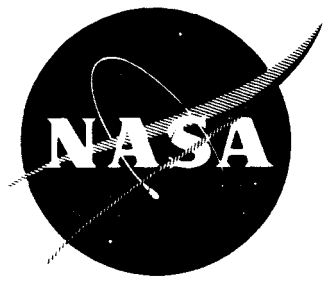


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IMPROVED CRYOGENIC
RESIN/GLASS-FILAMENT-WOUND COMPOSITES

by

A. Lewis, G. E. Bush, and J. Creedon

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

May 1966

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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Chemical Rocket Division
R. F. Lark

Von Karman Center
AEROJET-GENERAL CORPORATION
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FOREWORD

This interim report is submitted in partial fulfillment of the contract and in lieu of the third quarterly progress report at the request of R. F. Lark, Lewis Research Center, the NASA Project Manager, in a letter to A. Lewis, Aerojet-General Project Manager, dated 27 December 1965.

It documents the pertinent work involved in the preparation and evaluation of glass-monofilament-wound NOL rings in the development of improved cryogenic composites. It covers work performed by the Glass Technology Department of the Chemical and Structural Products Division of Aerojet-General from 29 June 1965 to 28 March 1966.



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IMPROVED, CRYOGENIC, RESIN/GLASS-FILAMENT-WOUND COMPOSITES

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A. Lewis, G. E. Bush, and J. Creedon

ABSTRACT

The use of NOL rings fabricated from monofilaments of Aerojet Hi-Stren glass drawn directly from the bushing provided an efficient and economical technique for interlaminar-shear testing. Specimens cut from the rings were tested at room temperature, after 6 hours in boiling water, and at -423°F to evaluate finish compositions, matrix resins, and flexibilizers for cryogenic application. The coupling agents used in the finish improved wet-strength retention more than the room-temperature or cryogenic shear strengths.

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GLOSSARY

	Definition
BDMA	Benzyl dimethylamine
BF ₃ -400	Boron trifluoride monomethylamine
DSA	Dodecanyl succinic anhydride
HHPA	Hexahydrophthalic anhydride
Hi-Stren	Aerojet-General proprietary high-performance glass
MEK	Methyl ethyl ketone
MOCA	4,4'-methylene-bis-(2-chloroaniline)
NMA	Nadic methyl anhydride
NOL	Naval Ordnance Laboratory
PPG	Polypropylene glycol
pphr	Parts per hundred of resin
Hand	Measure of the texture or feel of the glass

IMPROVED, CRYOGENIC, RESIN/GLASS-FILAMENT-WOUND COMPOSITES

by A. Lewis, G. E. Bush, and J. Creedon

Aerojet-General Corporation

SUMMARY

The objective of this work is the development of an improved glass/resin composite for cryogenic use through investigations of glass-filament finishes, suitable resins, and/or improved processing techniques for composite fabrication.

In Task I of the three-task program, state-of-the-art materials and techniques were evaluated with Naval Ordnance Laboratory (NOL) rings fabricated from newly formed glass monofilament. Task II, in progress, includes evaluations of the materials and/or techniques selected in the foregoing work; NOL rings made from single-end roving are being used. The approaches selected in Task II will be evaluated in Task III with uniaxially and biaxially wound composites made from single-end roving.

This interim report covers Task I. Filaments of Hi-Stren glass, a magnesia aluminosilicate developed by Aerojet-General, have been selected as reinforcing elements for all work in the program. The investigation thus far has shown that improved cryogenic properties can be obtained through the proper selection of finish and resin-matrix materials.

Coupling agent Z-6020 or Z-6040^{*} with Epon 828^{**} epoxy resin provided some of the best combinations of properties at room temperature, after a 6-hour water boil, and at -423°F in the work under Task I. The use of NOL ring composites, fabricated immediately after fiberization, was found to be an effective technique for evaluating the bond strength between the glass, finish, and resin matrix.

^{*} Respectively η -(trimethoxysilylpropyl)ethylenediamine and γ -glycidoxypropyltrimethoxysilane, manufactured by Dow Corning Corporation.

^{**} Manufactured by Shell Chemical Company.

I. INTRODUCTION

This study was undertaken to meet a National Aeronautics and Space Administration requirement for a high-performance cryogenic structure. Glass/resin composites are considered prime candidates for meeting this need. Limited data on the performance of such composites show higher performance at cryogenic temperatures than at room temperature. It is generally accepted that the room-temperature strength of a glass filament is approximately doubled and the elastic modulus is increased by approximately 10% at -423°F . Although the role of the resin matrix and finish is insignificant in terms of composite stress, crazing of the resin will result in reduced ability to transfer loads between adjacent fibers, thus causing premature composite failure.

The objective of this work is to develop glass/resin composites having improved cryogenic properties attained through the use of an improved finish, resin, and/or processing technique. Prime emphasis is being placed on finish investigations. Resin and processing-technique studies are allocated less important roles.

The program is divided into three tasks. Task I, covered in this report, involved the selection of 12 promising state-of-the-art materials and related techniques. The evaluation specimens were NOL rings fabricated from a newly formed monofilament of magnesia aluminosilicate glass (Hi-Stren, developed by Aerojet-General). The resin performance and interfacial-bond performance were determined by subjecting the rings to interlaminar-shear tests at room temperature, at room temperature after a 6-hour water boil, and at -423°F . In Task II the 12 selected materials and related processing techniques are being evaluated with NOL rings fabricated from single-end Hi-Stren roving. Task III will cover the final evaluation of the selections made in Task II; uniaxially and biaxially wound composites using single-end Hi-Stren roving will be fabricated and evaluated.

II. TECHNICAL DISCUSSION

A. APPROACH

Good bonding between the glass-fiber component and the resin-matrix component of a glass-reinforced composite is required to transfer stresses between the glass fibers in the composite. The bond strength is usually determined by interlaminar-shear measurements, which are used to evaluate parameters that affect the glass/resin interface. Parameters that can be studied include the composition of the finish and matrix and the effects of processing procedures. The NOL-ring test, which features easily fabricated specimens and is widely accepted in the industry, was chosen to determine shear strengths. Short-span horizontal-shear specimens were cut from cured NOL rings. Interlaminar-shear strengths were determined at room temperature (five specimens of each ring), at room temperature following a 6-hour water boil (five specimens), and at -423°F (three specimens).

B. ROLE OF FINISH IN GLASS-RESIN INTERFACE

Previous investigators have suggested that the composition of the finish and the method used for application to glass filaments have important effects on the glass/resin interface bond (Refs. 1 and 2). The finish, which is coated on the glass fiber immediately following fiberization, generally consists of a film former dissolved in a carrier (solvent), a coupling agent, a lubricant/wetting agent, and a plasticizer. Its function is to protect the fibers from abrasion, improve the bonding of the glass to the matrix resin, and protect the glass fibers from corrosive environmental elements, such as moisture.

The coupling agent, it is believed, contributes significantly to improving the interlaminar-shear strength of the composite. Functionally, it serves as a molecular bridge at the interface between the glass and the resin. It is synthesized in a manner that permits one end of the molecule to react or combine with the glass surface and the other with the resin matrix. Figure 1 shows a possible mechanism for attachment to hydroxyl sites on the glass surface.

Many investigations employing different approaches have been conducted to determine the nature of the glass/resin interface. The approaches included studies of (1) surface energy (determination of contact angles, measurement of surface-wetting behavior, investigation of the thermodynamics of spreading on glass, etc.), (2) adsorption phenomena (gas- and liquid-phase adsorption-isotherm measurements, adsorption of specific monomers and polymers, orientation of adsorbed materials, and anisotropy of adsorption), and (3) chemical phenomena (analysis of the glass surface before and after treatment with the bonding materials, radioactive-tracer determination of the extent of adsorption, and spectroscopic determination of adsorbants on glass). Direct physical measurements have been made to determine the strength of bonding between glass and resins. Many other tests and approaches have been used to determine the nature of the interfaces between the resins, the coupling agents, and the glass. Most of the results clearly imply that water is a major component adsorbed on the glass surface.

Inconclusive results were obtained in attempts to determine whether fresh, clean glass or chemically treated glass provided stronger bonds to resin materials. Some work has indicated that a freshly cleaved glass surface (one with no adsorbed water) demonstrates very poor bonding behavior, while water-covered glass surfaces exhibit bonding properties equal to those of glass subjected to prior coupling-agent treatment (Ref. 3). On the other hand, a recent study employing azeotropic distillation to remove the upper layers of adsorbed water (Ref. 4) supports the view that glass/resin bonding is improved as the amount of adsorbed water is reduced. It appears that the physical properties and behavior of the interface, as well as the surface structure of the glass, are not well understood. Similarly, the surface energy and the chemical behavior are insufficiently known to permit a clear understanding of the bonding mechanisms.

Because it is important to provide strong and impermeable bonding between the resins and the virgin uncoated glass fibers, a search for specific glass-fiber finishes (sizings) to improve the glass/resin bond was undertaken.

Most finishes in use today include a silane coupling agent (e.g., Union Carbide Corporation A-1100 and various vinyl and allyl silane compounds). The commercially successful finishes, however, have very diverse chemical structures. Among them are the original dextrin-oil emulsion (the first finish used on glass filaments), Volan types (chromium methacrylate complexes), and the most recently developed methacrylic-polymer type. Because the first reaction of all of these finishes involves hydrolysis, it may be concluded that hydroxyl interaction is important to the function of the finish.

