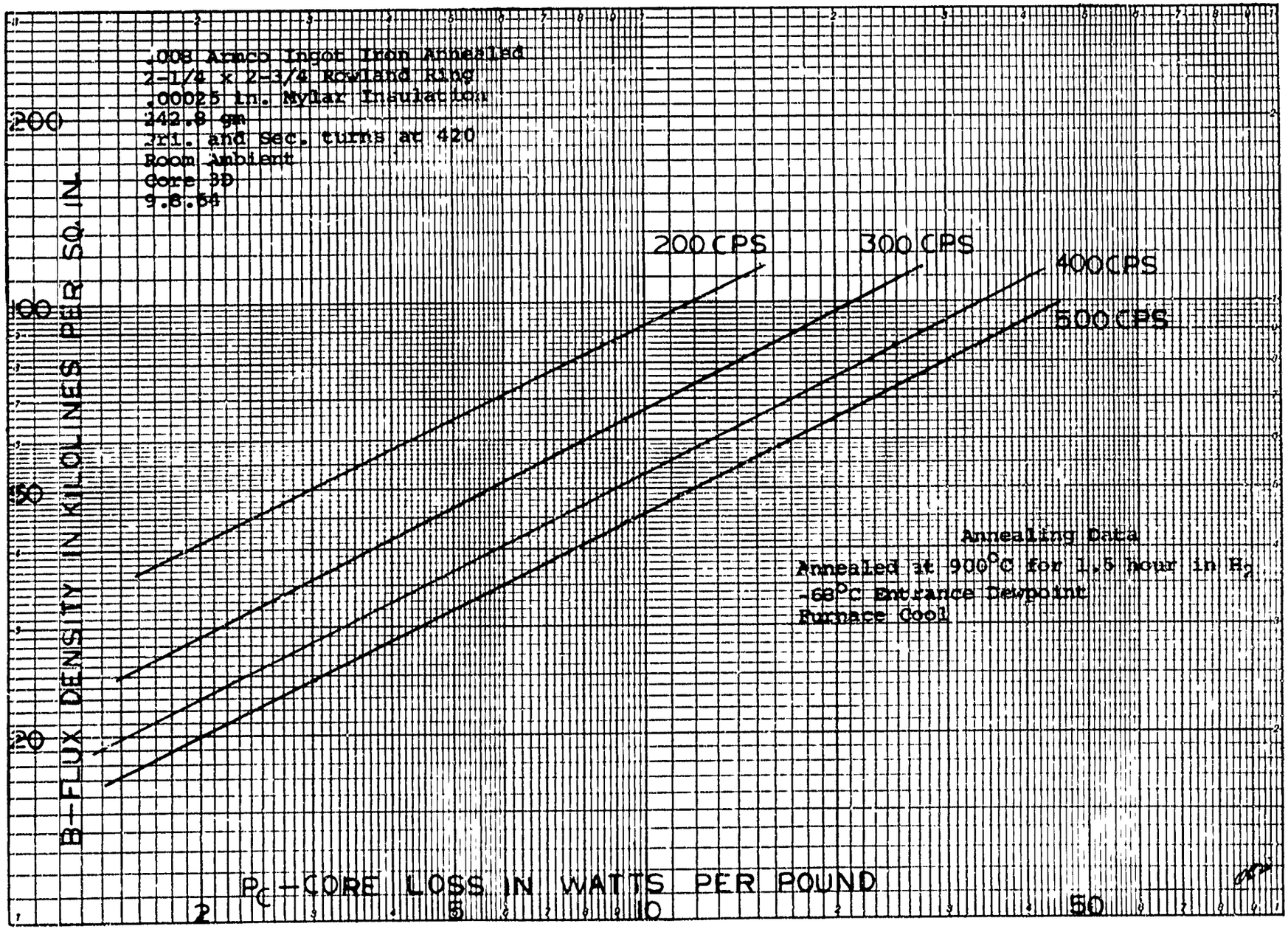

FIGURE 49. Core Loss of 0.008 Armco Ingot Iron Mylar Insulated

FIGURE 50. Apparent Core Loss