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FINAL REPORT

"DEVELOPMENT OF A CONTINUOUS SPINNING PROCESS
FOR PRODUCING SILICON CARBIDE - SILICON
NITRIDE PRECURSOR FIBERS"

CONTRACT NO. NAS8-34648

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CONCLUSIONS

The silicon carbide - silicon nitride precursor polymer produced by NASA's Huntsville laboratories can readily be fiberized, crosslinked and pyrolyzed. The product is a metallic black fiber, presumably of a composition of the type $C_xSi_yN_z$.

However, the properties of the resultant fiber have yet to be evaluated and knowledge of how the three steps, i.e. fiberization, crosslinking and pyrolysis, interact is almost nil.

OBJECTIVE

The objective of this research program is to design and construct an apparatus for the continuous production of silicon carbide - silicon nitride precursor fibers.

SUMMARY

The objective of the program was met by developing a small scale extruder based on a cylinder/piston assembly. The piston was caused to advance into the cylinder cavity at a precisely controllable rate by a variable speed DC motor via a differential screw mechanism. The resin in the cylinder cavity was extruded through variously sized spinneret plates, the fiber thus obtained being taken up onto a variable speed contact wheel.

Preliminary work with a sample of silicon carbide - silicon nitride precursor resin supplied by NASA demonstrated that the resin could readily be fiberized at 200-210^oF. It was found possible to fiberize the resin directly into ambient air, a controlled atmosphere cabinet not being necessary.

However, work with two subsequent batches of resin was rather less successful. These appeared to be gelled and also to contain substantial amounts of foreign material. Filtration of the resin was resorted to, and even then only small quantities of fiber could be obtained, with considerable difficulty.

The fibers so obtained could be readily crosslinked by maintaining them at 50^oC and 100% relative humidity. After 65 hours of this regimen, the fiber softened at about 400^oC, after 90 hours at 600^oC, and after 9 days full crosslinkage and a softening temperature of 800^oC was attained.

Fully crosslinked fibers were successfully pyrolyzed at 1000^oC, both with and without tension. Pyrolyzed fibers were of a metallic black color, with crystals (probably from an extraneous source) embedded in the surface.

RECOMMENDATIONS

1. Evaluate the $C_x Si_y N_z$ fibers obtained in this program with respect to such properties as thermal resistance, tensile strength, elongation, modulus, elastic recovery, oxidation resistance, electrical conductivity, and other characteristics of interest.
2. Explore the pertinent steps in the production of the precursor resin to determine how gelled product may be avoided and how resin properties such as composition and molecular weight may be controlled.
3. Determine how resin properties, fiberization, crosslinking, and pyrolysis parameters interact and define the optimum parameters for each of these with the goal of producing the optimum fiber.

INTRODUCTION

Carbon fibers have excellent physical properties, leading to their widespread use in high performance composite materials. However, their high electrical conductivity, while an advantage in some applications, is a distinct disadvantage in others.

The production of $C_xSi_yN_z$ fibers by the pyrolysis of suitable precursor resins of the polycarbosilazane type has been reported, both in the scientific and the patent literature. While the resultant shiny, black, amorphous fibers appear to have good physical properties, i.e. 1.9×10^5 psi tensile strength and 2.6×10^7 psi modulus, little else is known of their properties.

In order to determine if $C_xSi_yN_z$ fibers are a viable alternative to carbon fibers, considerable further information about their production and properties must be obtained. The present program represents preliminary efforts in that direction.

DISCUSSION

1. Fiber Extruder

Based on previous experience in these laboratories, a fiber extruder was designed. The operation of the design may be visualized by reference to Figure 1, a side view of the extruder.

The drive pulley (1) is powered by a main drive motor (not shown). A 1-16 screw (3) is locked to the drive shaft (2) by a key (5). Rotation of the pulley and drive shaft drives the 1-16 screw downward through the fixed nut (6). A 1/2-20 screw (7) with a removable piston (10) is threaded into the core of the 1-16 screw and restricted from rotation by a key (8). As the 1-16 screw is driven downward by the drive motor, the 1/2-20 screw is simultaneously withdrawn upward. The 1-16 screw advances downward 0.0625" per driveshaft revolution, while the 1/2-20 screw withdraws 0.0500". The net result is a 0.0125" per revolution piston advance.

By removing the heat shields (18), the main drive assembly (secured by four screws not shown), and withdrawing the 1/2-20 shaft key (8) the entire drive unit and piston can be removed from the extruder block. This permits manual loading of the resin in the melting cup (11).

Resin melting is accomplished by cartridge heaters (16) installed in the aluminum block (17). Temperature is maintained by a temperature controller unit (not shown) and thermocouples positioned in the melting pot and at the spinneret orifice. Hollow heat shields (18) thermally insulate the apparatus. A removable

socket head screw (15) secures the spinneret plate (14) and optional filters (13) at the base of the melting pot/extrusion cylinder cavity.

Figure 2 is a cross-sectional view of the unit (at Section AA in Figure 1). It illustrates positioning of the aluminum support beams (6) which span from just above the screw guides and key holder (4) to the 1-16 fixed nut (Figure 1). The gaps between beams allow access to the melting pot when the piston and drive unit are removed.

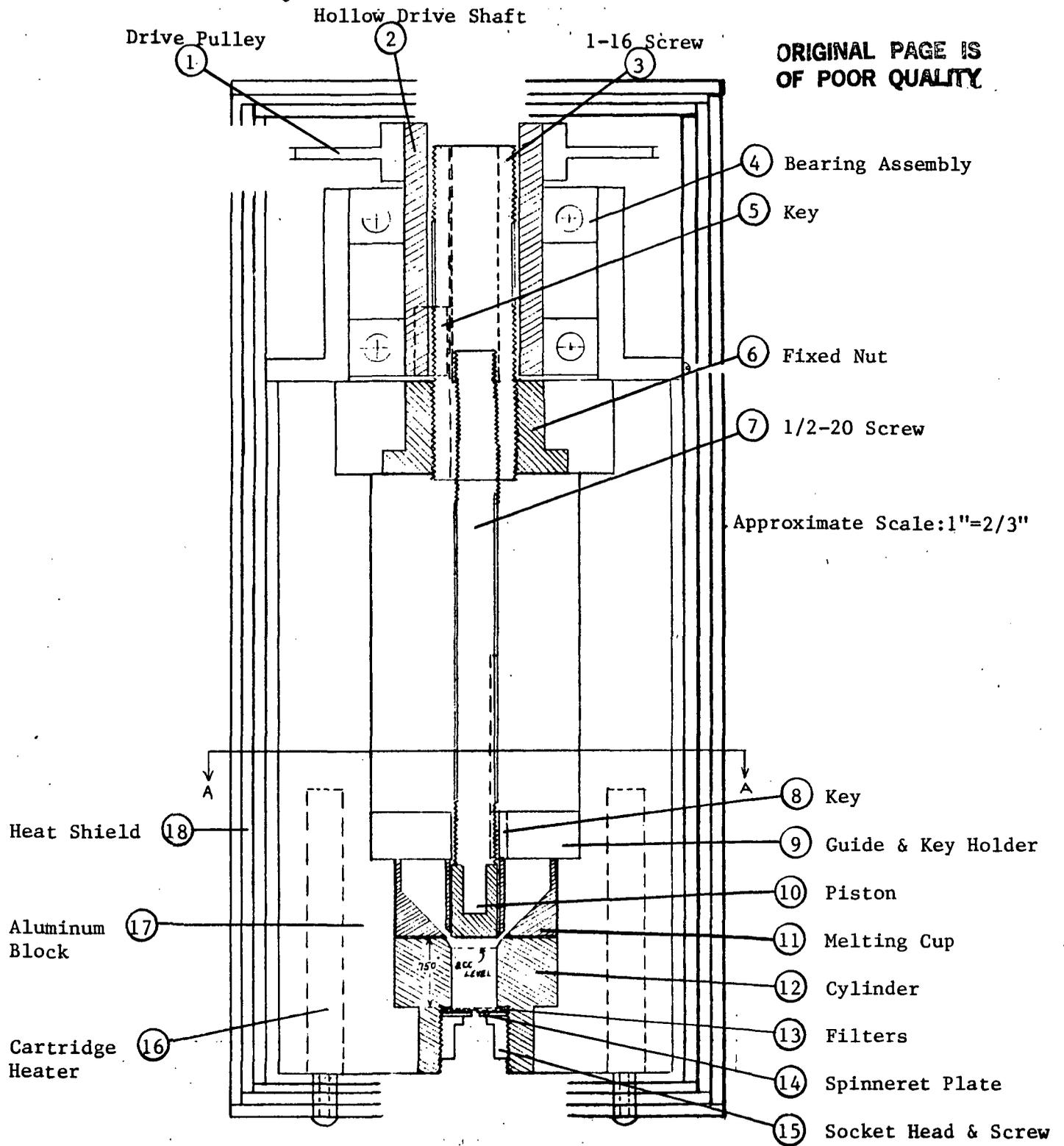


Figure 1. Extruder

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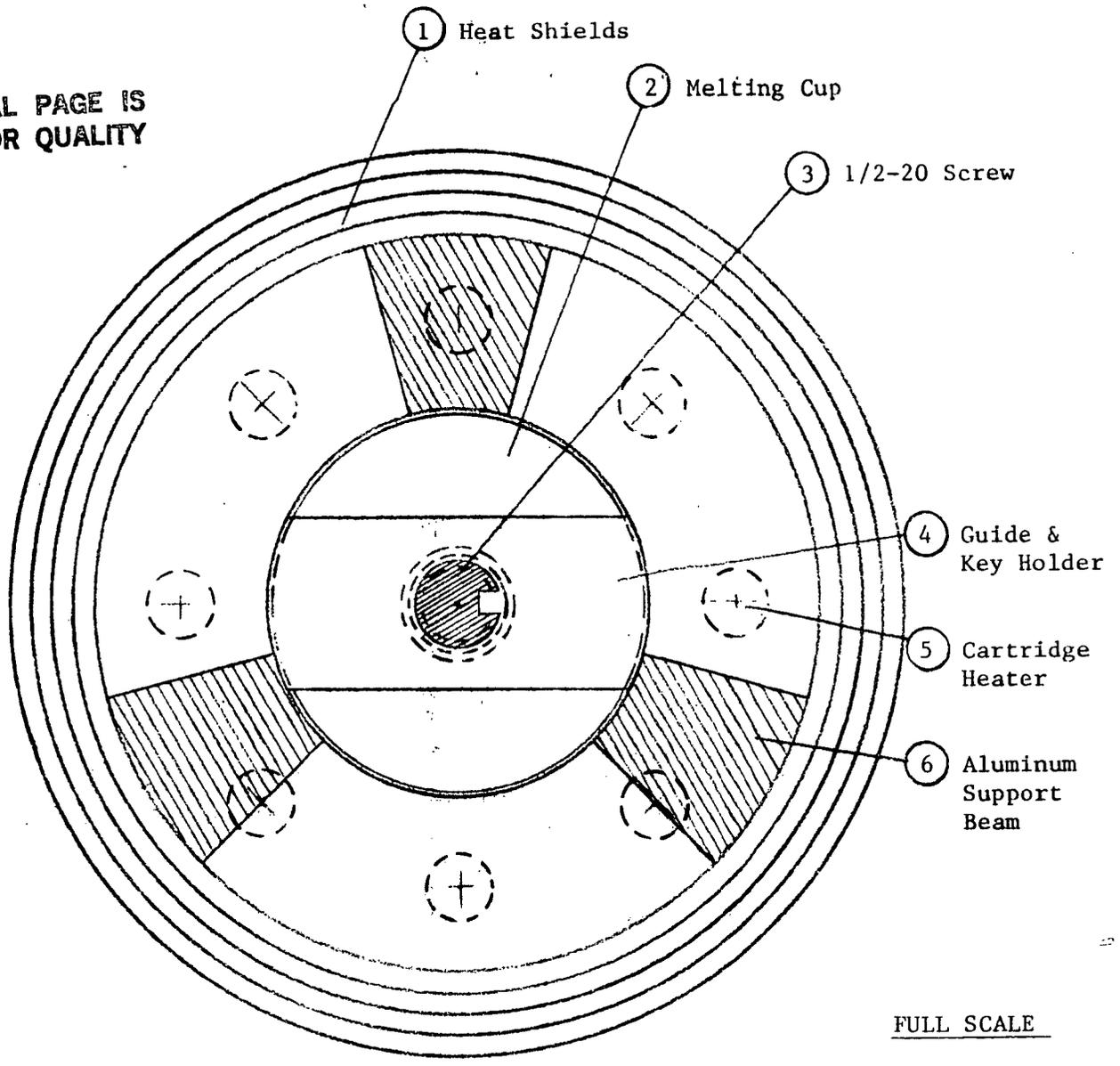
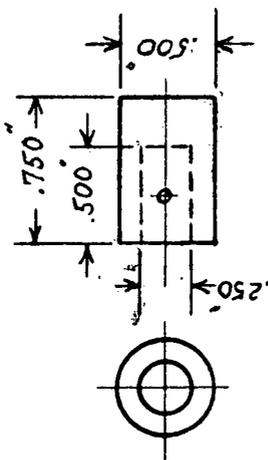
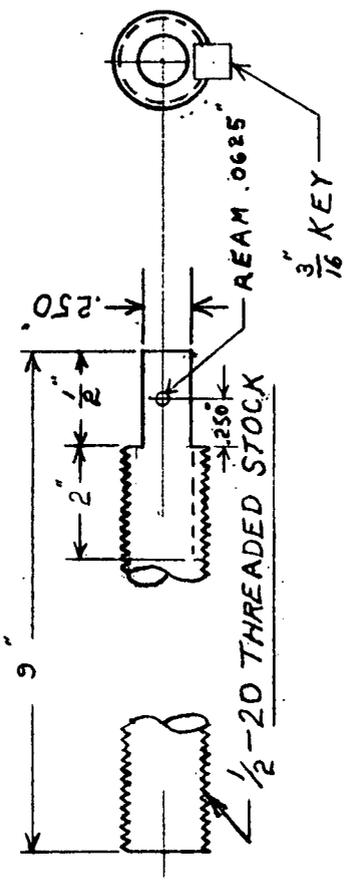