C. PROCESSING OF FINISH

The method of applying the coupling-agent component of the finish is an important aspect of the interaction between the finish and the glass filament. In the present study the coupling agent was applied (1) as part of the matrix resin in a "one-step process," or (2) as part of the finish, followed by application of the matrix resin in a "two-step process." A "combination process" (agent applied as part of the resin and the finish) is also possible.

Sterman and Marsden (Ref. 1) suggested that the silane coupling agents be dissolved in the resin instead of being applied directly to the fiber. They obtained higher interlaminar-shear values when γ -glycidoxypropyl-trimethoxysilane was used in a one-step process in an amine-cured epoxy laminate than when the finish was applied directly to the glass. Under the same conditions, an (epoxycyclohexyl)ethyltrimethoxysilane performed better when the finish was applied directly to the filament than in the one-step process. They believe that the bonding of the coupling agent in the one-step process involves silane migration to the filament interface, orientation of the silane, hydrolysis with bound surface water, and condensation with bonding.

More recently, Holtmann (Ref. 2) showed the coupling agent to be more effective in a two-step process with a polyester resin. He found also that further improvement could be obtained by using the coupling agent in both the finish and the resin matrix (i.e., the combination process). His evaluation was based on comparison of the effects of water boiling on horizontal-shear specimens.

D. SELECTION OF MATERIALS AND PROCESSING TECHNIQUES

1. Glass

Aerojet's Hi-Stren glass was selected for the reinforcing filament to ensure very high composite-strength values. The average room-temperature tensile strength and modulus of Hi-Stren are 700,000 psi (700 ksi) and 13.5×10^6 psi, respectively. These data were obtained with virgin filaments tested within 30 min after fiberization.

Hi-Stren monofilaments were tested at -320°F to establish a benchmark for use in comparison of composite-property data. Fifteen randomly selected, glass-fiber, control specimens tested at room temperature had an average tensile strength of 732 ksi and an average modulus of 13.4×10^6 psi.

Fifteen additional specimens were tested at -320°F by complete submersion in liquid nitrogen. The tensile strength was increased by approximately 50% to 1097 ksi; the tensile modulus was increased by approximately 10% to 14.7×10^6 psi. The data are given in Table 1.

2. Application and/or Processing Modification

Various techniques for the application and/or processing of the finishes and resins were selected to yield a minimum of entrained air bubbles and voids in the composite. Vacuum degassing and mechanical means such as vibration for air-bubble displacement were to be examined initially, but practical considerations forced a concentration of effort on other problems relating to resin and finish application on a monofilament fiber at the glass-fiber drawing furnace. The parameters that were considered included the resin and finish concentration, viscosity and temperature, glass-fiber tension, winding speed, finish and resin solvent carrier, and traversing methods. It was found that the use of the process that was developed caused the occlusion of very little air and drastically reduced the void content of NOL rings.

3. Finish Materials

Experience and an extensive survey of the suppliers and manufacturers listed in Table 2 formed the basis for the selection of finish materials. Samples of materials recommended by the suppliers were evaluated, and acceptable materials were used in the program. Some of the characteristics considered for acceptance were good abrasion resistance, low permeability and high stability to water vapor, good adhesion to and wetting of the glass filament and the matrix resin, high shear strength, and good handling properties.

The various components of the finish - coupling agents, film formers, plasticizers, and lubricant/wetting agents - are discussed individually below.

a. Coupling Agents

Table 3 lists the types of coupling agents considered for use in this program. Silane-type agents have been the most effective in promoting linkage between the glass and the resin matrix. Polyester and epoxy resins comprise most of the reinforced-plastics market today, and most coupling-agent investigations have been conducted with them.

The silane coupling agent is reported to bond to the glass fiber by condensation reaction of the active group on the silicon with the silanol on the glass surface (Ref. 1). Some typical active groups on a compound such as $\text{CH}_2=\text{CHSiX}_3$ where X may be Cl, OCH_3 , OC_2H_5 , or $\text{N}(\text{CH}_3)_2$, are used in finishes for polyester-resin composites. The hydrolyzable groups that form the silanol have little effect on the performance of the coupling agent as measured by composite strength. The choice is sometimes dictated by the handling properties, nature of the hydrolysis byproducts (HCl , ROH), and cost.

In most commercial applications, water is the preferred carrier for the film former in the finish. This restricts the film former in the finish to water-soluble or dispersible types. The water also serves to

hydrolyze the silane coupling agent to the silanol which is required for condensation with the silanol on the glass surface. The finishes evaluated in this program were in a solvent carrier since the film formers were not water soluble. The hydrolysis of the silane under these conditions is believed to be obtained with bound surface water or silanol groups on the glass fiber.

Chemical interactions of silane coupling agents with epoxy resins are obtained by reacting the active groups in these agents with the amine hardener (as for the Z-6040 coupling agent) or with the epoxy resin in the matrix (as for Union Carbide A-1100). The A-1100 agent was selected as the control for use in comparing various epoxy matrix systems in this program because of its widespread employment in the industry.

b. Film Formers

The film former in the finish provides the filament protection against mechanical damage during subsequent processing, in addition to a moisture-resistant barrier. The most effective types of film formers have been epoxy resins and the polyvinyl acetates. Selection of the film former is dictated primarily by the composite resin-matrix system. It is essential that compatibility and/or crosslinking be obtained between the film former and the matrix resin. In this program an epoxy-system film former was selected as the control.

c. Plasticizers and Lubricant/Wetting Agents

Plasticizers can be added to a resin to increase the flexibility and extensibility and to decrease the yield point, elastic modulus, and tensile strength.

Flow is caused by the movement of molecules. The ease with which movement occurs depends on the strength of the attractive forces between molecules. By decreasing these forces, a plasticizing agent increases the molecular mobility and in effect brings the substance closer to the liquid state at room temperature (Ref. 5). Increased temperature performs many of the same functions as the use of a plasticizer and was employed, as applicable, during this program.

The plasticizers must be compatible and capable of producing a stable solution with the resin (Ref. 6). Ordinarily, a plasticizer is not used in composites when high ambient strengths are desired, because maximum strength transfer cannot be accomplished through a flexible finish-resin matrix. In the present study, however, flexibilizers are of interest insofar as they affect the cryogenic performance of the composite. For a glass composite to perform effectively at cryogenic temperatures, the finish-resin interface must have some ability to strain. The urethanes are generally considered good candidates for flexibilizing resin systems for cryogenic applications.

Wetting agents, either cationic or non-ionic, can be added to the finish to reduce the surface tension and improve the wetting of the glass filament. Wetting agents may also function as lubricants, improving the processing characteristics of the finish. Bascom has reported (Ref. 7) that the type of wetting agent required varies with the type of epoxy resin

used. A lubricant serves an important processing function in reducing the friction between the monofilaments and the processing equipment; in addition, it frequently improves the "hand" of glass fibers.

Table 4 lists the plasticizers and the lubricant/wetting agents chosen for use with the selected film former in this program.

4. Matrix Resin

Matrix resins of a wide variety (Table 5) were selected for an evaluation of state-of-the-art systems for ambient and cryogenic temperature use.

a. Epoxies

Epoxy resins are used for ambient and cryogenic applications and have many desirable and useful properties. They can be cured with a variety of curing agents and provide a wide latitude in processing parameters and physical properties. Epoxies bond well to glass reinforcements, have less shrinkage than polyesters, and have low water-absorption properties. In addition, they possess high tensile strength with reasonably good extensibilities.

b. Epoxy-Nylon

The epoxy-nylon type of resin system should provide good cryogenic performance, based on adhesive-bonding studies reported by Kausen (Ref. 8). Tensile lap-shear strengths of 5 to 7 ksi have been obtained with these systems at -423°F , but they are somewhat sensitive to moisture.

c. Butadiene-Styrene

Butadiene-styrene resins were selected for study because of their ambient-temperature properties of low modulus and good adhesion.

d. Polyesters

Polyesters are low-cost, universally used, laminating resins and were evaluated for application as matrix material. They are not generally accepted for high-performance, aerospace, filament-winding applications because they do not bond as well as epoxy systems to nonmetallics, and have greater shrinkage and higher water absorption than epoxies.

e. Fluorocarbons

Published data (Ref. 9) indicate considerable increases in the strength of glass-cloth-reinforced laminates at -423°F , as compared with the room-temperature strength. The ultimate tensile strength of glass-reinforced fluorocarbons at -423°F is of the order of 85 ksi, vs 100 ksi for epoxy systems at the same temperature, but they cannot conveniently be used under the processing conditions of filament winding.

f. Urethanes

Polyurethanes appear to offer great potential for cryogenic applications. Although their room-temperature tensile strengths are low, Roseland has reported (Ref. 10) increased tensile lap-shear strength at cryogenic temperatures (390 psi at 180°F and 2000 psi at -423°F); in addition, polyurethanes exhibited peel strengths of 80 lb per inch of width at -423°F and provided excellent abrasion resistance.