of 0.008 Armco Ingot Iron Mylar Insulated

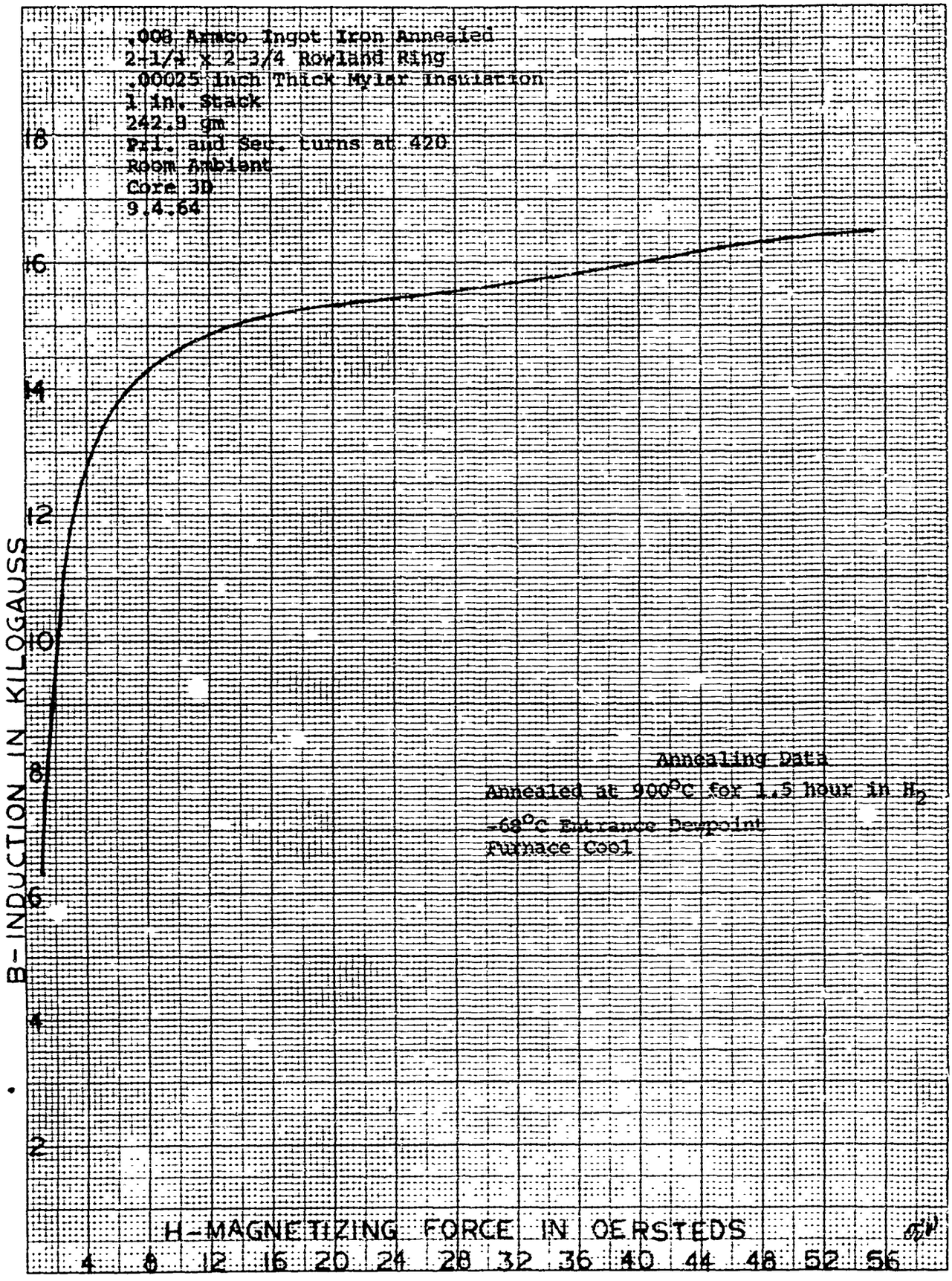

FIGURE 51. D-C Magnetization of 0.008 Armco