Figure 2. Cross-Section AA

Figures 3-15 provide detailed engineering drawings of the various subassemblies, as follows:

- Figure 3 - Differential screw and piston
- Figure 4 - Melting cup
- Figure 5 - Cylinder
- Figure 6 - Nut and holder
- Figure 7 - Lower guide and key holder
- Figure 8 - Body
- Figure 9 - Body
- Figure 10 - Bearing mount
- Figure 11 - Coupler assembly
- Figure 12 - Body - bottom view
- Figure 13 - Body - bottom view
- Figure 14 - Body - top view
- Figure 15 - Coupler, coupler sleeve and drive tube

Finally, Figures 16 and 17 depict the extruder in, respectively, assembled and disassembled states.



PISTON
STEEL

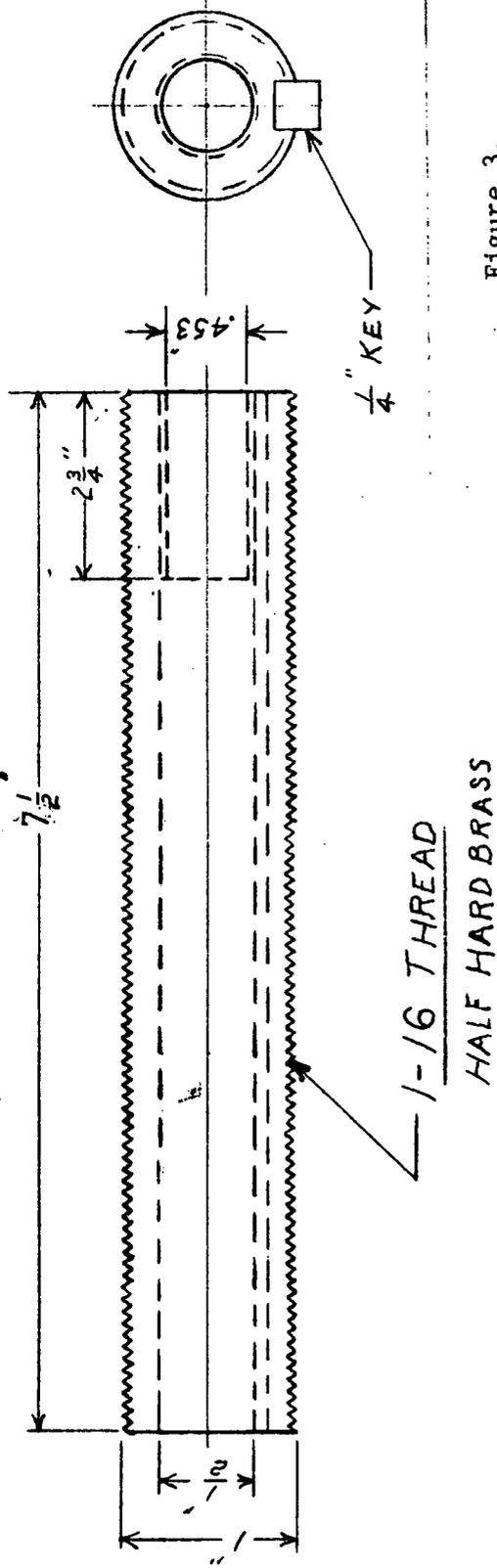


Figure 3.
Differential Screw
Full Scale

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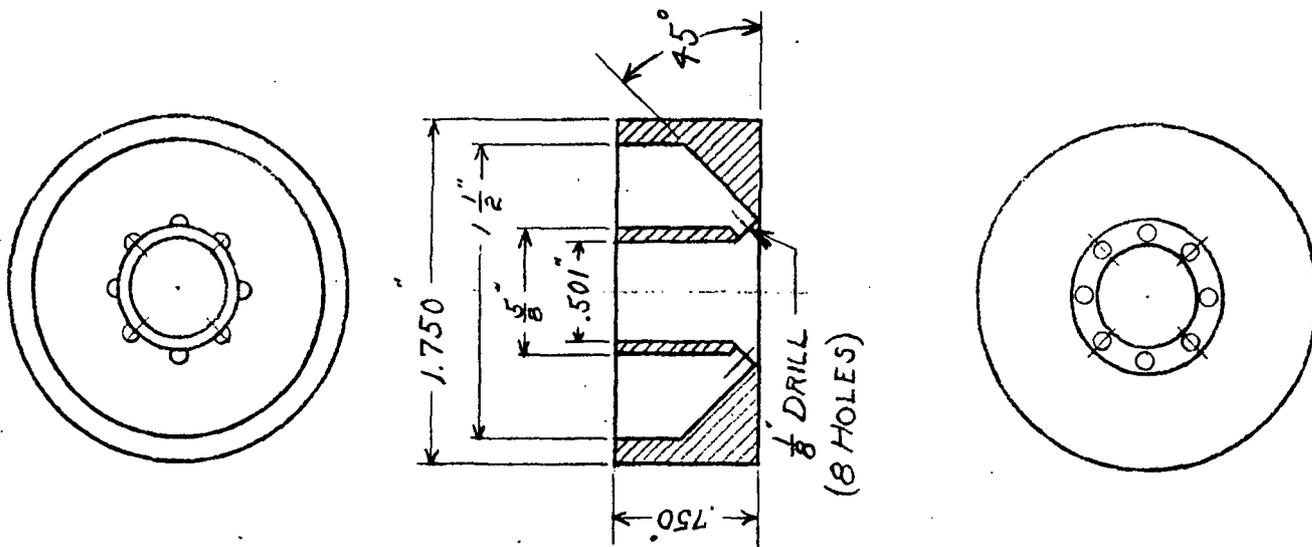


Figure 4.

Melting Cup

Full Scale

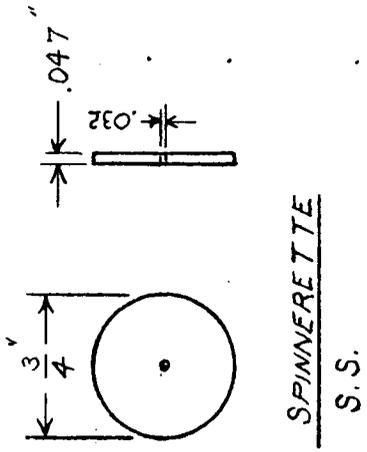
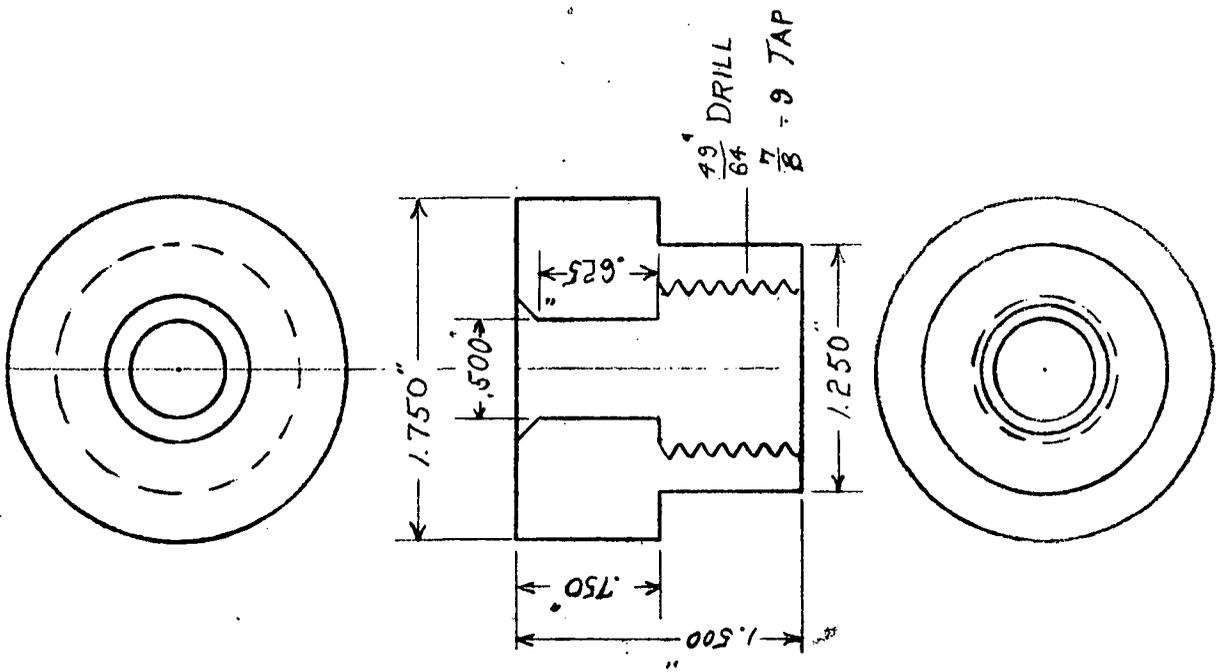