Roseland recently reported (Ref. 11) that he has obtained improved performance of urethane (Adiprene L-100, a urethane-based compound) in cryogenic applications through the use of the Union Carbide A-187 coupling agent. He reported that the addition of A-187 improved the shear and peel-strength properties of urethane-adhesive bonds to aluminum and glass, and that the peel strength was actually increased after a 48-hour soak in water. He also stated that too much silane (1.0%) seriously reduced the tensile strength and elongation of Adiprene L-100.

Good cryogenic properties for polyurethane-modified epoxies, as determined in tests of castings, have been reported in Aerojet work under Contract NAS 3-6287 (Ref. 12).

E. NOL-RING FABRICATION DIRECT FROM BUSHING (MONOFILAMENT)

1. Equipment

Specially designed fixtures were required for the fabrication of NOL rings from a glass monofilament immediately following fiberization. The equipment and tooling are described below.

a. Glass Making

The glass-manufacturing equipment includes glass-melting furnaces, a marble-making facility consisting of a fining furnace and a marble machine, and monofilament fiberizing furnaces.

(1) Melting

Raw batch materials are converted into Hi-Stren 19-S glass in either 1-lb-capacity laboratory furnaces or a 2000-lb-capacity pilot-plant furnace.

Laboratory furnaces (Figure 2) were used initially in the program. A batch of approximately 500 g of raw materials was melted into a homogeneous glass in approximately 24 hours. The glass was then poured into water, causing it to fracture into small particles, or frit. The particles were subsequently crushed and dried before being fed into the monofilament fiberizing furnace.

The laboratory melting furnaces are constructed of high-temperature refractories, and are heated with natural gas and compressed air. Furnace temperatures are automatically controlled and recorded by means of a thermocouple, controller, recorder, regulator, and gas-air mixer. The Hi-Stren glass is normally melted in a zirconia-alumina crucible.

The pilot-plant melting furnace (Figure 3) has a glass-melt capacity of 2000 lb and a melting area approximately 18 in. deep, 4 ft wide, and 6 ft long. The batch materials are charged into the furnace, are melted for approximately 48 hours, and are ladled into a stainless steel receptacle containing tap water. The fritted glass is then transported to bins for drying and storage.

(2) Marble Making

The marble facility consists of a remelt furnace (Figure 4) having a glass-holding capacity of 700 lb, and a marble machine having a production capacity of 35 lb/hour. The furnace is fired with natural gas and is controlled by an automatic firing mechanism consisting of temperature controllers and recorders, thermocouples, a gas-air mixer, and regulators.

Fritted glass is charged into the melt end of the remelt furnace. As the glass flows to the front (or discharge) end of the furnace, it is remelted and "fined" (i.e., trapped gases are removed). The glass then passes through an orifice and is sheared into "gobs" that fall onto rolls which form it into marbles.

(3) Fiberizing Furnace and Related Equipment

The monofilament fiberizing furnace consists of a precious-metal bushing having a 100-g remelt capacity (Figure 5) and is heated electrically, with the bushing acting as the heating element as well as the molten glass container. The glass is fed into the bushing in the form of frit and is conditioned prior to drawing at a temperature sufficiently high to ensure proper fining. Molten glass is discharged through an orifice at the bottom of the bushing.

The fiber thus formed is coated with finish material by a roller-coater applicator 12 in. below the orifice and/or a felt pad 36 in. below the orifice. The roller coater consists of a 4-in.-dia roll, 1 in. wide, that is rotated at a surface velocity of approximately 100 ft/min through a filament-finish bath by a variable-speed motor. The pad applicator consists of a felt pad mounted by means of two 1/16-in. steel pins welded to a 3-in.-long, V-shaped, metal holder.

The coated fiber is wound onto a 6-3/8-in. rotating drum 4 ft from the bushing. This "take-up" drum is driven by a variable-speed motor capable of operation at 0 to 10,000 ft/min (fpm).

The drum of the take-up machine was modified to accommodate an NOL-ring fabrication fixture and starting collar. To initiate fiberization, the filament is attached to the starting collar and the machine

speed is increased to the desired drawing speed. The machine is then traversed, placing the filament in the center of the winding mandrel. Approximately 45 min is required to fabricate a 1/8-in.-thick NOL ring.

b. NOL-Ring Processing Equipment

Winding fixtures were required for the fabrication of NOL rings directly from the monofilament furnace. They consist of four major components (see Figure 6). The center section has a 1-1/4-in.-dia hole that is used to fasten the unit to the shaft of the take-up machine. An insert was made for this hole to facilitate machining of the outside surface of the composite ring with a 1/2-in. router. The two flanges can readily be removed to permit removal of the composite from the fixture.

(1) Cutting Fixture

A jig was designed and fabricated for use in cutting the NOL ring into test specimens (Figure 7). It facilitates accurate preparation of specimens for interlaminar-shear testing and microscopic examination.

(2) Starting Fixture

A starting fixture (Figure 8), 6-1/4-in. in diameter and 4 in. wide, was designed and fabricated for use in starting the glass filament on the ring-fabrication fixture in order to provide a means of controlling the fiber diameter during start-up.

(3) Traversing Mechanism

A filament-traversing mechanism was designed and constructed to facilitate the fabrication of uniformly wound NOL rings. It consists of a brass guide attached to a 1/4-in.-dia rod that is fastened to a 1/4-in.-thick mounting plate using a single-barrel hinge. In the operating position, the rod is perpendicular to the mounting plate and is held firmly in a 3/8-in. groove in a Teflon cam by a coiled spring fastened to the rod and the mounting plate. The cam is designed to cause the rod to oscillate 1/4 in. or the width of the winding mandrel. This entire mechanism is attached to a mounting by means of a lead screw that permits easy alignment to the winding mandrel.

(4) Heated-Resin Container

To accommodate the application of a 100%-solid matrix resin independently from the finish or in an integral finish-resin mix, a resin-heating container 4 in. high by 3 in. in diameter was fabricated. A copper fitting is welded to the bottom; fastened to the fitting is a needle valve, which is connected to the applicator pad by a 1/4-in. copper tube. The top of the container is sealed with a polyethylene cover. The unit is heated by means of four resistance elements fastened to its exterior and connected to a 10-amp Powerstat that is used to adjust the temperature.

2. NOL-Ring Fabrication Process

The NOL rings were fabricated by drawing a monofilament directly from the monofilament furnace, passing it over the roller-coater and/or pad applicator, and winding the coated filament onto an NOL-ring fabrication fixture. Good processing techniques were required. The initial process used in NOL-ring fabrication directly from the fiber-forming furnace is described below.

The furnace was charged with glass, was heated to the glass-conditioning temperature, and was "conditioned" until the glass was properly fined. A glass level of 1-1/4 to 1-1/2 in. was maintained during conditioning and ring fabrication.

After conditioning, the glass filament was attached to the starting fixture of the take-up machine. The machine speed was slowly increased to the desired value. The filament was brought in contact with the roller coater and/or the felt pad, and the newly formed fiber was coated with a finish-resin solution by the rotating wheel of the roller and/or the pad.

The coated filament, after reaching the desired drawing speed, was traversed from the starting fixture to the winding mandrel. The reservoir of the roller coater was maintained at a constant level to ensure that an adequate amount of finish was applied to the fiber. A filament build-up of 1/32 in. over the prescribed ring thickness was added to ensure the proper ring dimensions. After the rings were cured, they were mounted on a router and were machined to the required thickness.

The NOL-ring composites (Figure 9) were cut into horizontal-shear specimens in accordance with ASTM Method D2344-65T. The ring was mounted on a shop aid tool (Figure 7) and was cut with a water-cooled diamond saw.

3. NOL-Ring Process Optimization

Before the candidate materials and techniques could be screened, it was necessary to (a) modify existing facilities and fixtures, (b) evaluate these modifications, and (c) determine the optimum fiberization parameters with Hi-Stren glass in the fabrication of NOL rings directly from the monofilament furnace.

Thirty NOL-ring composites were made to evaluate the facility modifications, fixture designs, and optimum fiberization parameters. The ring thickness was varied from 1/16 to 1/4 in. Two important criteria were determined in these experiments: the resin content of the composites and the packing density of the filaments. The filament packing was evaluated by microscopic comparison with NOL rings fabricated from 20-end roving. The wide data scatter in Table 6 results from varying the processing parameters to achieve a high-quality test specimen.

a. NOL Rings Fabricated from Hi-Stren Monofilament and S-994 20-End Roving

Starting with the first fabrication experiment, it was apparent that NOL rings fabricated directly from the furnace had filament packing superior to that of rings fabricated with 20-end roving.

Figure 10A reproduces a photomicrograph of the cross section of a ring fabricated with 20-end roving, and Figure 10B the cross section of a ring fabricated with a monofilament immediately following fiberization. The latter has closer packing and substantially fewer voids; its improved quality indicates good wetting of the nascent filament.

b. Evaluation of Starting Fixture

Figure 11 reproduces photomicrographs of two rings made to evaluate the fiber-starting fixture. In Figure 11B, the fiber was started directly on the winding mandrel; it produced large-diameter filaments and resin-rich areas as seen at the left.