Ingot Iron Mylar Insulated

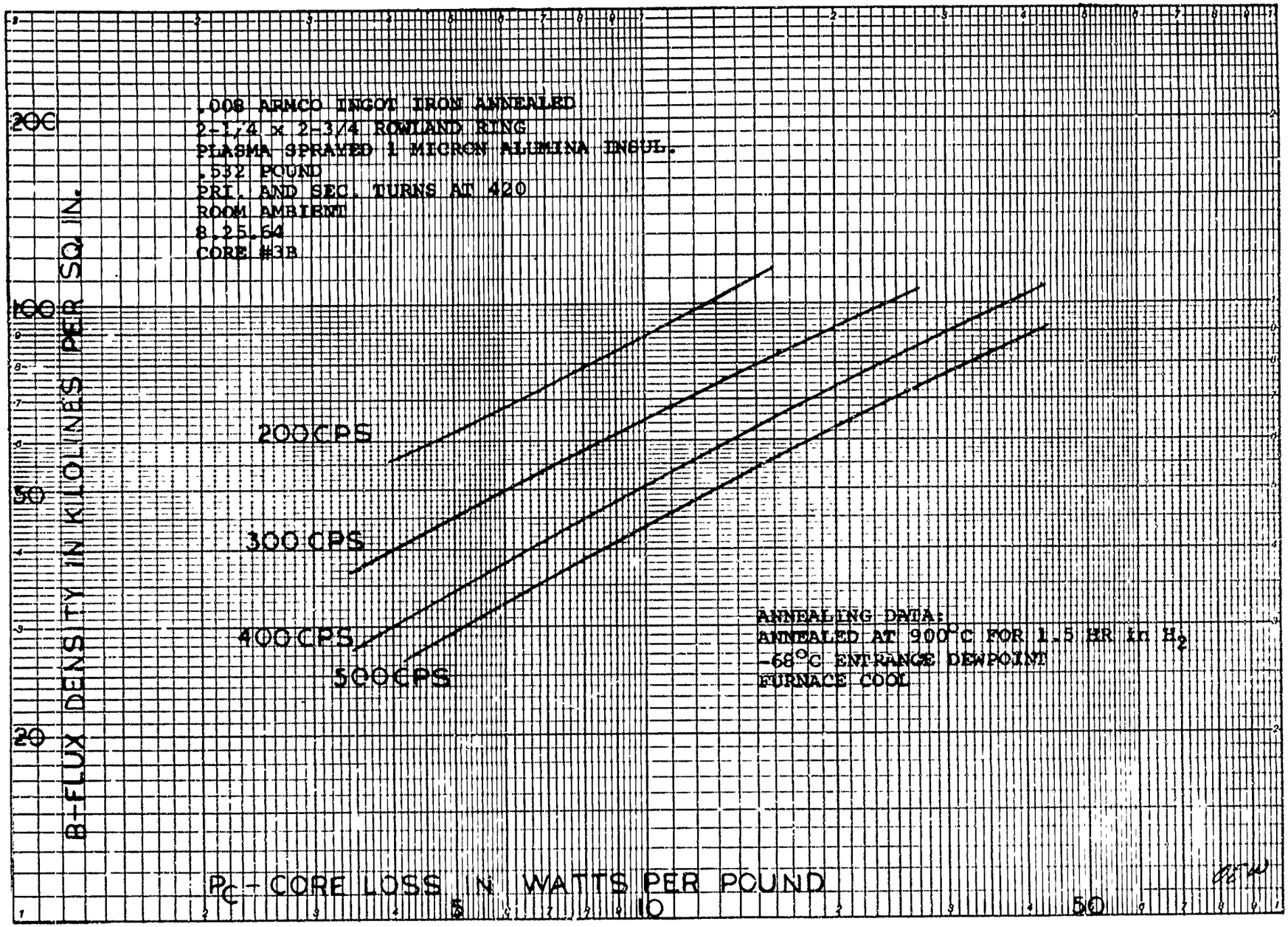

FIGURE 52. Core Loss of 0.008 Armco Ingot Iron Al_2O_3 (99.99%) Insulated