Figure 5.
Cylinder
Full Size

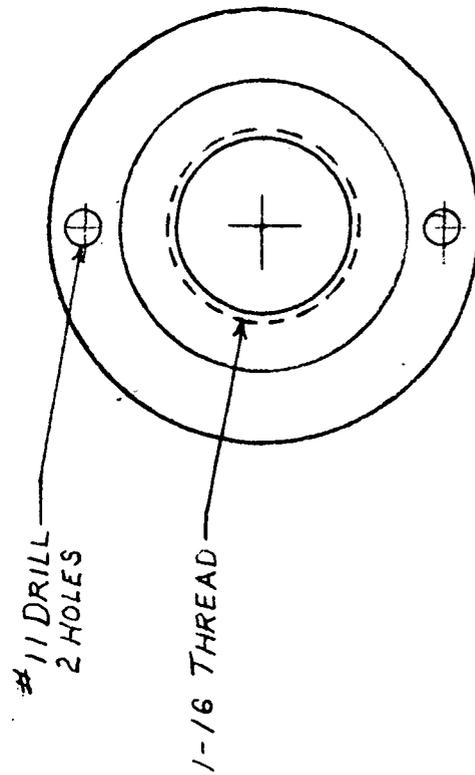
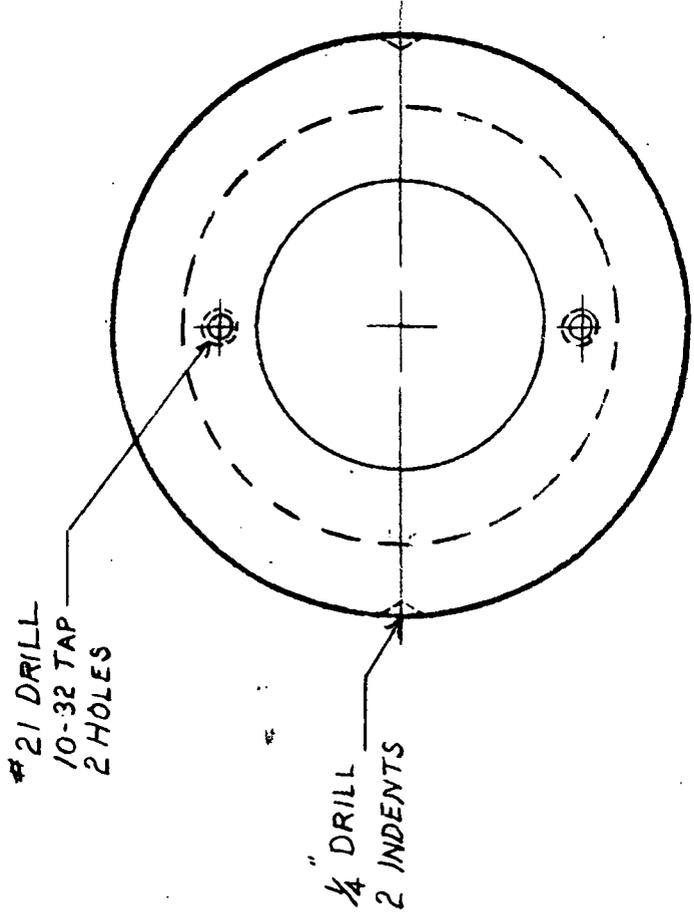
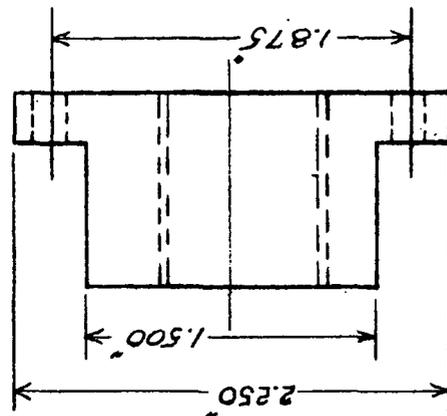
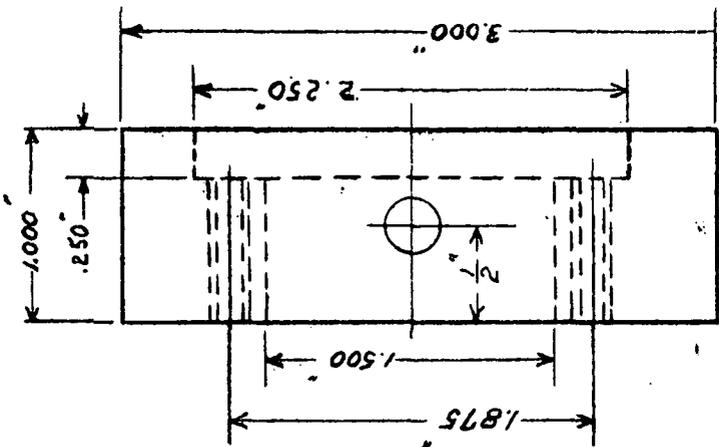
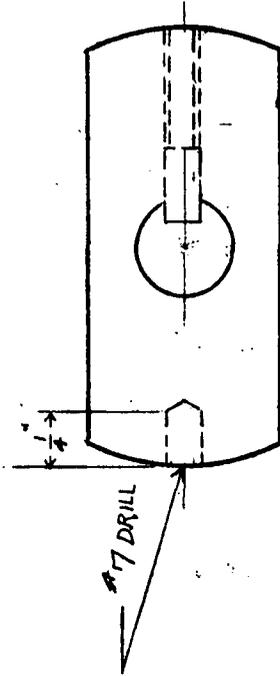
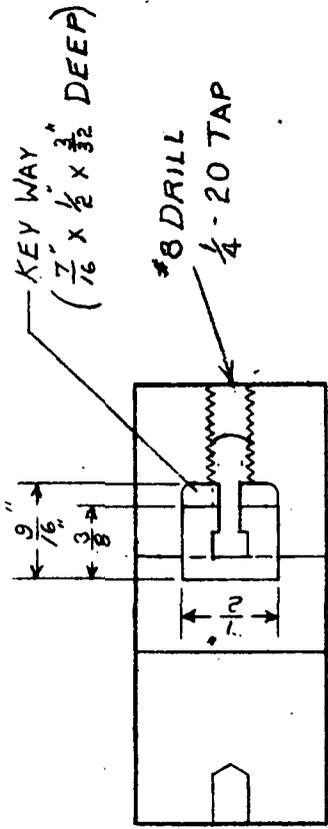


Figure 6.

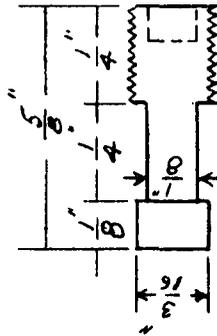
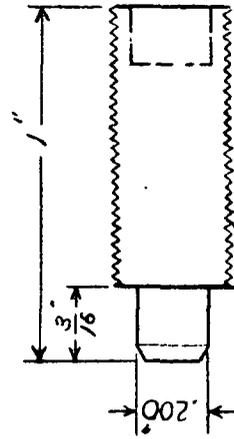
Nut and Holder
(Steel)

Full Size

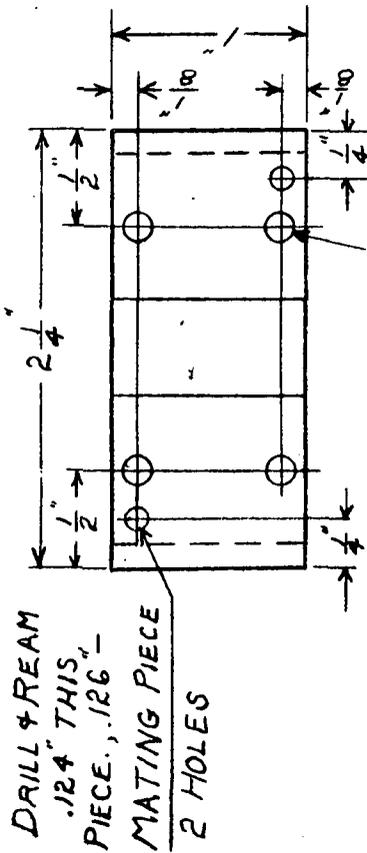
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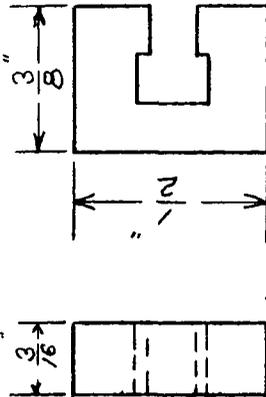
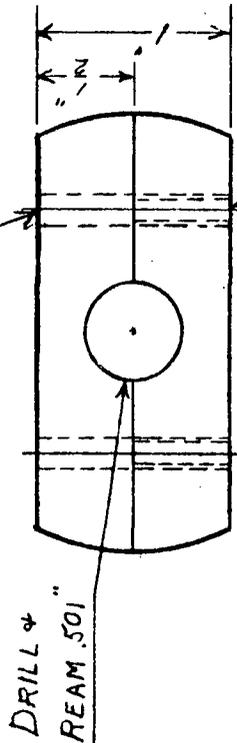
LOWER GUIDE & KEY HOLDER
A.L. FULL SCALE



KEY SCREW



#19 DRILL (4 HOLES)



BRASS KEY

Figure 7.

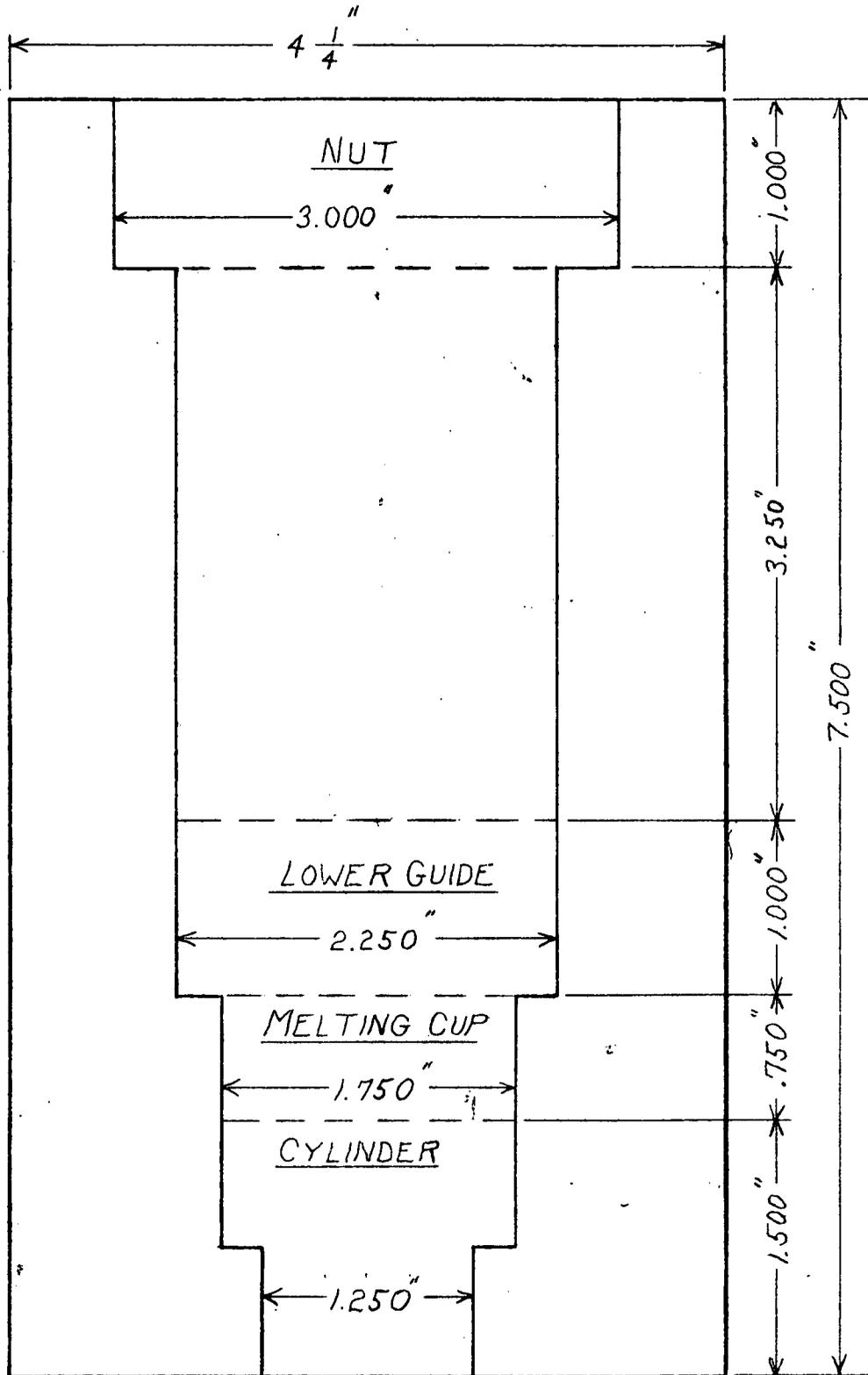


Figure 8.