The slow speed at which the fiber must be started (1000 fpm) results in excessive resin pickup and a loosely packed ring. The starting fixture shown in Figure 8 was designed to overcome this problem; Figure 11A shows a ring fabricated with its aid. Uniform fiber diameter and resin distribution are obtained by reducing the fiber diameter (i.e., by increasing the drawing speed) while the fiber is attached to the starting fixture.

After it was determined that the fixture and fiber-furnace modifications were adequate to ensure suitable test specimens, an experiment was designed to determine the optimum fiberizing parameters.

c. Study of Optimum Fiberizing Parameters

Optimum conditions are required for the production of glass fibers having a high tensile strength and modulus of elasticity. The parameters selected for study in this experiment were the drawing speed, glass temperature, and fiber-furnace glass level.

Optimum Hi-Stren fiber properties had previously been obtained with a glass temperature of 2920°F, a glass level of 1-1/2 in., and a drawing speed of 5750 fpm. The first ring made with these parameters (Table 6) had a loosely packed composite. After subsequent rings were fabricated at various speed, levels, and temperatures, the following parameters were selected: a drawing speed of 10,000 fpm, a glass temperature of 2920°F, and a glass level of 1-1/4 in.

Both tensile and shear rings were fabricated. A few were tested for mechanical properties in accordance with ASTM specifications (see Appendix); the results are shown in Table 6. Most of the rings were examined photomicrographically for filament packing and voids (see Figures 12 and 13). The resin content and voids were determined by density and resin-

burnoff measurements. Subsequent studies (Table 7) resulted in the selection of a drawing speed of 3500 fpm to handle the wide range of physical properties of the various matrix materials.

4. Methods of Finish Application

a. One-Step Application (Integral Mix)

An experiment was undertaken to evaluate nine coupling agents (see Table 8), using a one-step process to apply the finish resin. The coupling agent and the Epon 828 resin system were blended into a homogeneous 100%-solids mixture, which was applied by the felt-pad technique. The resin was supplied to the pad at a constant, predetermined temperature selected to yield an optimum viscosity for good coating and wetting. The finish-resin composition was as follows:

	<u>Parts by Weight</u>
Epon 828 epoxy resin	52.0
Nadic methyl anhydride (NMA)	42.0
Benzyl dimethylamine (BDMA)	0.5
Coupling agent	5.5 (i.e., 5.5 wt%)

The ring fabricated using A-1100 (Ring 10, Table 8) was selected as the control. Its average interlaminar-shear strength was 10.8 ksi. An extremely low 6-hour water-boil strength was obtained from Ring 26, fabricated without a coupling agent. Figure 14 shows the horizontal-shear-test specimens before and after the water boil; it demonstrates the edge effect and reveals the appearance after boiling for the various coupling agents.

b. Two-Step Application

In the two-step process, the finish was applied by the roller coater 12 in. below the bushing, and the heated matrix resin was applied by the felt pad 36 in. below the bushing as a 100% solid. This approach produced a ring (Ring 31, Table 9) yielding the highest average interlaminar-shear strength (13.4 ksi). When subjected to a 6-hour water boil, however, rings from this experiment yielded lower interlaminar-shear strengths and wet-strength retentions than comparable rings made by the one-step-application process. This difference is attributed to the coupling-agent concentration (1.2 wt% for the two-step process vs 5.5 wt% for the one-step process).

The coupling agents were substituted in the following formulation:

	<u>Parts by Weight</u>
Epon 828 epoxy resin	52.0
NMA	42.0
BDMA	0.5
Acetone solvent	350.0
Coupling agent	5.5 (i.e., 1.2 wt%)

F. EXPERIMENTAL RESULTS

1. Process Evaluation

The general improvement in wet-strength retention resulting from the use of coupling agents is shown in Figure 15; consistently higher horizontal-shear values are evident. There is some indication that one-step finish application provides higher strengths than the two-step process, perhaps because the coupling-agent concentrations for the one- and two-step processes were 5.5 and 1.2%, respectively, based on the total weight of the finish and resin-matrix solids.

An NOL ring was fabricated by the two-step process with a coupling-agent concentration of 5.7 wt% to determine whether the shear-strength difference could be attributed to process difference or coupling-agent concentration. The results shown for Ring 105 in Table 10 indicate comparable wet-strength retention for the one- and two-step processes when the coupling-agent concentrations are equivalent.

Figure 16 appears to indicate that the use of coupling agents does not improve the horizontal-shear strength at room temperature. It also appears that a higher coupling-agent concentration (i.e., 5.5 wt% for one-step application vs 1.2 wt% for two-step application) resulted in a lower interlaminar-shear strength at room temperature (Figure 16) and at -423°F (Figure 17). The Z-6030 coupling agent, which exhibited excellent cryogenic-shear properties, was an exception; the value presented in Figure 17 is an average of six separate determinations. This performance may be an indication that this coupling agent contributes to high shear strengths at -423°F.

Figures 15 through 17 and Tables 8 and 9 appear to indicate that the use of coupling agents has a greater influence on wet-strength retention than on room-temperature and cryogenic shear strengths.

The Z-6040 coupling agent, a glycidoxypropyltrimethoxysilane, provided the highest wet-strength-retention value (89.0%) of the coupling agents evaluated (Table 8). Its good performance was expected, but it is difficult to explain the good performance of A-172 (76.3%), which is a vinyl-silane designed for use with polyester resins.

2. Water Absorption

Figures 18 and 19 show a definite correlation of horizontal-shear strength with water absorption. The one-step process appears to offer greater shear strength after a water boil than the two-step process, but this is explained on the basis of difference in coupling-agent concentrations (5.5 vs 1.2 wt%). In general, Z-6040 consistently provided the most favorable wet-strength-retention properties.

3. Effect of Voids on Interlaminar-Shear Strength

Figure 20 shows the effect of voids on composite strength; the data were taken from Tables 8 and 9. The void content was calculated from

the specific gravity of the glass and the resin matrix. Because the specific gravity of the glass can vary according to the thermal history, the void-content calculations are subject to considerable uncertainty; when the void content was very low, the calculated values were negative for many specimens. The data in Figure 20 nevertheless indicate a definite correlation between void content and the interlaminar-shear strength of the Epon 828/NMA/BDMA system with various finishes. Specimens with zero-void content exhibit a range of room-temperature shear strengths between 11.4 and 13.4 ksi; the variation in type of finish probably contributed to this spread. When an appreciable void content was calculated, the specimens showed much lower horizontal-shear strengths.

The use of a single-end glass roving for NOL-ring fabrication is expected to make the reduction of voids more difficult. Bascom (Ref. 13) reports that a low void content in a single-end-filament, epoxy-resin composite requires the use of a surface-active agent to reduce the contact angle, and that oscillation of the strand mechanically releases the occluded air.

4. Performance of Resin Systems

The epoxy-resin systems evaluated showed a shear-strength range from 1.87 to 11.4 ksi at room temperature (Table 11). The systems that have high ambient values also have high interlaminar-shear strengths at -423°F (e.g., Rings 43, 46, 55, 65, 71, and 72). It does not appear possible, however, to predict the cryogenic-shear-strength performance from ambient-strength data. Systems in which the resin solids were less than 100% showed a tendency toward low shear strengths at ambient and cryogenic temperatures (e.g., Rings 40, 48, 50, 57, 58, 61, 66, and 74). Relatively low strength was obtained from the polyester resins (Rings 64, 75, and 76), but it is believed that higher resin contents are required with these systems than with the epoxies. Flexible systems (epoxy, polyester, butadiene-styrene, and urethane-modified epoxy) yielded substantially increased strengths at cryogenic temperatures as compared with the room-temperature values.

Rings 67 and 68 had an epoxy-nylon film former in the finish with the standard Epon 828/NMA/BDMA system; it was believed that the good low-temperature properties reported for the epoxy-nylon (Ref. 9) would improve the cryogenic performance, but no significant improvements were obtained. The low values reported for Ring 69 using Union Carbide ERRA-300 reflect the processing and curing difficulties encountered. This resin requires special curing and handling to obtain the high interlaminar-shear strengths reported in the literature.

Wet strength is considered a satisfactory measure of interfacial-bond strength, and the strength retention after a 6-hour water boil is very high for a few systems (Rings 50, 66, 69, 74, and 75). These rings also have low ambient-temperature shear strengths, and the results are therefore considered indications of resin-processing difficulties rather than coupling-agent performance.

The results presented in Table 11 reflect the effects of the resin system and curing agent on interlaminar shear, because only two coupling agents were used in this phase of the work. The A-1100 was used for all epoxy, phenolic, urethane, and modified-epoxy resins, and the A-172 was used with polyesters and styrene-butadiene in integral-mix systems. Because of the relatively narrow range of room-temperature horizontal-shear effects shown in Tables 8 and 9 (one resin system and many coupling agents), it is believed that a change in coupling agent for the various systems reported in Table 11 would have little effect in this regard and that Table 11 can therefore be used to select the most likely resin candidates for cryogenic study and for optimization in a coupling-agent study.