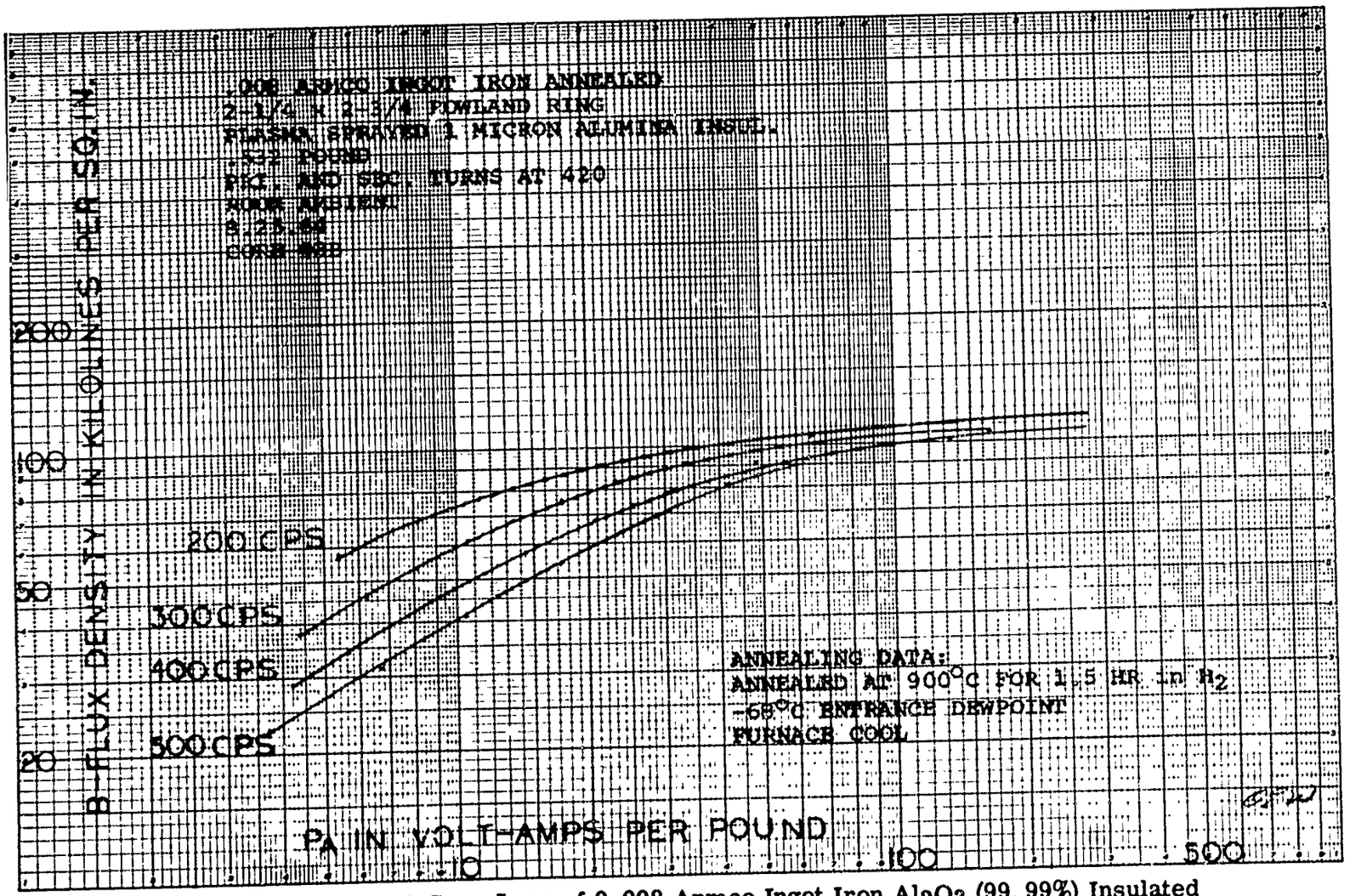

FIGURE 53. Apparent Core Loss of 0.008 Armco Ingot Iron Al_2O_3 (99.99%) Insulated