Body

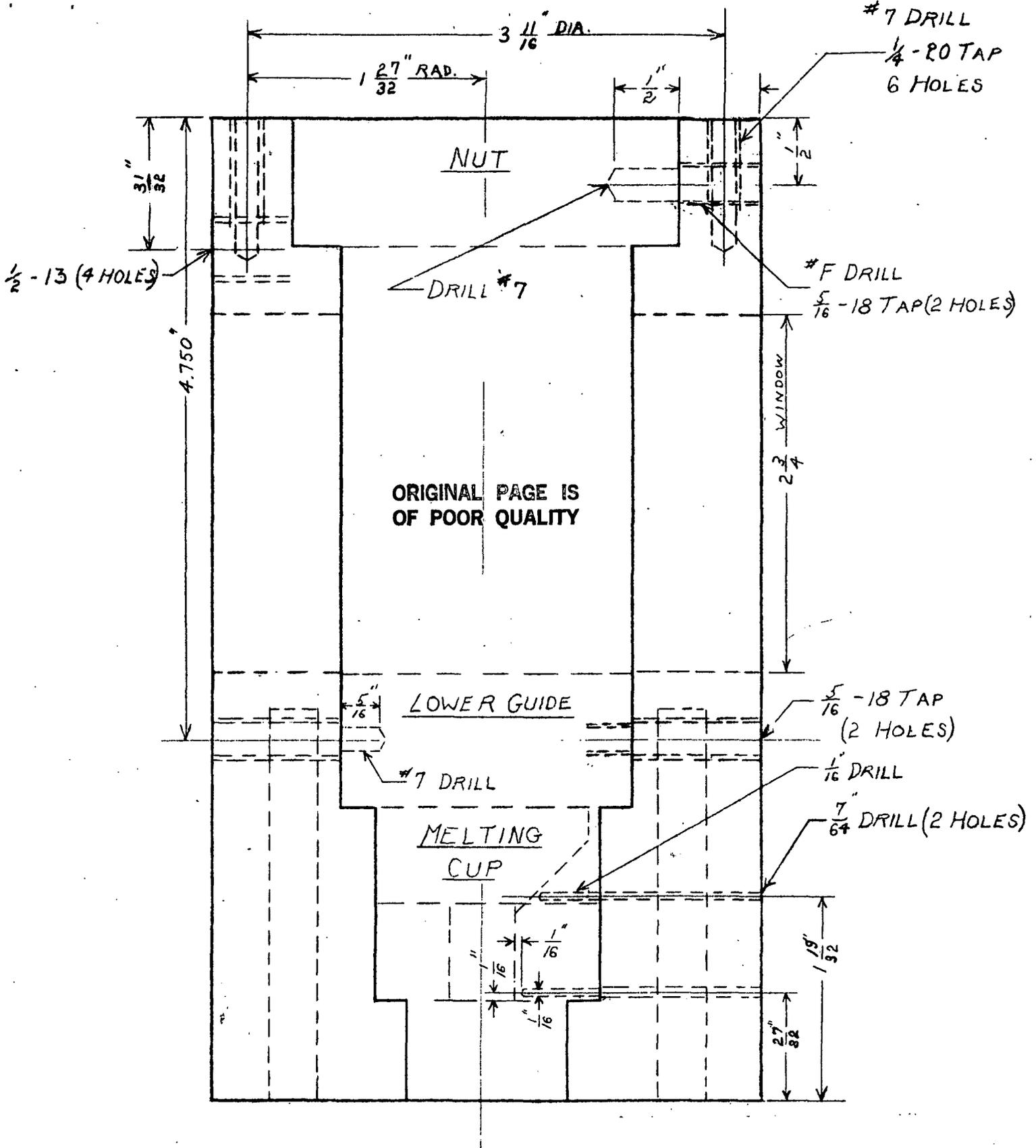


Figure 9.

Body

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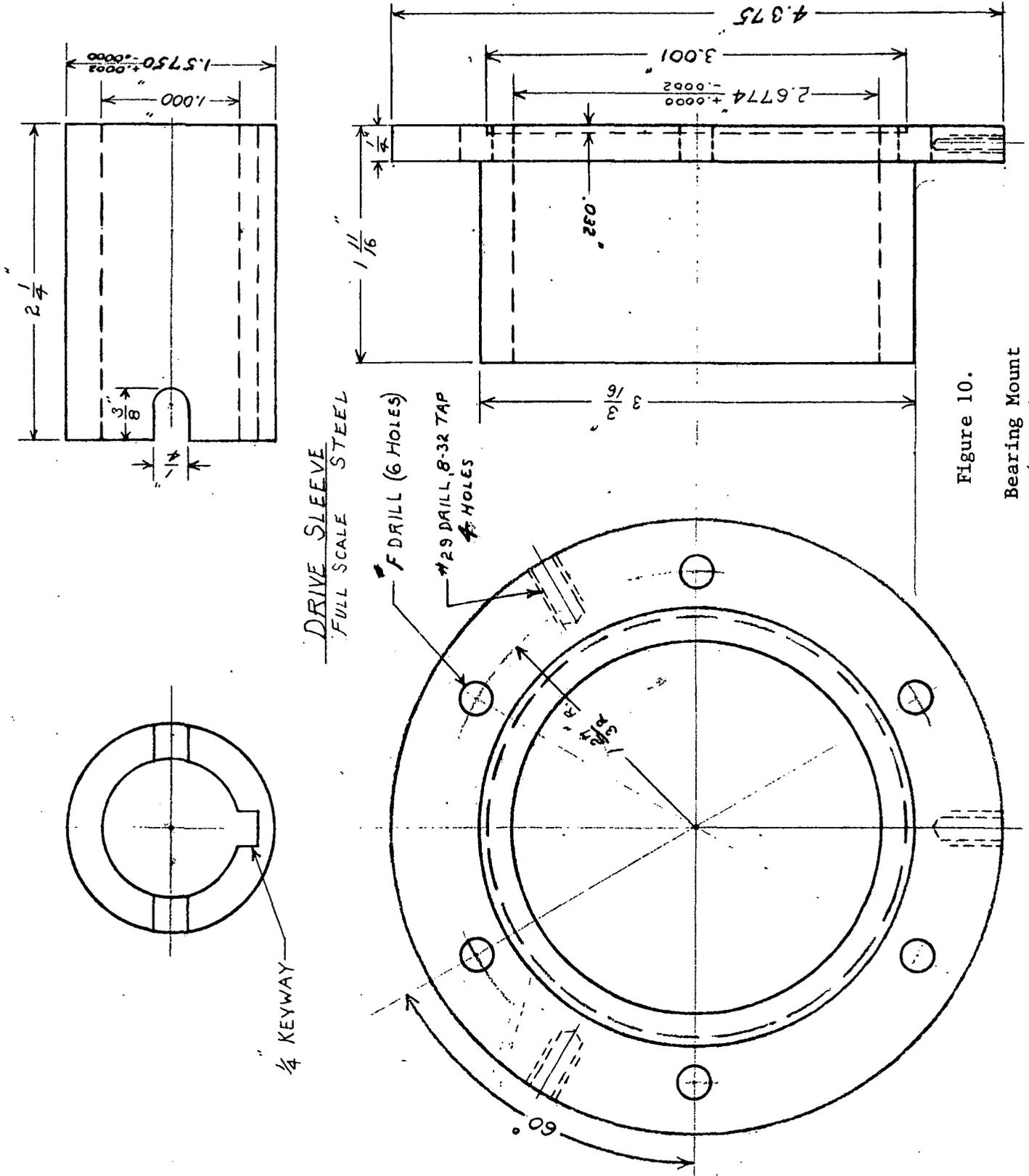
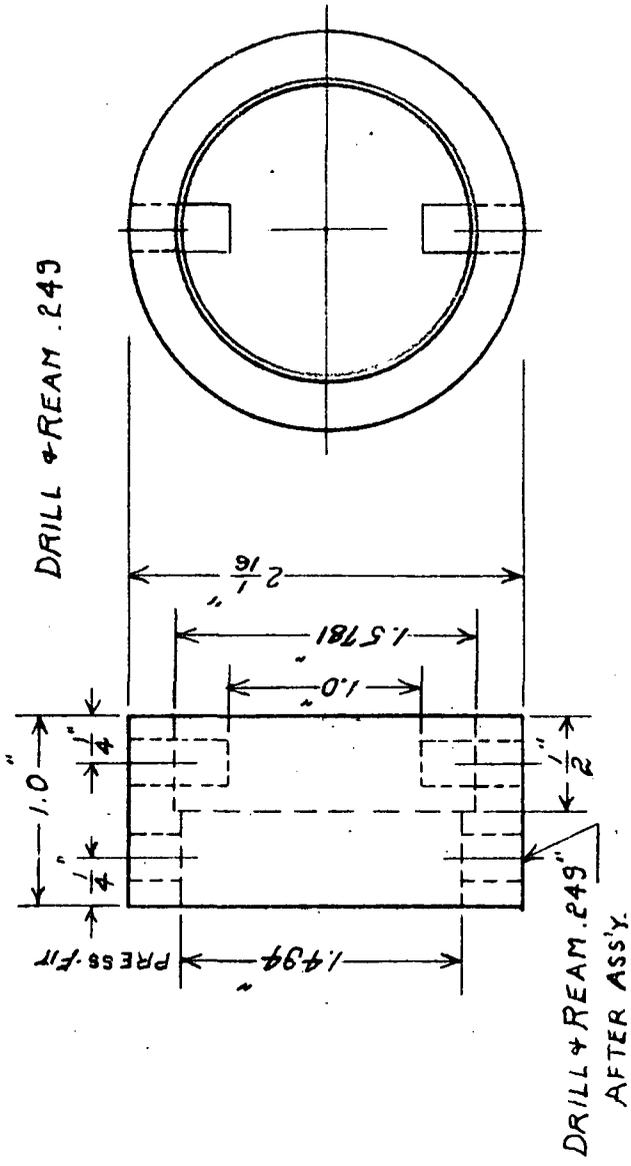


Figure 10.

Bearing Mount
(Steel)

Full Scale

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COUPLER SOCKET
STEEL 1:1

HOLD-KROME #15046

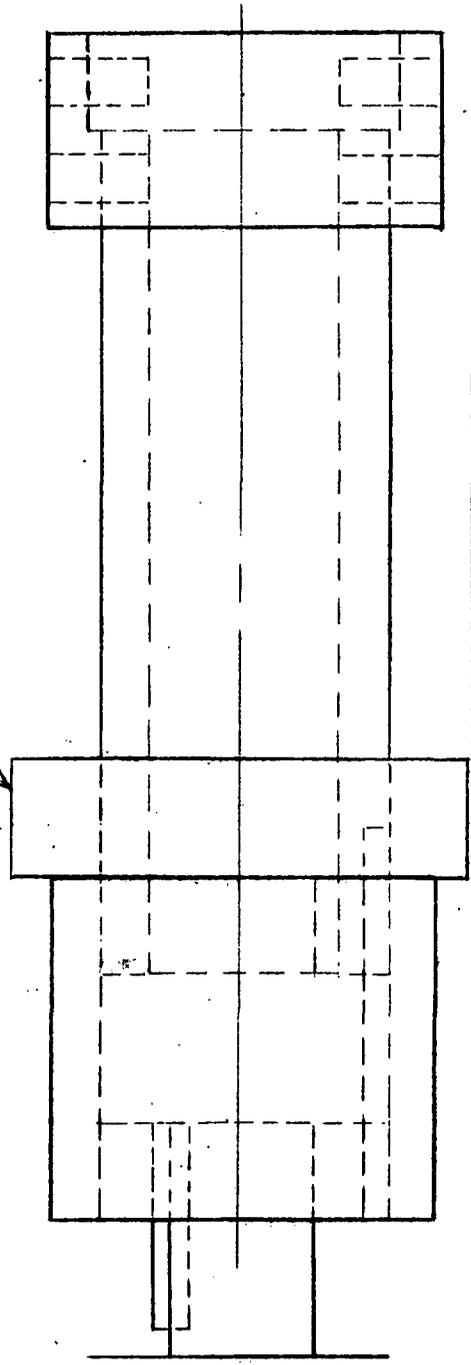


Figure 11.

Coupler Assembly

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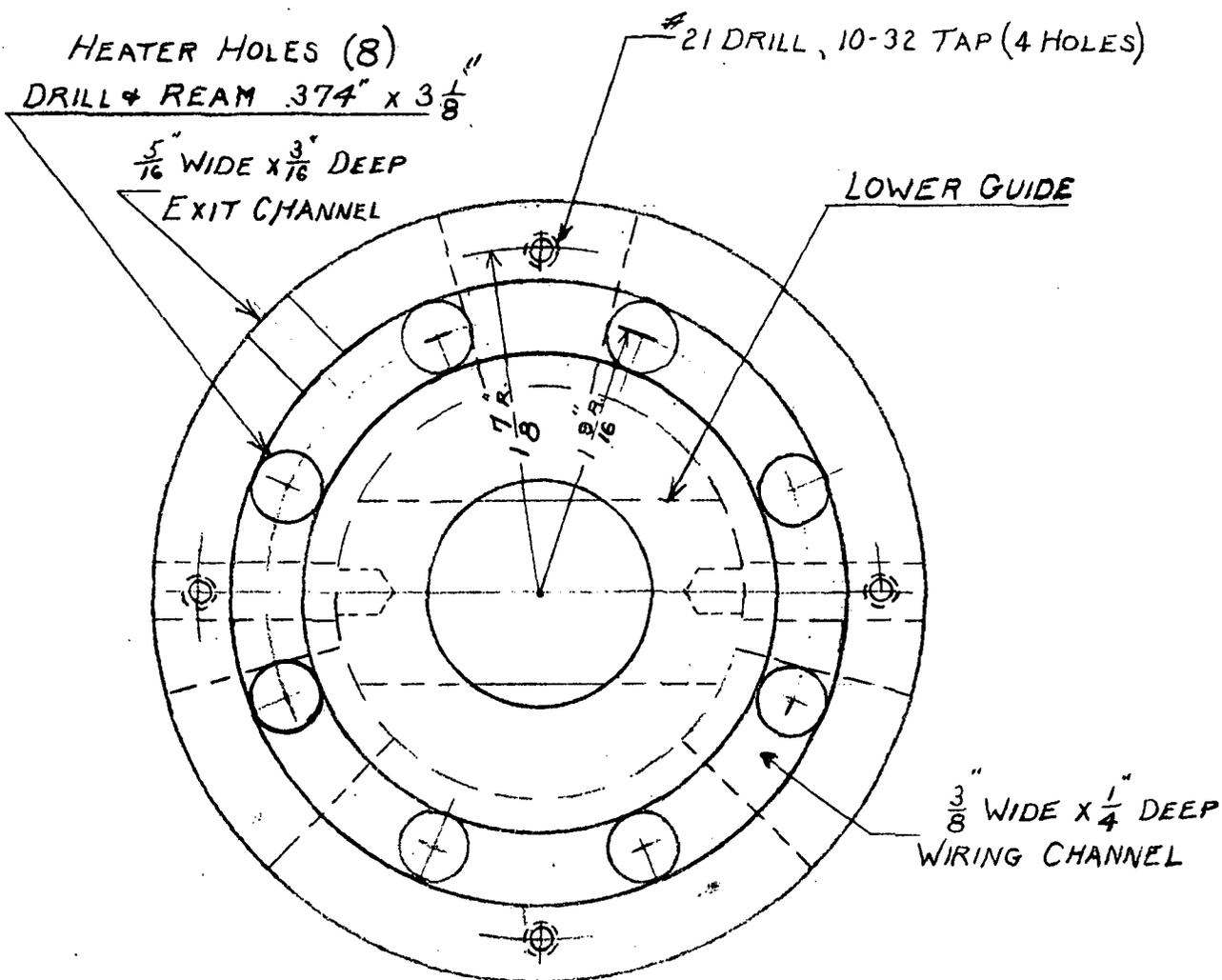


Figure 12.