5. Water-Displacement Study

This experiment was designed to determine the effect of displacing water from the surface of glass fibers by means of compounds containing polar and nonpolar groups. The compounds were applied ahead of the finish and the matrix resin. Zisman has reported (Ref. 14) that such compounds spread rapidly over the water surface as a result of their high spreading coefficients and low viscosities. The spreading compound readily displaces a thin water layer (no greater than a few millimeters thick) from the glass surface. This condition exists for a short period until the compound has evaporated; after evaporation, water fills in the dry spaces.

The results of the water-displacement study are presented in Table 12. The selected compounds were applied by the roller coater located approximately 12 in. below the glass bushing. The felt-pad applicator approximately 36 in. below the bushing was used to apply a homogeneous finish-resin mixture to the fiber. The Epon 828/NMA/BDMA resin system and A-1100 coupling agent in a 100%-solid solution were used.

Comparison of the data presented in Tables 8, 9, and 12 indicates that the room-temperature and 6-hour water-boil strengths are approximately the same and that the use of polar-nonpolar compounds yielded no apparent benefits.

The vapor pressure of the water-displacing agent should be considered in evaluating the data in Table 12. In this experiment, the agent was applied in close proximity to the fiberizing bushing, which operates at 2700°F. The selected agents have low boiling points, and it is possible that they had partly evaporated by the time the finish-resin matrix was applied. Higher-boiling-point displacing agents may prove more effective than the present data indicate.

6. Lubricant/Wetting Agents

Typical lubricant/wetting-agent compounds used in the industry were tested and the results are shown in Table 13. The compounds used in Rings 82, 83, and 84 (all ICI Organics Company materials) provided comparable strength retention after a 6-hour water boil.

Experimentation provides the only basis for selection of lubricant/wetting-agent compounds. The resin, the concentration, and the process all influence the performance. Cirrasol 220 provided the best characteristics for the present application, as measured by wet-strength retention (Table 13).

7. Plasticizers

Table 14 shows the cryogenic performance of flexibilized epoxy systems. An integral blend of Epon 828, Shell Curing Agent "D," flexibilizer, and coupling agent was used in the preparation of NOL rings. The A-1100 coupling agent was initially used, but was found to react with the system.

The data in Table 14 show that the greatest percentage of increase in cryogenic shear strength is obtained by the low-modulus systems, but the absolute values were much greater for the higher-modulus resins. Increasing the percentage of flexibilizer decreases the room-temperature shear strength as well as the cryogenic. The A-186 coupling agent used in this experiment did not seem to offer much advantage, as measured by strength retention after a water boil.

The data in Table 14 indicate that the Versamid and polysulfide modified epoxies are suitable candidate flexibilizers.

III. CONCLUSIONS AND RECOMMENDATIONS

It can be concluded that (a) coupling agents have a far greater effect in improving wet strength than they do in improving room-temperature or cryogenic properties, (b) epoxies and modified epoxies offer the greatest potential for cryogenic applications, (c) the selected plasticizers demonstrated good cryogenic properties, (d) the lubricant/wetting agents selected for study have little or no effect on composite properties, and (e) the monofilament-wound NOL ring is a satisfactory and inexpensive tool for use in evaluating the interfacial-bond strength of glass/resin composites.

It is recommended that the Task II and III material evaluations be confined to five matrix resins, in addition to Epon 828/NMA/BDMA with A-1100 coupling agent as the control system; four film formers; and three coupling agents. This would yield 61 combinations for NOL-ring fabrication with single-end Hi-Stren roving.

Processing studies will be conducted in addition. They will include (a) fabrication-parameter studies, (b) the effect of ultrasonics on the mechanical properties of composites, and (c) the effect of fillers (silicon-carbide whiskers, etc.) on interlaminar-shear strength.

The resins, film formers, and coupling agents suggested for the ensuing work are listed below, together with reasons for their selection.

A. MATRIX RESINS

The resin systems recommended for evaluation include the following:

1. Araldite 6005 resin and Araldite 957 curing agent as representing a system that has good interlaminar-shear strength at room and cryogenic temperatures as well as after a 6-hour water boil.

2. Epon 815/Versamid 140, a slightly more flexible system having ambient-temperature and cryogenic (23.2 ksi) shear strengths equivalent to those of the foregoing system.

3. Epon 815/LP-3 (polysulfide), a still more flexible system having slightly reduced cryogenic-shear properties (21.0 ksi).

4. Epon 826/Epon 871/Adiprene L-100/MOCA, a system developed in a concurrent program (under Contract NAS 3-6287), reported to have promising cryogenic properties, and included at the request of NASA.

5. Epon 828/DSA/3162-D/BDMA, another development under Contract NAS 3-6287 reported to have promising cryogenic properties and included by NASA request.

B. FILM FORMERS

Film formers based on the Araldite 6005, Epon 815/Versamid 140, and Epon 815/LP-3 resin systems are recommended for further evaluation, in addition to urethane-modified epoxy resin. These film formers are compatible with the matrix resins, cover a range of room-temperature flexibility, and have good cryogenic-shear properties.

C. COUPLING AGENTS

The coupling agents recommended for further evaluation include the following:

1. Z-6040, which demonstrated good shear properties at room temperature, after a 6-hour water boil, and at -423°F .

2. Z-6020, which demonstrated good interlaminar-shear properties when evaluated in a two-step application process under all three test conditions.

3. A-186, which demonstrated good compatibility with the flexibilizers evaluated in Task I.

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TABLE 1

STRENGTH AND MODULUS VALUES FOR HI-STREN GLASS
MONOFILAMENTS AT ROOM TEMPERATURE AND -320°F*

Fiber No.	Fiber Diameter in.	Tensile Properties				Ratio of Properties at -320°F and Room Temp	
		At Room Temp		At -320°F		Tensile Strength	Tensile Modulus
		Strength ksi	Modulus 10 ⁶ psi	Strength ksi	Modulus 10 ⁶ psi		
1	0.000361	594	13.05	1054	14.64	1.77	1.12
2	0.000361	739	13.69	No test	-	-	-
3	0.000361	767	13.58	1261	14.37	1.71	1.06
4	0.000361	771	14.15	1318	15.57	1.71	1.10
5	0.000354	301**	13.09	1099	14.46	-	1.10
6	0.000354	709	13.13	647**	14.38	-	1.10
7	0.000355	688	13.10	826	14.62	1.20	1.12
8	0.000377	857	15.22**	1024	17.50**	1.19	-
<u>Av</u>	<u>0.000361</u>	<u>732</u>	<u>13.40</u>	<u>1097</u>	<u>14.67</u>	<u>1.51</u>	<u>1.10</u>

* Gage length = 1.00 in. Strain rate = 20%/min. Room-temperature tests at 100°F and a relative humidity of 60%.

** Value considered not representative of batch and not included in averages or ratios.

TABLE 2

RESIN MANUFACTURERS AND SUPPLIERS SURVEYED

<u>Firm</u>	<u>Location</u>
Allied Chemical Corporation, Plastics Division	Morristown, N.J.
American Cyanamid Company, Plastics and Resins Division	Wallingford, Conn.
Armstrong Products Company, Inc.	Warsaw, Ind.
Catalin Corporation of America	New York, N.Y.
Ciba Products Company, Technical Sales Department	Fair Lawn, N.J.
Dow Corning Corporation	Midland, Mich.
Durez Plastics Division, Hooker Chemical Corporation	North Tonawanda, N.Y.
Emerson & Cuming Corporation	Canton, Mass.
Enjay Chemical Company	New York, N.Y.
Epoxylite Corporation	South El Monte, Calif.
FMC Corporation, Organic Chemicals Division	New York, N.Y.
Freeman Chemical Corporation	Port Washington, Wisc.
Furane Plastics, Inc.	Los Angeles, Calif.
General Electric Company, Chemical Materials Department	Pittsfield, Mass.
Glidden Company, The	Cleveland, Ohio
Interplastics Corporation (George Woloch Company, Inc.)	New York, N.Y.
Isochem Resins Company	Providence, R.I.
Jones-Dabney Company, Resin and Chemical Division	Louisville, Ky.
Monsanto Chemical Company, Plastic Division	St. Louis, Mo.
Narmco Research and Development Division. Whittaker Corp.	Costa Mesa, Calif.
Pittsburgh Plate Glass Company, Coatings and Resin Division	Pittsburgh, Pa.
Reichhold Chemicals, Inc.	White Plains, N.Y.
Rohm & Haas Company	Philadelphia, Pa.
Shell Chemical Company, Plastic and Resin Division	New York, N.Y.
Union Carbide Plastic Company, Division of Union Carbide Corporation	New York, N.Y.
United States Rubber Company, Naugatuck Chemical Division	Naugatuck, Conn.