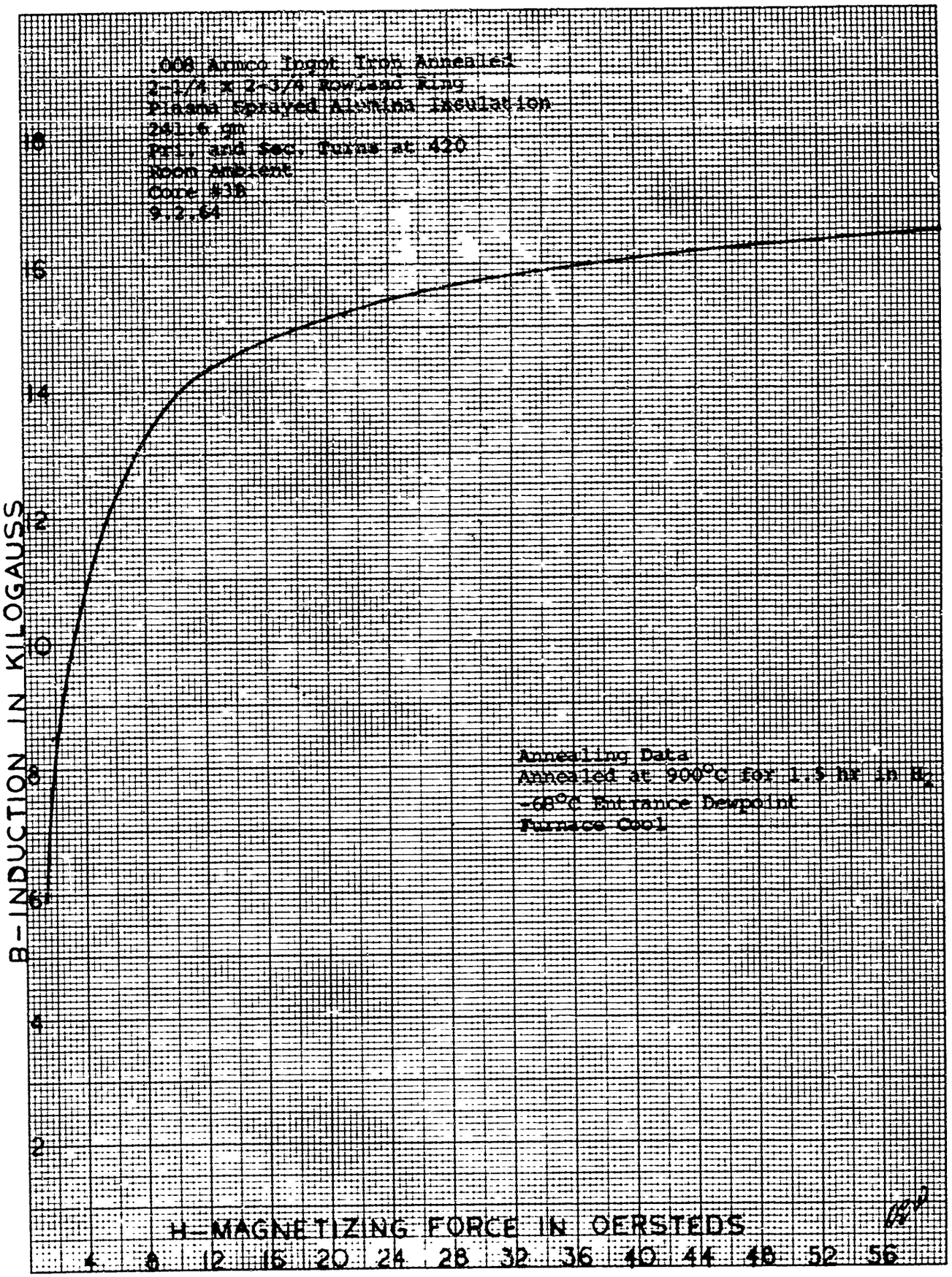

FIGURE 54. D-C Magnetization of 0.008 Armco Ingot Iron Al_2O_3 (99.99%) Insulated

tests will be run at resistive loading. The other tests will be run by "Loading Back" or "Opposition" loading because the variable frequency supply is limited in output power. A number of variable frequency supplies are available and since only transformer losses will be supplied, the "Opposition" loading should present no problem. Figure 55 is a diagram of the test set-up for the "Opposition" loading.