Body

Bottom View
See Sheet "A" for Heater
Angular Location

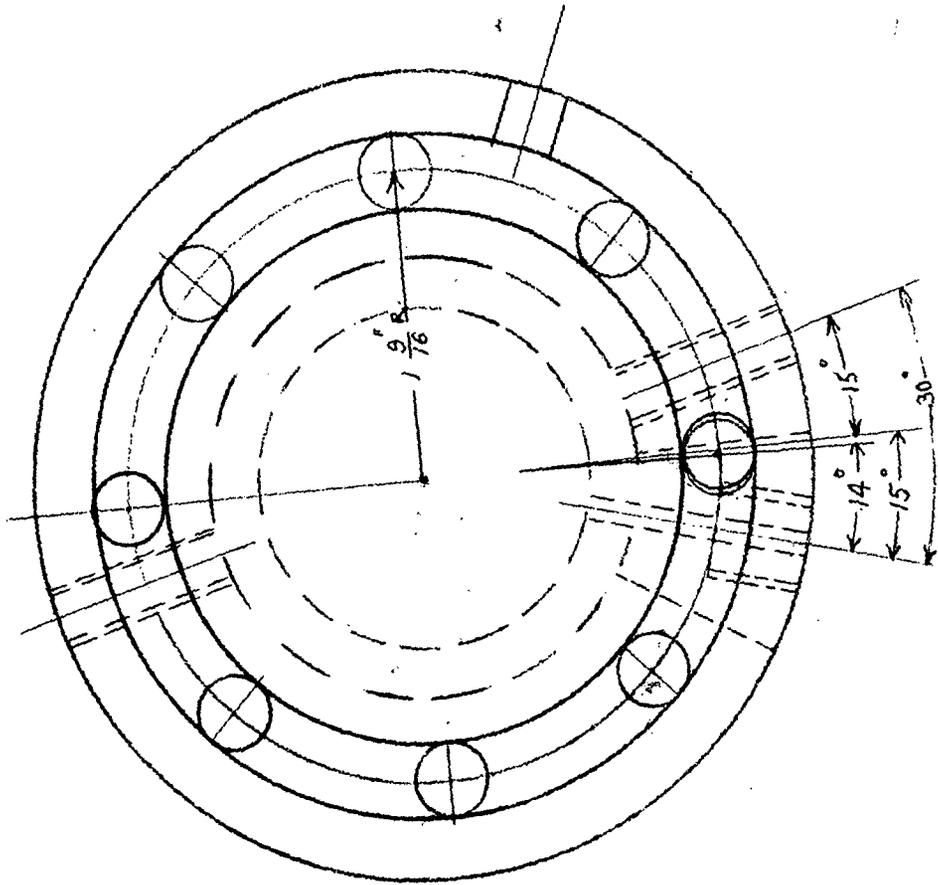


Figure 13.

Body

"Sheet A"
Bottom View

#8 DRILL x 1" DEEP
(8 HOLES)
 $\frac{1}{4}$ - 20 TAP x $\frac{3}{4}$

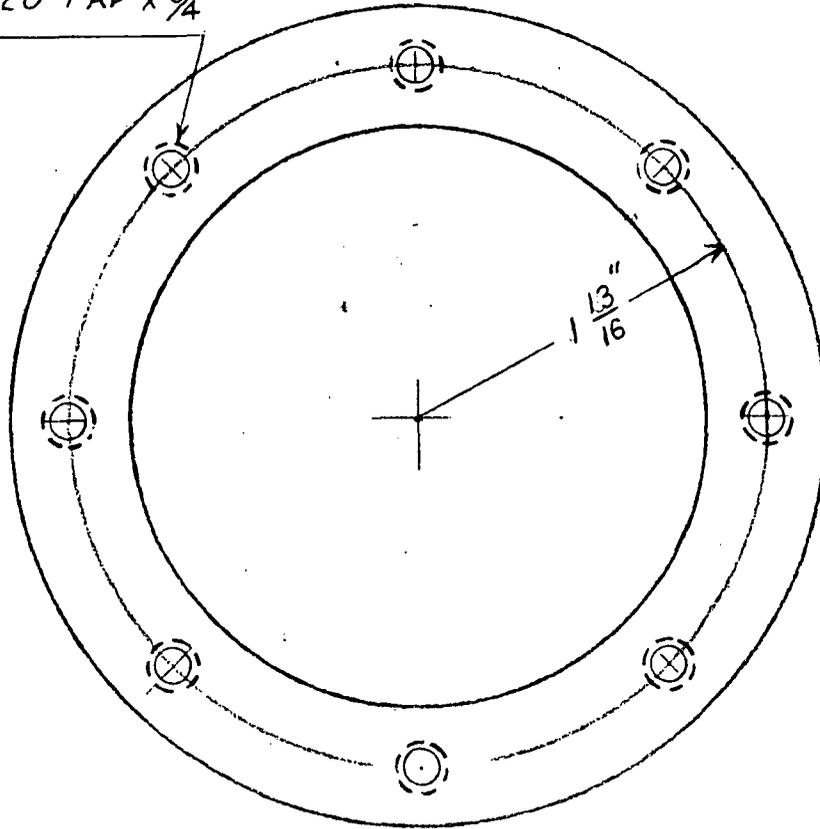


Figure 14.

Body

Top View

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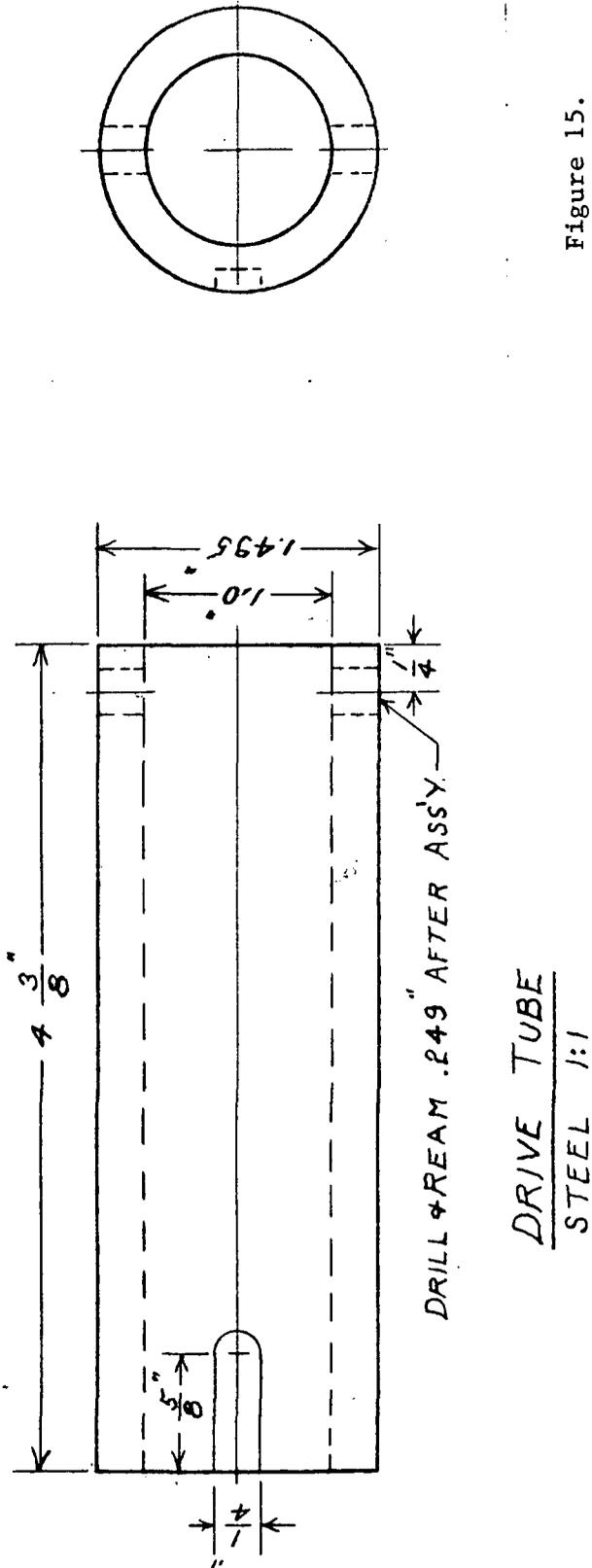
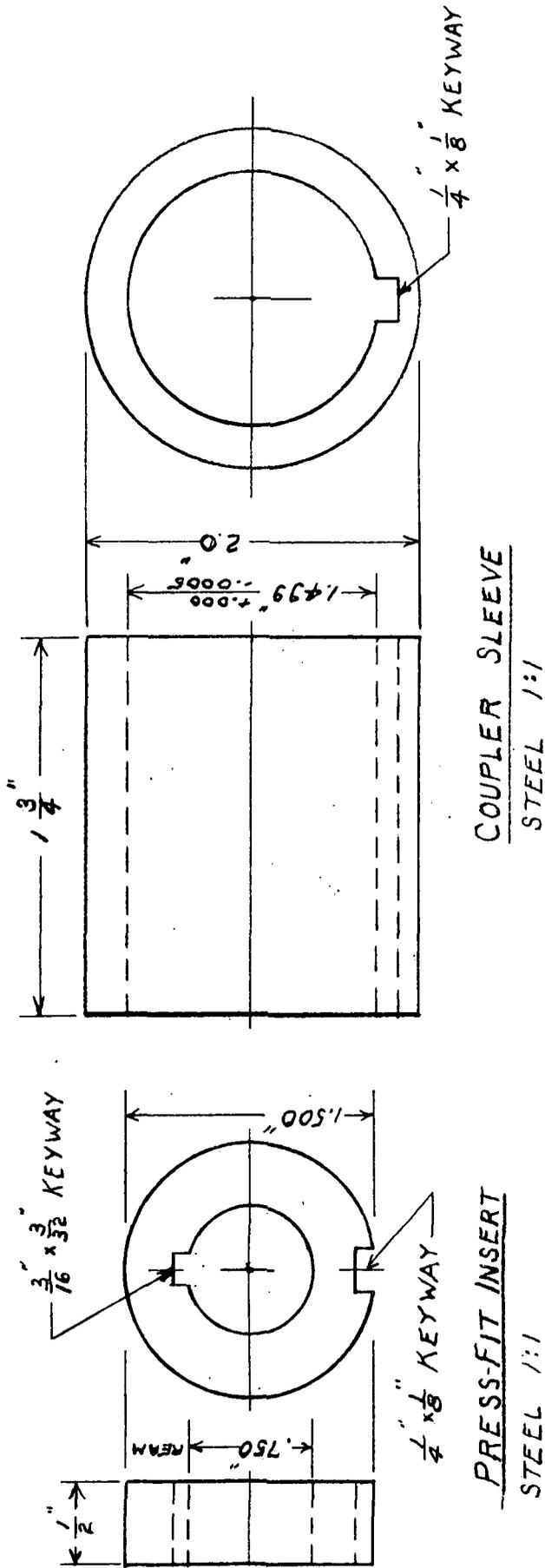


Figure 15.