TABLE 3

CANDIDATE COUPLING AGENTS

<u>Trade Designation</u>	<u>Chemical Name and Formula</u>	<u>Manufacturer</u>
A-1100	γ -aminopropyltriethoxysilane $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	Union Carbide Corporation
A-172	Vinyltris(2-methoxyethoxy)silane $\text{H}_2\text{C}=\text{C}-\text{Si}(\text{OC}_2\text{H}_4\text{OCH}_3)_3$	Union Carbide
A-174	γ -methacryloxypropyltrimethoxysilane $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \end{array} \text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$	Union Carbide
A-186	β -3,4-(epoxycyclohexyl)ethyltrimethoxysilane $\text{O} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_{10} - \text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	Union Carbide
Z-6020	η -(trimethoxysilylpropyl)ethylenediamine $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$	Dow Corning Corporation
Z-6030	γ -methacryloxypropyltrimethoxysilane $\begin{array}{c} \text{CH}_2=\text{C}(\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3) \\ \\ \text{CH}_3 \end{array}$	Dow Corning
Z-6040	γ -glycidoxypropyltrimethoxysilane $\text{OCH}_2\text{CH}(\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3)$	Dow Corning
Volan E	Organic acid chrome complex*	E. I. du Pont de Nemours & Company
Volan L	Methacrylato chromic chloride*	Du Pont

* Structural formula for Volan E and L (which respectively contain 17-19 and 19-21% chrome complex):

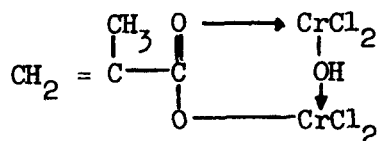


Table 3

TABLE 4

CANDIDATE PLASTICIZERS AND LUBRICANT/WETTING AGENTS

	<u>Trade Designation</u>	<u>Supplier</u>
	Plasticizers	
Aliphatic amide amine	Epi-cure 855	Jones-Dabney Company
Polyamides	Versamid 100, 115, 125, and 140	General Mills, Inc.
Polysulfides	LP-3, LP-8, and LP-33	Thiokol Chemical Corporation
Trimer acid	3162-D	Emery Industries, Inc.
	Lubricant/Wetting Agents	
-	AHCO-185	ICI Organics Company
-	Cirrasol 220	ICI Organics
-	Cirrasol 838	ICI Organics
-	Y-4186	Union Carbide Corporation
-	L-527	Union Carbide

TABLE 5

CANDIDATE RESINS

<u>Type</u>	<u>Trade Name</u>	<u>Supplier</u>
Epoxy	Epon 815, 826, 828, 871, 872, 949A & B, 1028-B-70	Shell Chemical Company
↑	Isochemrez 405, 408	Isochem Resins Company
	DEN 438, DER 331	Dow Chemical Company
↓	Araldite 6005	Ciba Products Company
	ELS-3001, ERRA 0300	Union Carbide Corporation
Epoxy	Oxiron 2000	FMC Corporation
Urethane	Uralane 5721-A	Furane Plastics, Inc.
Urethane	Adiprene L-100	E. I. du Pont de Nemours & Company
Urethane	Narmco 7343	Narmco Materials Division
Silicone	DC-2106	Dow Corning Corporation
Polyamide	XPI-182	American Cyanamid Company
Polyamide	XPI-185	American Cyanamid
Butadiene-styrene	Buton-100	Enjay Chemical Company
Polybutadiene	Buton-150	Enjay
Phenolic	SC 1008	Monsanto Chemical Company
Phenolic elastomer	Narmco 2021	Narmco
Epoxy-nylon	Epon 949	Shell
Polyester	Paraplex P-13	Rohm & Haas Company
Polyester	Paraplex P-43	Rohm & Haas
Polyester	Selectron 5016	Pittsburgh Plate Glass Company
Fluorocarbons	Teflon T-30	Du Pont

TABLE 6
NOL-RING FABRICATION STUDY

Group* No.	Ring No.	Type of Test Specimen	Thickness in.	Type of Glass	Strength at Room Temp ksi**	Remarks	Winding Speed fpm	Resin Content wt%
1	1	Horizontal shear	3/16	4H-1	7.281 (av)	Poor wrap, fila- ments loose on top surface	5,750	13.3
1	2	Horizontal shear	3/16	4H-1	8.274	Good wrap	8,000	13.3
1	3	Tensile strength	3/16	4H-1	130.4	Good wrap	10,000	13.0
2	4	Horizontal shear	3/16	Hi-Stren	Not tested	Poor wrap	7,000	12.8
2	5	↑	3/16	↑	↑	Very loose	4,600	-
2	6	↓	1/4	↓	↓	Extremely loose	7,300	-
2	7	↓	1/4	↓	↓	Extremely loose	2,200	-
2	8	↓	1/4	↓	↓	Extremely loose	2,200	-
2	9	Horizontal shear	3/16	↓	↓	Fair wrap	10,000	-
2	10	Tensile strength	1/8	↓	Not tested	Fair wrap	10,000	-
3	11	↑	1/8	↑	124.6	Good wrap	8,600	11.6
3	12	↓	1/16	↓	Not tested	Fair wrap	10,000	-
3	13	↓	1/8	↓	Not tested	Good wrap, dam- aged on removal from fixture	↑	-
3	14	Tensile strength	1/8	↓	199.1	Good wrap	↑	13.4
4	15	Horizontal shear	1/4	↓	Not tested	Poor wrap, loose	↑	-
4	16	↑	↑	↑	5.000 (av)	Good wrap	↑	11.2
4	17	↓	↓	↓	5.074 (av)	Good wrap	↑	11.3
4	18	Horizontal shear	↓	↓	Not tested	Damaged on re- moval from fixture	↑	11.9
4	19	Horizontal shear	1/4	↓	2.235	Good wrap	↑	10.0
4	20	Tensile strength	1/16	↓	169.4	↑	↑	8.7
4	21	↑	↑	↑	220.3	↓	↑	8.6
4	22	↓	↓	↓	207.9	Good wrap	↑	-
4	23	Tensile strength	1/16	↓	Not tested	Damaged on re- moval from fixture	↑	-
4	24	Horizontal shear	1/4	↓	3.683 (av)	Good wrap	↑	10.2
4	25	Horizontal shear	1/4	↓	3.631 (av)	↑	↑	10.8
4	26	Horizontal shear	1/4	↓	5.242 (av)	↓	↑	10.9
4	27	Tensile strength	1/16	↓	237	Good wrap	↑	11.6
5	28	Horizontal shear	1/4	↓	Not tested	Damaged on re- moval from fixture	↑	8.25
5	29	Horizontal shear	1/4	↓	Not tested	↑	↑	-
5	30	Horizontal shear	1/4	Hi-Stren	Not tested	Damaged on re- moval from fixture	10,000	8.6

Group No.	Application
1	Initial development of NOL-ring winding directly from bushing
2	Development and modification of NOL-ring mandrels
3	Development of starting-collar winding technique
4	Study of fiberization parameters
5	Establishment of range of resin-finish solids content

** (Av) = average as determined from five tests.

Table 6

Ring No.	Resin-Finish Solids, wt%	Composite Properties		Horizontal-Shear Strength		
		Resin Content wt%	Specific Gravity	At Room Temp	After 6-Hour Water Boil	At -423°F
1	-	-	-	-	-	-
2	25	13.3	2.09	6.67	-	-
3	25	12.9	-	5.09	-	-
4	50	10.6	2.19	6.20	-	-
5	50	13.4	-	5.26	-	-
6	50	12.05	2.17	7.92	6.96**	21.4
7	50	10.1	-	4.07	-	-
8	75	10.7	-	7.20	-	-
9	75	11.6	-	8.74***	7.21**	19.2
10	100	13.4	2.18	10.8	8.79	19.2
11	75	10.65	2.17	6.28	-	-
12	100	-	-	6.37	-	-
13	100	11.3	-	6.26	-	-
14	100	14.0	2.14	10.6	8.20	23.0
15	100	12.9	-	9.01**** 8.82	7.58	21.5
16	100	12.0	-	10.4**** 10.6	7.94	19.6
17	100	-	-	-	-	-

* All rings were fabricated of Epon 828/NMA/BDMA in a weight ratio of 52/42/0.5 of the total finish-resin mix. All rings were cured for 1 hour at 200°F and 2 temperature and after a water boil are averages from five tests for each condition.

** Tested after a 2-hour water boil; all other tests followed a 6-hour water boil.

*** Average based on ten tests.

**** The two members of each of these pairs of values represent averages from room-temperature (1) an Instron tensile tester normally used for room-temperature tests, and (2) a Instron tensile tester used for -423°F testing. This was done to provide a comparison between the two methods and the results were again averaged.

70

ONE-STEP APPLICATION)*

Bond Retention, %		Composite Properties			
After 6-Hour Water Boil	At -423°F	Resin Content wt%	Specific Gravity	Water Absorption wt%	Void Content vol%
81.0	177	13.4	2.18	0.09	0.052
63.0	190	11.7	-	0.09	-
69.7	169	12.5	2.18	0.07	0.53
76.3	186	12.6	2.18	0.125	0.76
89.0	193	11.8	2.20	0.032	0.25
-	-	-	-	-	-
67.7	193	12.3	2.18	0.095	2.03
67.0	195	12.2	2.13	0.24	3.09
9.3	196	11.6	2.22	0.124	Negligible
66.8	345	11.8	2.20	0.22	Negligible
89.5	239	11.2	2.21	0.19	0.726

tested for horizontal-shear strength at room temperature and after a 6-hour
 for -423°F are averages from three tests per ring. Water absorption was
 coupling agent was 5.5 wt% of the finish-binder integral mix. Ring 100 was

components and coupling agent under the basic conditions adopted for this

Table 8

COUPLING-AGENT STUDY (

Ring No.	Coupling Agent	Resin Solids wt%	Horizontal-Shear Strength, ksi			Strength
			At Room Temp	After 6-Hour Water Boil	At -423°F	
10	A-1100	100	10.8	8.79	19.2	100
18	A-174	100	10.4	6.53	20.5	100
19	A-186	100	11.9	8.32	20.1	100
21	A-172	100	10.5	8.02	19.5	100
22	Z-6040	100	10.9	9.72	21.0	100
23**	Z-6020	-	-	-	-	-
24	Volan E	100	10.6	7.17	20.5	100
25	Volan L	100	8.83	5.91	17.2	100
26	-	100	11.9	1.10	23.2	100
52	Z-6030	100	8.19	5.47	28.2	100
100	Z-6030	100	10.4	9.34	24.9	100

* Epon 828/NMA/BDMA resin system in a weight ratio of 52/42/0.5. Values reported at room temperature and after water boil are averages from five tests for each condition per ring; values reported at -423°F were determined from the 6-hour water-boil horizontal-shear specimens. The coupling agent used for a data-reproducibility check.