Three transformers have been designed and are being manufactured to aid in the test program. The transformers are for the specific function or functions as follows:

No. 1 Transformer

This transformer is to be utilized to step up the supply voltage to input test voltages for 500 and 1000 volts. It is capable of supplying full power to the transformer under test where it is operating with a resistive load. This transformer will also be used to supply the excitation or no load losses for opposition loading.

No. 2 Transformer

This transformer is to be used to supply the excitation for load losses in opposition loading. It will step up the current from the power supply to the 50 amperes load current required.

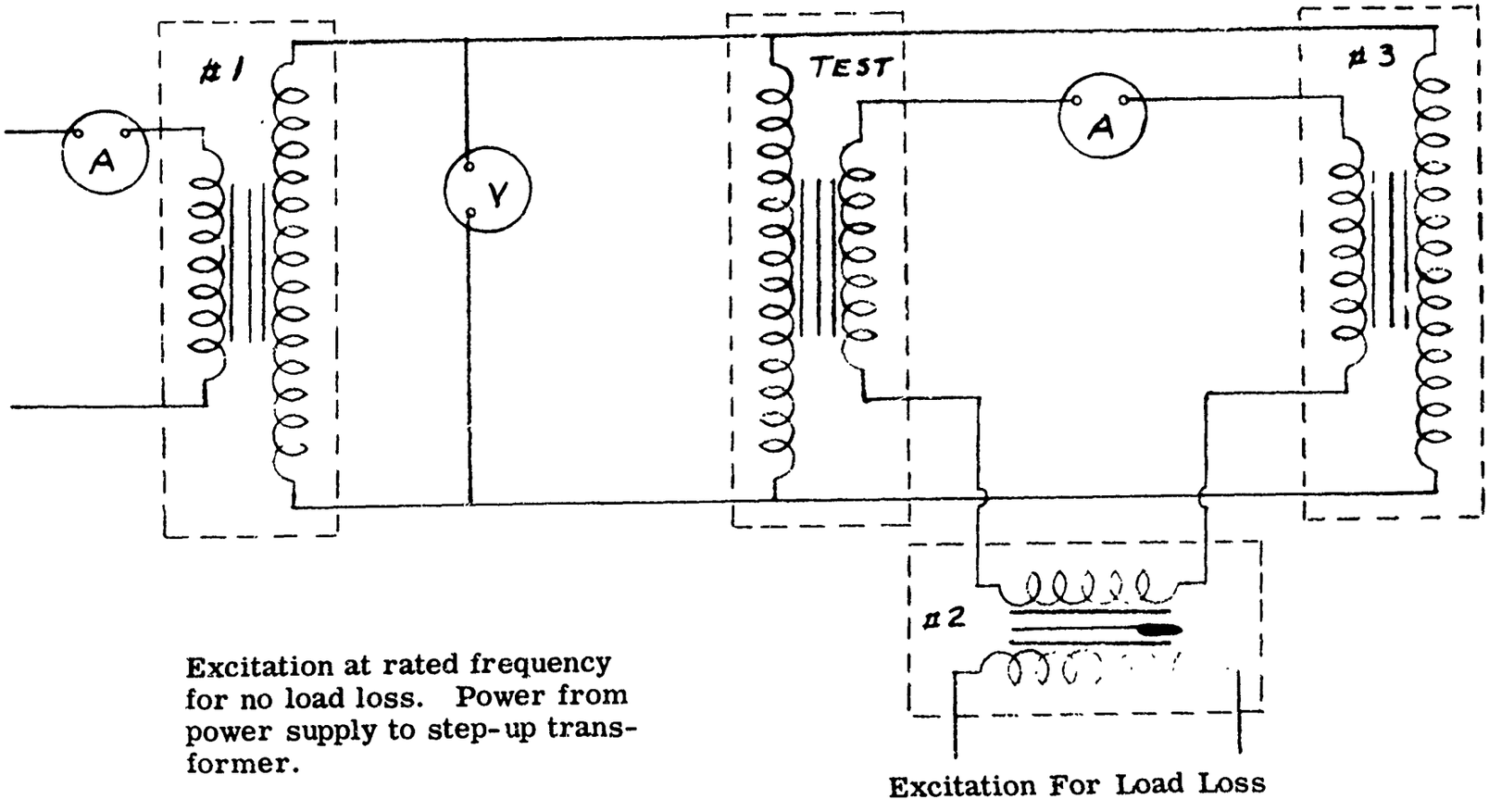

FIGURE 55. Diagram of Opposition Loading Test Set-Up

No. 3 Transformer

This transformer is to be similar to the transformer under test and will be used in opposition to the test transformer for opposition loading.

During the opposition loading test, the transformers will have the excitation for no load losses applied to the high voltage, and excitation for load losses applied to the low voltage winding. It is possible to reverse the method of supplying the losses, but this would require an additional testing transformer. If load losses were supplied on the high voltage winding, the current could be supplied directly from the power supply but an isolation transformer would have to be between the power supply and the high voltage to prevent the application of the high voltage to the power supply. A step up ransformer is required to step-up the supply voltage for resistive loading.

IV. FUTURE WORK

A. Conductors - Insulating With Ceramics

The small wire size of the conductor for the primary winding of the transformer dictates a different method of applying high-purity potassium resistant ceramics than plasma-arc spraying. The ceramic, 99.99% alumina or ball milled Alite A-610 (99.0% alumina-1% magnesium), will be dispersed in a plastic vehicle such as polyvinyl acetate etc. The resultant slurry will be applied to conductors by spraying or dip coating techniques. The coating will then be baked at ~90 C for a period of time sufficient to either cure the plastic or eliminate the organic solvent. Preliminary experiments that have been conducted on such coatings show it is possible to wind a conductor insulated in this manner. The crucial point occurs when the organic binder is burned out of the insulation leaving a loosely adhering ceramic powder.