Coupler

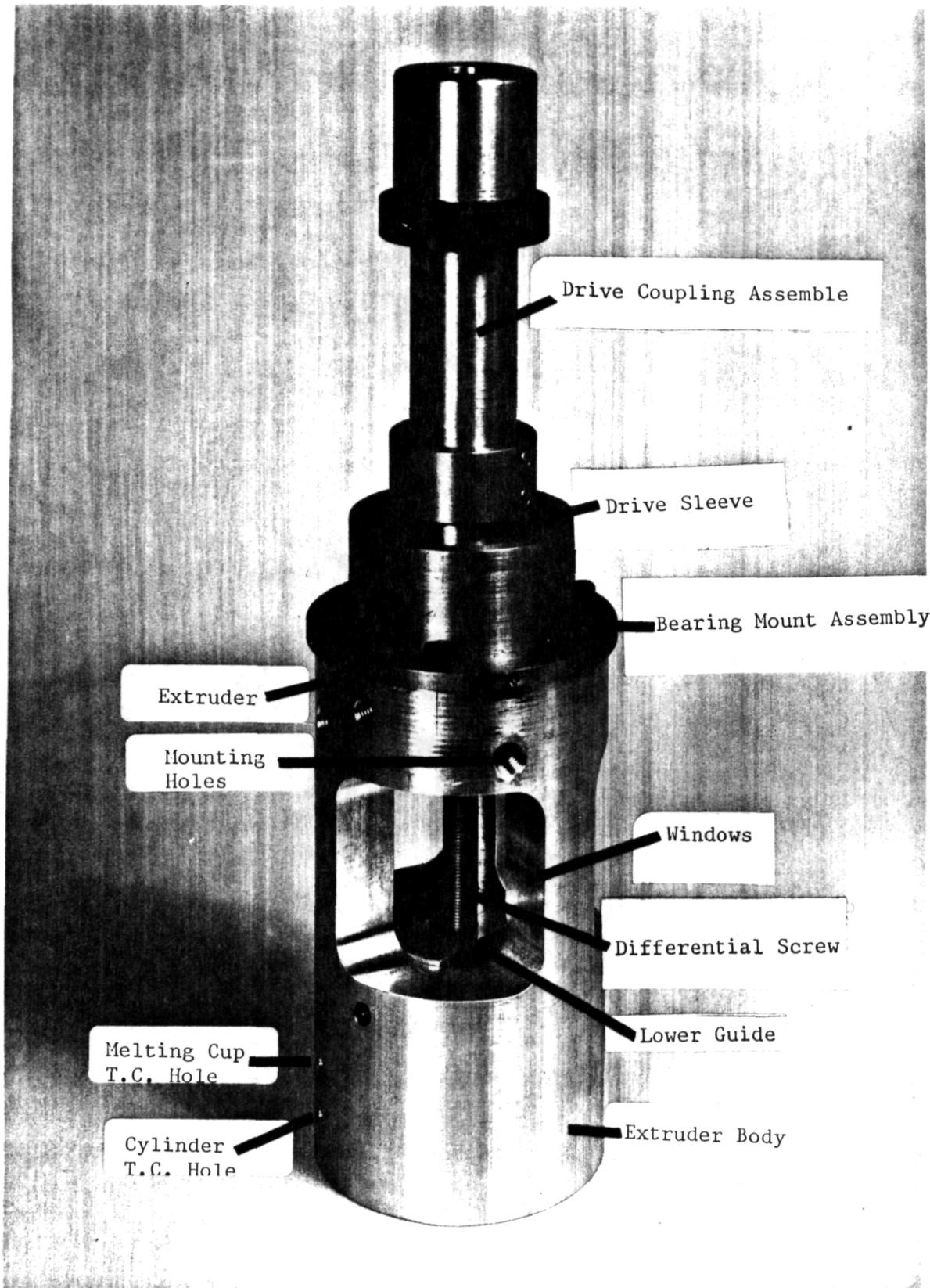


Figure 16.

Assembled Fiber Extruder

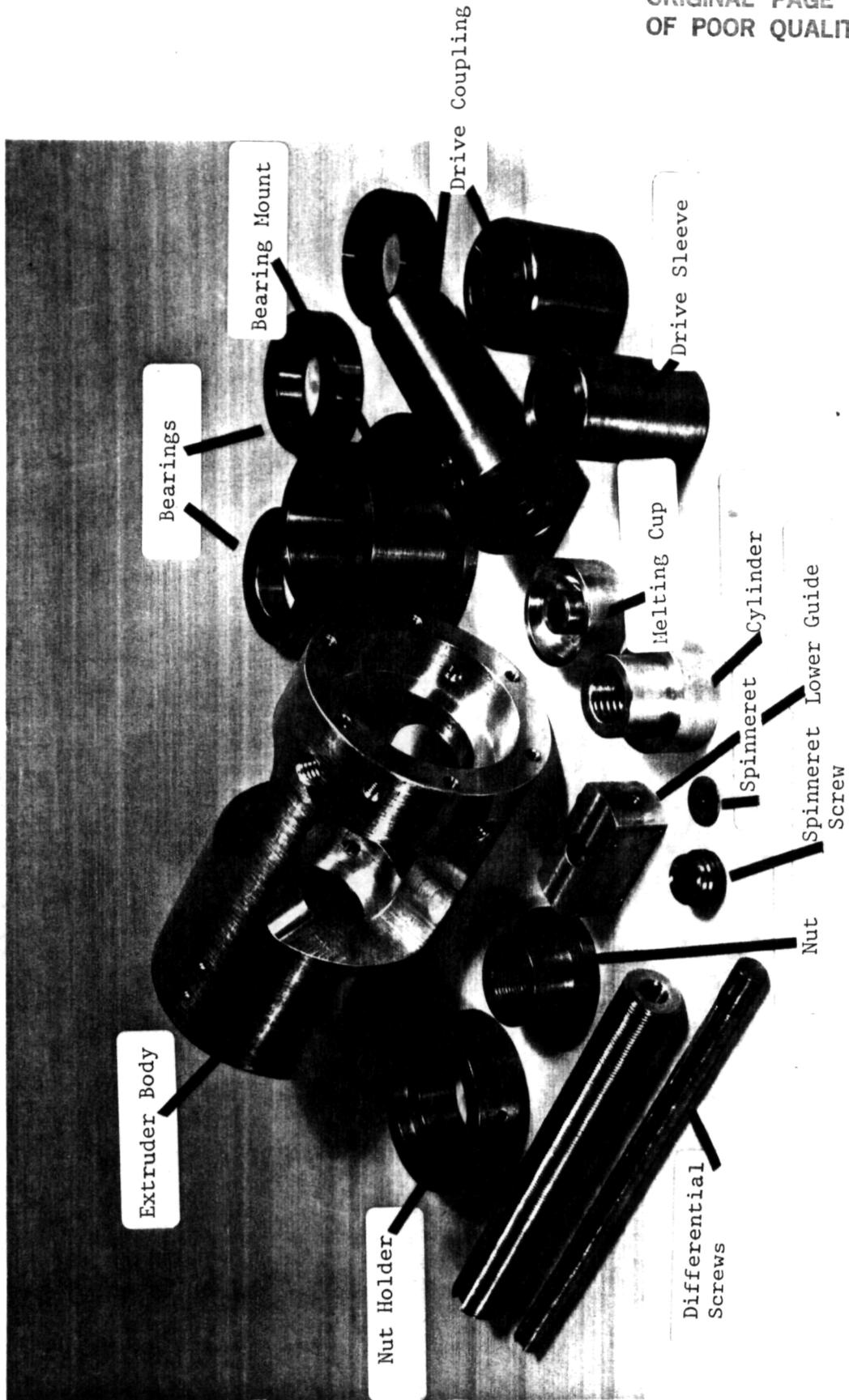


Figure 17.

Extruder Components

The extruder was driven by a 1/4 horsepower, 1750 rpm Graham DC motor with a variable speed (variable voltage) controller. An SM-cyclo double speed reducer was used to gear the motor output down in a 121:1 ratio. The system so fitted provided extrusion rates from 0.051 cc/min to 0.740 cc/min.

Heat was supplied to the extruder by eight 100 watt cartridge heaters in the main extruder body (see Figure 12). These were controlled by an Omega model 149 proportioning temperature controller. Temperature control of the extruder was found to be excellent, the maximum excursion from the control point being no more than 1^oF (either with or without the annular and top heat shields in place).

It was felt that a safety shut-off switch was necessary in order to prevent mechanical damage to the extruder. However, the compact design and the inaccessibility of the moving parts relating to position penetration made any kind of limit switch impossible. The problem was solved by installing a cam on the input shaft to trigger a count mechanism which would shut the unit off after a predetermined number of revolutions. By carefully calibrating the differential screw the counter prevents the piston from "bottoming out". In addition, the displayed count provides an exact indication of the piston position within the extrusion cylinder.

A 1/8 horsepower, 1750 rpm Graham DC motor with a variable speed control was utilized for the take-up function. This was coupled directly to a 11" diameter, 4" wide expanding contact wheel, upon which the fiber was wound. The entire take-up system was mounted on a rolling cartridge mount to permit traversing the take-up. This system provided take-up rates from 500 ft/min to 5,000 ft/min.

Spinneret plates were punched from 0.042" thick molybdenum and 0.046" stainless steel. Several plates were provided with 100 and 200 micron orifices via an electron beam process, while 400 and 800 micron orifices were produced by microdrilling.

Finally, the system was calibrated in terms of readily observable parameters, namely the armature voltages of the extruder and take-up motors. These voltages are good indicators of motor speed. Charts were prepared relating these two parameters in terms of their respective armature voltages for each of three fiber diameters, 15, 25 and 30 microns. The speed dependency of each motor as a function of armature voltage was determined. The volumetric rate of extrusion was then directly relatable to the extrusion motor speed and armature voltage through the piston cross-section area and the differential screw thread ratios and pitches. Similarly, the linear rate of take-up was relatable to the corresponding motor parameters through take-up wheel diameter. By implementing the armature voltages in the table, reasonable speeds for the extruder and the take-up can be achieved to produce fiber of a predetermined diameter.

A system evaluation was undertaken with polystyrene resin. A spinneret plate with a 0.032" orifice was installed. However, molten polystyrene resin did not flow freely from the melting cup into the extruder piston cavity. The problem apparently was caused by an air lock, and was alleviated by the installation of two vent pipes in the melting cup. Thereupon, once the optimum temperature had been defined, a full charge of polystyrene resin was extruded and wound onto the take-up wheel with no fiber breakage.

The entire extruder assembly, without heat shields but with the control panel, is depicted in Figure 19.