** An NOL ring could not be fabricated due to a reaction between the resin components during the study.

8 (1)

TABLE 7

APPLICATION STUDY*

Strength Retention, %			Winding Speed fpm	Remarks
At Room Temp	After Water Boil	At -423°F		
-	-	-	-	Very loose wrap, ring not completed
-	-	-	2000	Traverse 6 in. above winding mandrel
-	-	-	2000	Traverse 3/4 in. above mandrel
100	-	-	8000	Preheated ring mandrel, 200°F
-	-	-	3000	Poor wrap, voids on side walls
100	87.8	397	4600	Very good appearance, very uniform
-	-	-	8000	4H-1 glass
-	-	-	3500	4H-1 glass
100	82.5	220	3500	Uniform wrap
100	81.0	177	3400	Resin-finish reservoir heated to reduce viscosity
-	-	-	3500	Repeat of Ring 9
-	-	-	-	A-1100 was applied at roller coater, resin finish was applied at pad
-	-	-	3500	Repeat of Ring 12
100	77.7	218	3400	Repeat of Ring 10
100	85.0	241	3400	Repeat of Ring 10
100	75.5	187	3400	Repeat of Ring 10
-	-	-	3400	Repeat of Rings 12 and 13, rings damaged, no test

The A-1100 coupling agent was used for all rings at a concentration of 5.5 wt% hours at 350°F. Except as noted below, the horizontal-shear strengths at room temperature, and the strengths at -423°F are averages from three tests per ring.

temperature testing of five ring segments each (all ten segments from one ring) (2) another Instron tester in the Von Karman Center Cryogenic Facility that was used for strength-retention calculations, the two average values were

COUPLING-AGENT STU

Ring No.	Coupling Agent	Solids, wt%		Horizontal-Shear Strength, ksi			At Room Temp
		Finish (Roller Coat)	Resin (Pad)	At Room Temp	After 6-Hour Water Boil	At -423°F	
27	A-1100	22	100	10.9	2.40	22.1	10
98	A-1100	22	100	11.0	6.44	21.8	10
28	A-174	22	100	11.3	1.27	23.8	10
99	A-174	22	100	11.2	3.24	25.8	10
29**	A-186	22	100	11.4	5.43	20.2	10
30	A-186	22	100	12.3	3.65	22.4	10
102	A-186	22	100	11.4	8.94	21.9	10
31	A-172	22	100	13.4	6.65	27.1	10
32	Z-6040	22	100	12.9	7.55	27.6	10
103A	Z-6040	22	100	10.7	8.52	26.0	10
103B	Z-6040	22	100	10.9	8.62	25.9	10
33	Z-6020	22	100	12.8	8.84	26.0	10
34	Volan E	22	100	13.1	7.54	25.5	10
35	Volan L	22	100	11.9	7.13	24.1	10
26***	-	-	100	11.9	1.10	23.2	10
51	Z-6030	-	100	12.0	6.32	23.8	10

COUPLING-AGENT CONCENTR

Ring No.	Concentration, wt%		Horizontal-Shear Strength, ksi			At Room Temp
	Coupling Agent (Roller Coat)	Resin Solids (Pad)	At Room Temp	After 6-Hour Water Boil	At -423°F	
79	37.5	100	11.2	7.90	22.0	100
80	20.0	100	11.4	5.49	23.7	100
81	3.6	100	10.7	3.79	24.8	100
105	5.7	100	11.2	8.33	25.4	100

* Epon 828/NMA/BDMA resin system in a weight ratio of 52/42/0.5. Values reported are averages from five tests for each condition per ring. Water absorption with agent was 1.2 wt% of the finish and binder resin. Rings 98, 99, 102, 103A, and

** Excessive filament breakage during winding; this evaluation was repeated with

*** The results for Ring 26, wound without a coupling agent, are included for comparison

**** Epon 828/NMA/BDMA resin system in a weight ratio of 52/42/0.5.

TABLE 9-10 (1)

UATION STUDY

ds, wt%	Finish	Horizontal-Shear Strength, ksi			Strength Retention, %			Composite Properties		
		At Room Temp	After 6-Hour Water Boil	At -423°F	At Room Temp	After 6-Hour Water Boil	At -423°F	Resin Content wt%	Specific Gravity	Water Absorption wt%
-		2.23	2.17	-	100	-	-	10.2	2.19	0.36
-		7.16	4.14	24.8	100	57.7	346	13.7	2.12	0.54
-		7.17	3.91	17.5	100	54.4	243	10.7	2.20	0.26
-		10.6	8.30	21.0*	100	-	-	-	-	0.15
		ged on removal from mandrel			-	-	-	-	-	-
-		-	-	-	-	-	-	-	-	-
22		9.10	3.55	22.5	100	39	247	12.8	2.18	0.29
22		6.05	3.46	20.5	100	57.2	338	11.3	2.20	0.20
22		4.05	2.16	11.6	100	53.5	286	11.5	2.22	0.13
-		-	-	-	-	-	-	-	-	-
22		2.32	2.30	13.0	100	99.5	564	7.1	2.12	1.11
-		1.87	No test	No test	100	-	-	26.9	1.59	8.2
-		11.4	6.00	22.8	100	52.7	200	-	-	0.16
5	None	Damaged on removal from ring mandrel			-	-	-	7.5	-	-
	None	2.35	Damaged on removal from ring mandrel			-	-	13.2	-	-
0	None	1.48	No test	10.7	100	-	720	7.4	2.08	-
5	None	Rings unsatisfactory on inspection			-	-	-	10.9	1.96	-
	None	2.71	No test	11.2	100	-	414	8.5	2.12	1.1
5	None	4.32	No test	8.43	100	-	195	6.2	2.04	14.5

Table 11, Sheet 1



Ring No.	Resin		Coupling Agent	Hardener		Cure		Sol. Resi
	System	Type		Material	Amount pphr	Time hours	Temp °F	
40	ELS-3001	Phenolic	A-1100	BDMA	1.5	1 2	200 350	70
41	Isochemrez 408	Epoxy	A-1100	Isochem 408	22	0.67	212	100
42	Isochemrez 405	Epoxy	A-1100	Isochem 50	18	1	212	75
43	Epon 826	Epoxy	A-1100	NMA	80	1	200	100
				BDMA	0.5	2	350	
44	Epon 871	Epoxy	A-1100	BF ₃ -400	3.0	1 2	200 350	Dama
45	Epon 872	Epoxy	A-1100	BF ₃ -400	3	Set up in pot		-
46	Epon 828/872 (50/50 wt%)	Epoxy	A-1100	NMA	80	1	200	100
				BDMA	0.5	2	350	
47	Epon 828/871 (50/50 wt%)	Epoxy	A-1100	NMA	80	1	200	100
				BDMA	0.5	2	350	
48	Epon 1028-B-70	Epoxy	A-1100	NMA	80	1	200	70
				BDMA	0.5	2	350	
49	Isochemrez 405	Epoxy	A-1100	Isochem 50	18	Set up in pot		-
50	Epon 826/Epon 871/ Adiprene L-100 (35/25/50 wt%)	Epoxy-urethane	A-1100	MOCA	27.6	5	285	70
54	Araldite 6005	Epoxy	A-1100	Araldite 907	85	2 2	212 300	100
55	Araldite 6005	Epoxy	A-1100	Araldite 830	60	2 2	210 300	100
56	SC-1008	Phenolic	A-1100	None	-	0.5 0.5 0.5 0.5	200 250 300 350	60-6
57	Selectron 5003	Polyester	A-172	Benzoyl peroxide	4.0	0.5 1.0	170 250	66
58	Buton-100	Butadiene-styrene	A-172	Dicumyl peroxide	4.0	2 3	300 320	50.
59	Buton-500	Butadiene-styrene	A-172	Dicumyl peroxide	4.0	2 3	300 320	52.
60	Buton-150	Polybutadiene	A-172	Dicumyl peroxide	4.0	1	320	50
61	SC-1008	Phenolic	A-1100	None	-	0.5 0.5 0.5 0.5	200 250 300 350	60-6

* Test conducted at -320°F.