The techniques of circumventing this powdery insulation are as follows:

1. The coil will be wound green after the ceramic insulation is bound with the plastic material. A plasma-arc spray of high purity alumina will be applied over the outer surface of the coil. The whole coil will then be fired at 600-700 C.
2. The alternate dip or spray coatings of alumina base ceramic and calcium fluoride-barium fluoride eutectic will be applied in a plastic binder to a columbium clad (20-28%) dispersion-

strengthened copper conductor. After curing the plastic or removing the solvent, the conductor will be wound into a coil. The temperature will be increased to 1030 C. At this temperature, the eutectic melts and binds the ceramic insulating material. The result will be a ceramic insulated coil.

These coils will be tested in potassium vapor for their corrosion resistance and electrical properties.

B. Transformer Fabrication

Transformers will be fabricated using the concentric coil design.

The coil fabrication methods described in the preceding paragraphs on conductor insulation will be adapted to transformer windings.

C. Preliminary Transformer Testing in 600 C Potassium Vapor

The transformers will be sealed in a stainless steel capsule equipped with electrical potassium resistant feed-throughs. Potassium will be introduced and the whole assembly will be placed in an inert atmosphere (argon) furnace for exposure at 600 C.

D. Ceramic-to-Metal Seals

More evaluation of ceramic-to-metal seal corrosion resistance in 600 and 850 C potassium vapor will be done.

E. Magnetic Material Evaluation After Potassium Vapor Exposure

The Cubex, Armco Iron and Hiperco 27 Rowland Ring samples will be examined for corrosion effects and changes in magnetic properties after 500 hours exposure to 600 C potassium vapor.

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1. R. W. Ure, Jr., J. Chem. Phys., Vol. 26 No. 6, 1957
2. Walter J. Tarnicke, Alite Division, U. S. Stoneware, Private Communication.
3. P. E. Kueser et al, Research and Development Program on Magnetic Electrical Conductor, Electrical Insulation and Bore Seal Materials, Third Quarterly Report NASA-CR-54089 June, 1964.