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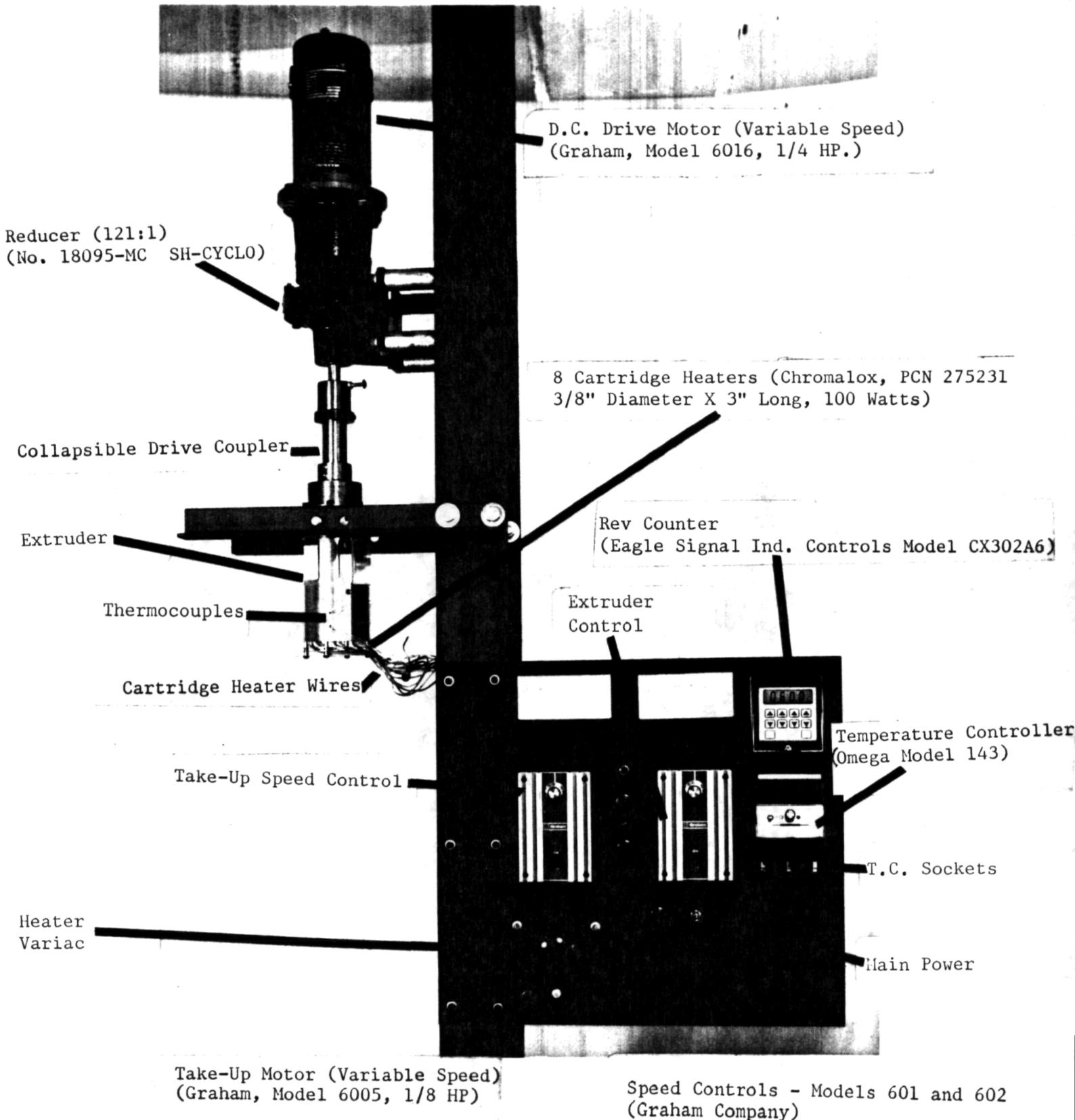


Figure 19.

Extruder Assembly With Control
Panel (Heat Shields Removed From
Extruder Body)

2. Spinning of Silicon Carbide - Silicon Nitride Precursor Fibers.

For preliminary trials with silicon carbide - silicon nitride precursor polymer the extruder was fitted with a 0.016" orificed spinneret plate.

Two small chips of the MW-3468 resin were placed in the extruder melting cup and the temperature was raised to 200°F. The resin softened but did not melt. The temperature was raised by 5° increments and allowed to stabilize for fifteen minutes at each setting. At 215°F the resin was fully melted but was too viscous to flow. The temperature was increased by 10° increments to 260°F at which point the resin slowly ran down the melting cup ports into the extruder piston cavity. At 300°F the resin flowed freely down the piston cavity walls onto the spinneret plate.

A new charge of resin was placed in the melting cup and melted at 300°F, filling the piston cavity. As extrusion began the resin dripped from the spinneret orifice, indicating the resin was too hot. The temperature was reduced to 225°F and allowed to stabilize. Extrusion at this temperature yielded a fiber that started to draw nicely, but broke frequently.

A new charge of resin was placed in the melting cup, melted at 274°F and extruded. The extruder motor voltage regulates extrusion speed and was set at 25 volts for this as well as the prior run. Take-up wheel speed was maintained at 240 feet per minute. Several hundred feet of 60 micron diameter fiber were drawn with a 210°F extruder temperature with occasional fiber breakage. The extruder voltage was cut to 20 volts and fiber diameter decreased to 30 microns. Occasional fiber breakage continued.

The extruder temperature was cut back to 200^oF and the fiber take-up speed was increased to 290 feet per minute. The resulting fiber measured 26 microns in diameter and several hundred feet were drawn with very few fiber breaks.

The drawn fiber was very brittle and hard to handle. Slight pressure caused the fiber to disintegrate.

Further fiberization runs demonstrated that the MW-3468 resin requires a melt temperature in the range of 200-210^oF for optimum fiberization. Two sets of conditions to produce ca. 30 micron fiber are given in Table 1.

Table 1.

<u>Extrusion</u>		<u>Take-up</u>		
<u>Del. rate</u>	<u>Armature potential</u>	<u>Speed</u>	<u>Armature potential</u>	<u>Extruder</u>
<u>cc/min</u>	<u>volts</u>	<u>ft/min</u>	<u>volts</u>	<u>Temperature, ^oF</u>
0.0612	10	275	4.5	200
0.117	18	478	8.0	210

Some fiber breakage was experienced. A few of the breaks appeared to be caused by "gelled" resin, rather than foreign material. It was decided to counter this problem with the use of filters on subsequent runs. Temperature control was excellent, usually within $\pm 1^{\circ}$ F of the control point. Speed control was satisfactory.

Initial attempts to spin fiber from a second resin shipment were unsuccessful due to a gelled component in the resin. At 225^oF, a temperature at which fiber was successfully drawn from the first resin sample, the resin exited the 0.032" spinneret orifice in spurts of grainy, bubble impregnated rods, 0.032" in diameter and approximately 0.50" long (see photograph). The gelled resin's high viscosity caused high resistance to extrusion which deformed the threads of the extruder main drive screw. A new screw with more thread surface contact was constructed to improve the durability of the extruder.

The extruder temperature was slowly increased to find the melting point of the resin. At 350^oF resin was observed dripping from the spinneret orifice. Within a few minutes, all the nongelled resin had dripped out of the piston cylinder and only the unmelted gelled resin remained. The temperature was increased to 400^oF and extrusion was attempted. Once again, the resin exited the orifice as grainy, bubble-filled rods. It became apparent that the resin would have to be filtered prior to extrusion to separate the gelled component.

A portion of the remaining resin sample was filtered directly into the extrusion cylinder through an 0.008" mesh screen. Filtration was done under an inert nitrogen atmosphere at 375^oF. The gel remaining on the screen, about 25% of the initial amount, was pale yellow, grainy and bubble filled. A section of hollow glass tube remained on the screen as well, apparently a stirring rod tip which broke off during resin manufacture.

The filtrate resin was dark amber, clean and homogeneous in appearance. Extrusion at 225^oF yielded resin that drew into fiber smoothly with only occasional fiber breakage. Twenty-five to thirty micron diameter fiber was

drawn continuously in two to three minute periods several times. Two pirns of 2000 to 3000 feet each were drawn.

A third batch of resin from Huntsville was filtered through an 0.008" mesh screen at 375^oF under an inert atmosphere. Fiberization was unsuccessful, however, as the resin seemed too weak to draw. It was easily started by hand drawing from the spinneret orifice, but drew down in diameter quickly and broke before reaching the take-up wheel. The limited amount of resin after filtration made it difficult to determine the nature of the fiberization problem.

Half of the remaining resin was filtered and drawn into fiber. It drew fairly easily but the limited amount of resin after filtration yielded only a few hundred feet of fiber, approximately 40 microns in diameter.

3. Crosslinking Studies

Preliminary crosslinking studies were conducted with the 26 micron fiber which was obtained at an extruder temperature of 200^oF and a take-up rate of 290 ft/min from the first batch of polymer.

One sample was placed in a desiccator at 100% relative humidity (RH) while another sample was placed in a 0% RH desiccator. After five days the samples were compared. The 100% RH exposed fiber seemed slightly less brittle than the 0% RH exposed fiber. The 100% RH sample desiccator was placed in an oven at 60^oC to foster fiber crosslinking. Examination after 24 hours showed increased fiber flexibility and improved tolerance to pressure.

These results prompted a comparison of resin melted in a 40% RH room atmosphere with resin melted in a 0% RH nitrogen atmosphere. Both samples had the same degree of brittleness when cooled. These results led to the conclusion that there appeared to be no advantage to drawing the fiber in an inert atmosphere. At this point the planned construction of an inert gas fiberization cabinet was abandoned, and all fiberization studies were conducted at ambient humidity conditions.

As already indicated, fiberization studies with the second batch of resin yielded two pirns of 2,000 - 3,000 feet each. The first pirn was placed in an oven at 75^oC (165^oF), 100% relative humidity to crosslink the fiber. Examination after 40 hours exposure indicated that the oven temperature was too high, as the fiber had become tacky and had agglomerated into a multi-fiber mass. The second pirn was crosslinked at 50^oC (122^oF), 100% relative humidity. Daily examination indicated increasing tensile strength and decreasing brittleness.

To determine if a fiber was fully crosslinked, an individual fiber was suspended across a channel in a metal block. The fiber was observed as the block was heated. When the fiber softened, it sagged, indicating the melting point. After 65 hours at 50°C, 100% relative humidity, the fiber softened at 400°C. After 90 hours exposure, the fiber withstood 600°C, at which point the aluminum block supporting the fiber began to soften and blister.

To counter this problem a high temperature melting point device was set up using an induction heater to evaluate hydrolyzed fiber and to determine whether it had been crosslinked sufficiently to sustain pyrolysis temperatures without intolerable deformation. Eight short fibers were suspended over a 5/8" channel in a one inch graphite block. A quartz tube housed the block during the heating process which was performed under an inert atmosphere. The fiber, which had been exposed to 50°C, 100% relative humidity for nine days, was heated slowly. At approximately 800°C (block temperature) the fiber began to curl. Examination of the fiber in contact with the block revealed a darkening in color with a tapering color density gradient toward the cooler suspended portion. The fiber had been pyrolyzed without melting, indicating a high degree of crosslinking. The nine day hydrolysis period was probably more exposure than was necessary, but budgetary constraints limited further evaluation of crosslinking parameters.

4. Pyrolysis Studies

Pyrolysis studies were conducted with a Fisher No. 472 furnace. This was modified with two vacuum sphere assemblies, one at each end, which made it possible to place the fibers under suitable tension in a controlled vacuum/atmosphere. The furnace so modified is depicted in Figure 20.

A trial run found the temperature controller to be malfunctioning, but manual control proved adequate for our experiments. The temperature profile of the 8" heat zone was examined at 750°C with the aluminum combustion tube in place. The half profile is outlined at one inch intervals below:

Thermocouple Distance From

Center of Heat Zone	0	1"	2"	3"	4"	5"
Temperature (Degrees C)	750	745	733	707	653	568

Considering the 100°C difference from center to either end, the center temperature of the furnace was run to 1000°C to assure fiber pyrolysis over the entire 8" heat zone.

A bundle of approximately 40 of the hydrolyzed fibers, 12" in length, was placed on a molybdenum fiber guide tray and pyrolyzed in the high temperature furnace under an inert nitrogen atmosphere. No tension was applied to the fibers. The temperature was slowly increased from 600°C to 1000°C over a three hour period. Little shrinkage or curling was apparent in the pyrolyzed fiber which was shiny black in appearance. Clear crystals were apparent on the surface of the fibers in random positioning (Figure 21).

A second bundle of hydrolyzed fiber was prepared for pyrolysis. Tungsten wire, 0.002" in diameter, was tied around each end of the 12" fiber bundle to

facilitate tensioning of the short fibers during pyrolysis. The entire bundle was tensioned as a whole in this first experiment because the brittleness of the fibers made individual handling very difficult. A steel machine nut weighing approximately 1.3 grams was attached to the tungsten wire on one end of the fiber bundle and the wire on the other end was secured to a fiber guide. The weighed end was suspended over a pulley in the guide system, thus positioning the fibers within the heat zone while maintaining them under tension (Figure 22). Fiber shrinkage due to pyrolysis was monitored by following the height of the suspended nut with a cathetometer.

During initial heating the fiber expanded approximately 0.5 centimeters. The fiber began to shrink at a center temperature of approximately 650°C and continued to do so at a fairly constant rate as the temperature approached 900°C. At 900°C the rate of shrinkage decreased, but shrinkage continued as pyrolysis extended to the material in the heating zone boundaries. Total fiber shrinkage was approximately 3.5 centimeters at the 1000°C shutdown point. Microscopic examination revealed a 20% decrease in fiber diameter accompanying pyrolysis; 25 to 30 micron diameter fibers decreased to 20 to 24 microns. This examination also showed crystals present on the straight metallic black fiber (Figure 23).

A second attempt to pyrolyze a fiber bundle under tension was interrupted by a break in the fiber at 830°C. In addition to removing tension, the break caused the fiber bundle to move partially out of the heat zone and removed the tension. As a result, only about 4" of the fiber bundle was fully pyrolyzed.

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Helium Inlet

T.C.

Combustion
Tube End

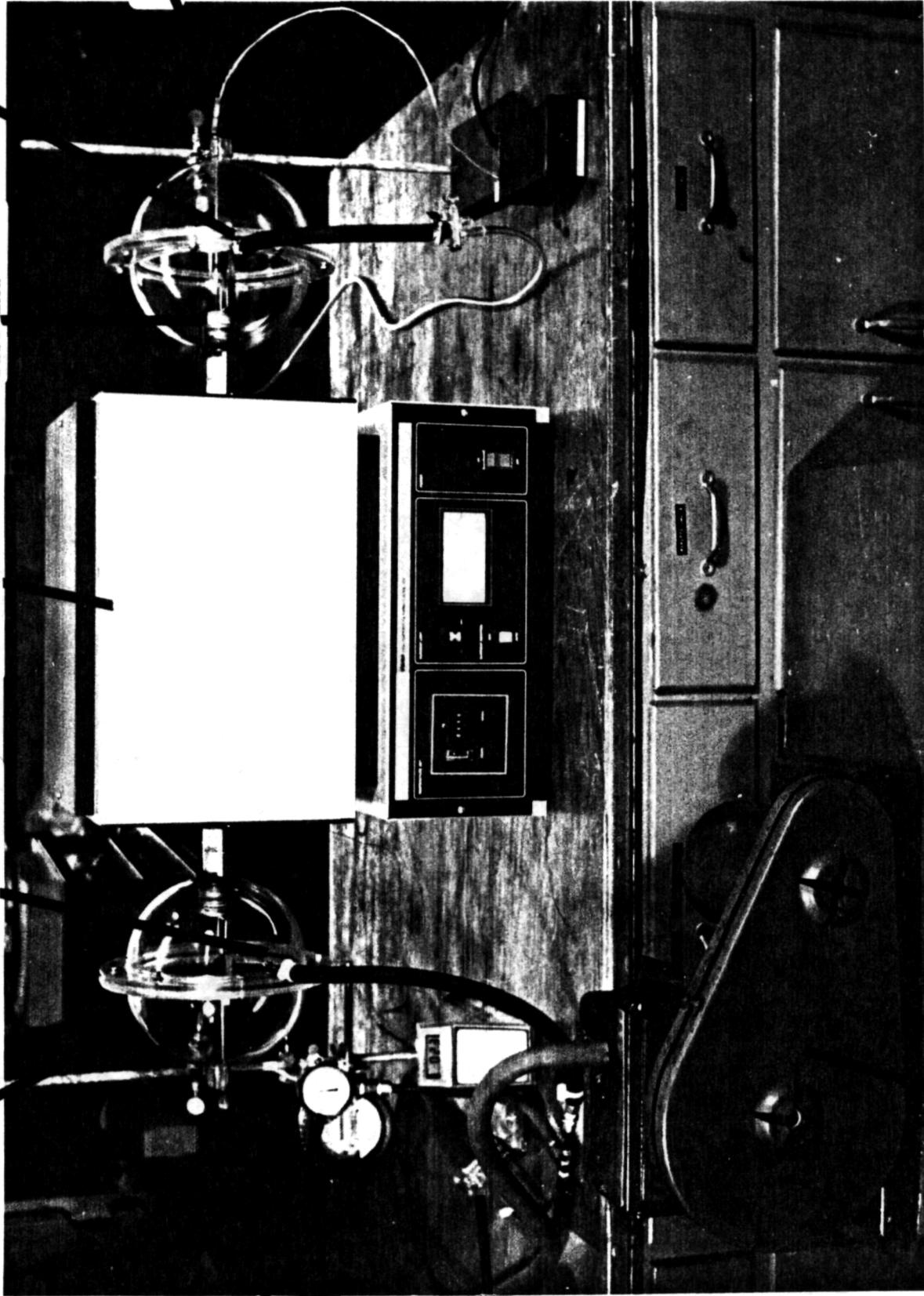
Furnace
(Fisher #472)

Vacuum
Port

Spherical Termination for Combustion Tube

Vacuum and
Positive
Pressure
Gauge

Vacuum Shut-Off
Valve



Vacuum
Pump

Figure 20.

High Temperature Furnace Vacuum
Sphere Assembly

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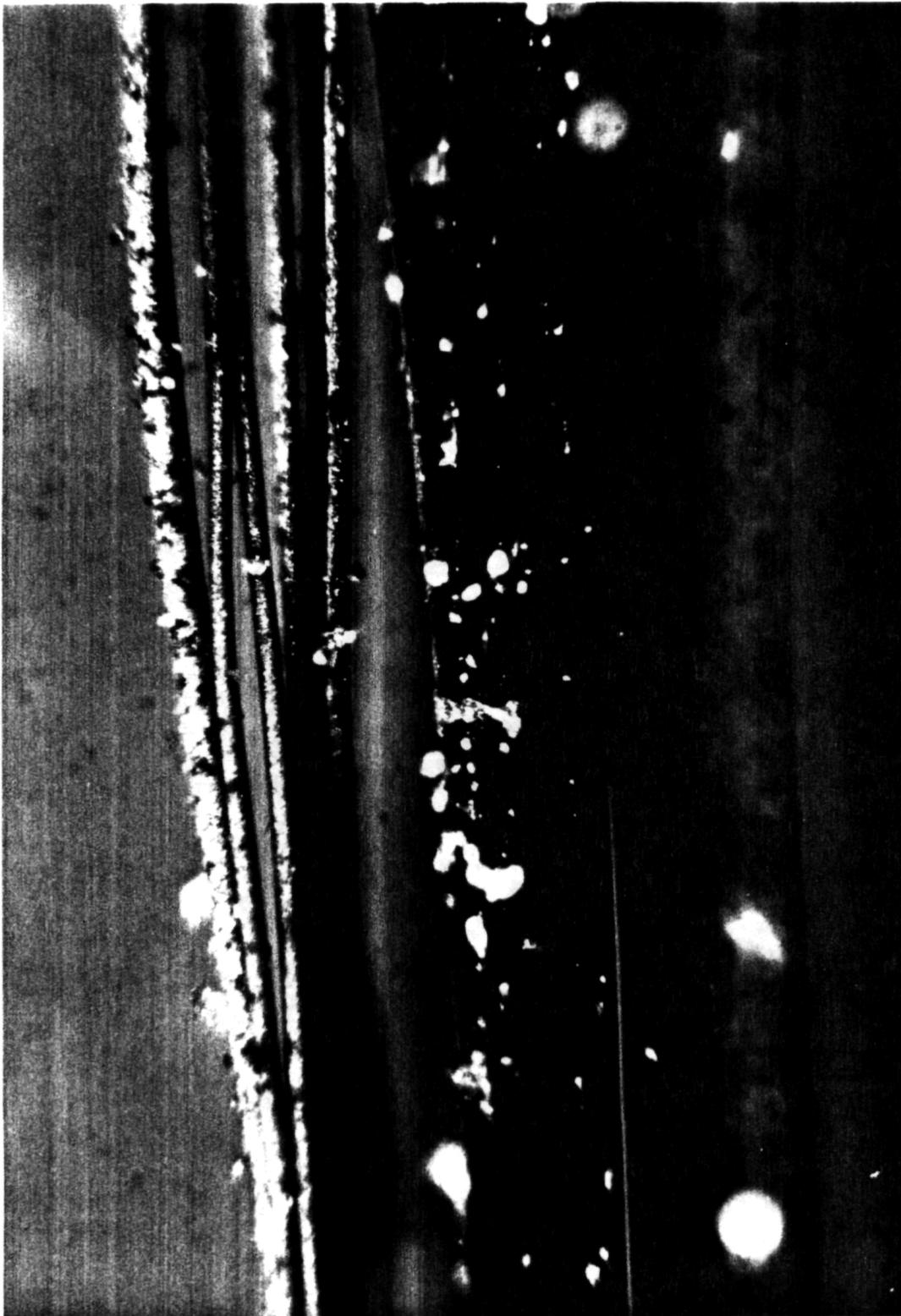


Figure 21.

Crystals Present on Pyrolyzed
Fiber 125X Magnification

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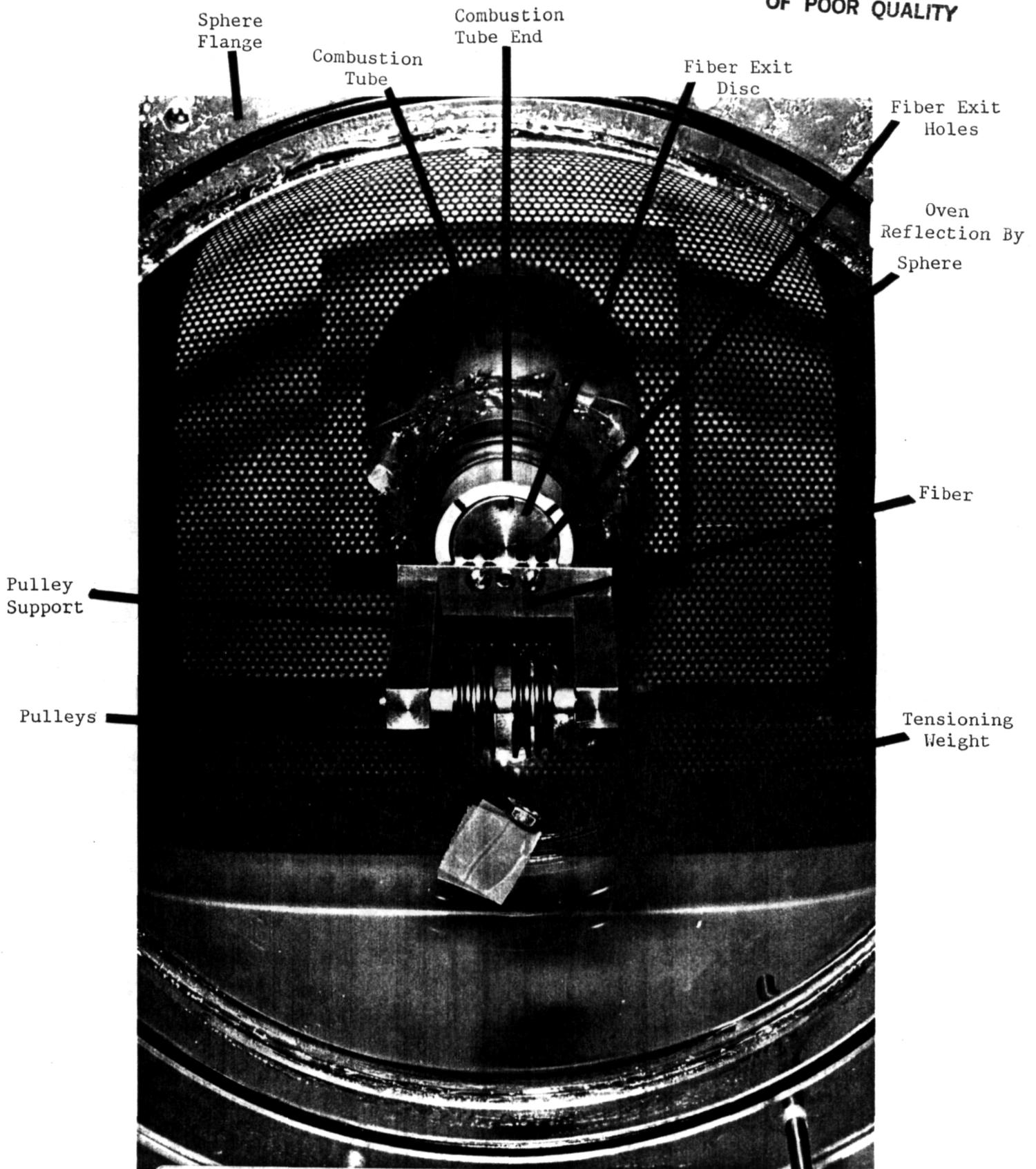


Figure 22.

Weight Attached to Tungsten
Wire to Tension Fiber Bundle
During Pyrolysis

* 2 Mil
Tungsten Wire
Interface
Between Fibers
and Weight

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Figure 23.

Fiber Bundle Pyrolyzed Under
Tension 65X Magnification

An examination of both untreated and hydrolyzed fiber revealed particulate impurities attached to the fiber surface. It was not determined whether these were crystalline or noncrystalline, nor whether they were related in any way to the definitely crystalline outcroppings noted on the pyrolyzed fibers. While they were indeed small enough to pass through the 0.008" resin screen, they were attached only superficially at the fiber surface and appeared not to have been wet by the matrix when it was in the fluid state. It seems likely that they represent detritus picked up through electrostatic attraction during or after fiberization.