TABLE II, SHEET 1 (1)

TABLE 9

BY (TWO-STEP APPLICATION)*

<u>Strength Retention, %</u>			<u>Composite Properties</u>			
	<u>After</u> <u>6-Hour</u> <u>Water Boil</u>	<u>At</u> <u>-423°F</u>	<u>Resin</u> <u>Content</u> <u>wt%</u>	<u>Specific</u> <u>Gravity</u>	<u>Water</u> <u>Absorption</u> <u>wt%</u>	<u>Void</u> <u>Content</u> <u>vol%</u>
0	22.0	202	11.6	2.21	0.15	0.04
0	58.0	197	11.5	2.22	0.144	0.00
0	11.3	211	11.7	2.21	0.24	0.015
0	28.8	229	12.0	2.22	0.25	Negligible
0	48.0	178	11.7	2.22	0.22	Negligible
0	29.6	182	11.2	2.23	0.19	Negligible
0	78.2	192	12.5	2.18	0.13	0.522
0	49.6	202	11.5	2.22	0.094	Negligible
0	58.5	216	11.8	2.22	0.092	Negligible
0	80.0	244	11.8	2.21	0.24	Negligible
0	78.6	236	11.6	2.23	0.18	Negligible
0	69.0	203	11.9	2.21	0.054	0.075
0	57.4	194	12.6	2.20	0.07	Negligible
0	59.7	203	11.3	2.22	0.24	Negligible
0	9.3	195	11.6	2.22	0.124	Negligible
0	52.5	197	11.7	2.21	0.192	Negligible

TABLE 10

BY (TWO-STEP APPLICATION)****

<u>Strength Retention, %</u>			<u>Composite Properties</u>			
	<u>After</u> <u>6-Hour</u> <u>Water Boil</u>	<u>At</u> <u>-423°F</u>	<u>Resin</u> <u>Content</u> <u>wt%</u>	<u>Specific</u> <u>Gravity</u>	<u>Water</u> <u>Absorption</u> <u>wt%</u>	<u>Void</u> <u>Content</u> <u>vol%</u>
	70.6	197	11.9	2.23	0.19	Negligible
	48.3	209	11.5	2.23	0.23	Negligible
	35.2	231	11.3	2.23	0.35	Negligible
	74.3	225	11.5	2.22	0.118	-

tested for horizontal-shear strength at room temperature and after a 6-hour water boil as determined from the 6-hour water-boil horizontal-shear specimens. The coupling and 103B were used for data-reproducibility checks.

Ring 30.

comparison.

TABLE 1

Ring No.	Resin		Coupling Agent	Hardener		Cure		Sol. Resi.
	System	Type		Material	Amount pphr	Time hours	Temp °F	
62	Paraplex P-13	Polyester	A-172	Benzoyl peroxide	1.0	0.5 0.5 0.5 2.0	200 250 300 350	46.
63	Narmco 2021	Nitrile phenolic	None	None		System cobwebbed		20
64	Paraplex P-13/P-43 (50/50 wt%)	Polyester	A-172	Benzoyl peroxide	4.0	1 2	200 250	100
65	Araldite 6005	Epoxy	A-1100	Araldite 957	20	2 2	175 300	100
104A	Data-reproducibility test, composition and cure same as Ring 65				-	-	-	-
104B	Same				-	-	-	-
66	Epon 949A	Epoxy-nylon	A-1100	Epon 949B	12	0.25 1.0	200 350	17.
67	Finish: Epon 949A Resin: Epon 828	Epoxy-nylon Epoxy	A-1100	Epon 949B NMA BDMA	12 80 1	1 1 2	200 250 350	100
68	Finish: Epon 949A Resin: Epon 828	Epoxy-nylon Epoxy	A-1100	Epon 949B NMA BDMA	12 80 1	1 1 2	200 250 350	100
69	ERRA 0300	Epoxy	A-1100	Shell Curing Agent "Z"	20	2 2	175 300	100
70	DER 331	Epoxy	A-1100	NMA BDMA	80 0.5	1 1 2	200 250 350	100
71	DEN 438	Novolac epoxy	A-1100	NMA BDMA	101 0.5	1 2	250 380	100
72	DEN 438/DER 331 (55.6/44.4 wt%)	Epoxy	A-1100	NMA	100	1 2	250 380	100
73	DC-2106	Silicone	None	Dow Corning 15	5	16 2 2 2	200 260 325 400	59
74	DC-2106	Silicone	A-1100	Benzoyl peroxide	4.5	16 2 2 2	200 260 325 400	59
75	Paraplex P-43	Polyester	A-172	Benzoyl peroxide	4.0	1.5 0.5	260 325	-
76	Oxiron 2000	Epoxy-polyester	A-1100	HHPA PPG	80.0 8.0	4	310	-
77	Narmco 7343	Urethane	A-1100	Narmco 7139	11	1	290	-

* Epon 949 (epoxy-nylon) with A-1100 and methyl alcohol used as finish solution.

** Same finish as above, except pH adjusted to 5.0 with formic acid.

TABLE 11, SHEET 2 (1)

12
 (STEP FINISH APPLICATION)*

Strength Retention, %		Composite Properties			
After 6-Hour Water Boil	At -423°F	Resin Content wt%	Specific Gravity	Water Absorption wt%	Void Content vol%
81.0	-	11.0	2.2	0.13	Negligible
67.0	-	-	-	0.17	0.663
68.5	-	-	-	0.244	0.439
81.8	-	-	-	0.13	Negligible

13
 (ONE-STEP APPLICATION)**

ksi	Strength Retention, %			Composite Properties			
	At Room Temp	After 6-Hour Water Boil	At -423°F	Resin Content wt%	Specific Gravity	Water Absorption wt%	Void Content vol%
8	100	77.2	239	11.3	2.22	0.18	0.144
6	100	71.3	236	11.2	2.23	0.19	Negligible
2	100	69.0	247	9.9	2.21	0.28	0.906
4	100	52.5	270	10.1	2.22	0.217	1.12
9	100	51.0	219	11.3	2.21	-	0.661

14
 (ONE-STEP APPLICATION)***

ksi	Strength Retention, %			Composite Properties				
	At -423°F	At Room Temp	After 6-Hour Water Boil	At -423°F	Resin Content wt%	Specific Gravity	Water Absorption wt%	Void Content vol%
System	-	-	-	-	-	-	-	-
23.2	100	52	237	11.3	2.20	0.104	-	
7.05	100	-	2560	10.2	2.13	-	5.65	
12.4	100	78	1160	10.7	1.97	0.197	11.65	
mandrel	-	-	-	-	-	-	-	
21.0	100	42	443	10.5	2.20	0.29	1.31	
19.5	100	44	473	11.3	2.22	0.082	Negligible	

MA in a 52/42/0.5 weight ratio and A-1100 coupling agent (5.5 wt% of the
 A-1100 coupling agent (5.2 wt% of the total mix), and the lubricant/
 Agent "D" were combined with coupling agent A-186 (5.5 wt% of total mix).

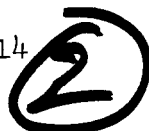


TABLE 1

SURFACE-WATER DISPLACEMENT (ONE

Ring No.	Displacing Agent	Horizontal-Shear Strength, ksi			Stress At Room Temp
		At Room Temp	After 6-Hour Water Boil	At -423°F	
36	Isopropyl alcohol	10.0	8.12	20.7	100
37	Methanol	10.6	7.12	21.1	100
38	MEK	10.4	7.14	23.0	100
39	Acetone	10.2	8.34	20.5	100

TABLE 1

LUBRICANT/WETTING-AGENT STUDY

Ring No.	Agent		Horizontal-Shear Strength, ksi		
	Material	Concentration wt%	At Room Temp	After 6-Hour Water Boil	At -423°F
82	Cirrasol 220	0.1	10.4	8.02	24
83	AHCO-185	0.1	10.1	7.13	24
84	Cirrasol 838	0.1	9.38	6.46	23
85	Y-4186	1.0	9.04	4.75	24
86	L-527	0.5	10.0	5.12	21

TABLE 1

STUDY OF FLEXIBILIZERS (

Ring No.	Epon Resin	Material	Wt% of Total Mix	Horizontal-Shear Strength	
				At Room Temp	After 6-Hour Water Boil
87	-	Versamid 125	Ring could not be wound from this s		
88	815	Versamid 140	30.0	9.79	5.11
89	815	LP-3	45.5	0.275	No test
90	815	LP-3	23.0	1.08	0.837
91	815	LP-3	70.0	Damaged on removal from	
92	815	LP-3	5.0	4.72	1.98
93	828	LP-3	22.0	4.14	1.81

* Displacing agent applied by roller coater. Epon 828/NMA/BDMA finish-binder mix) applied by the pad technique.

** Epon 828/NMA/BDMA resin system in a 52/42/0.5 weight ratio wetting agent were applied by the pad technique.

*** 100 parts by weight of Epon resin to 10 parts of Shell Cur:

TABLES 12, 14, 17

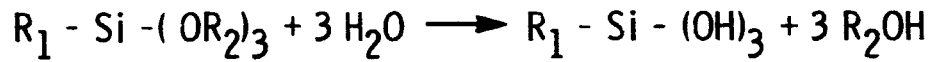
1 (cont.)

Finish	Horizontal-Shear Strength, ksi			Strength Retention, %			Composite Properties		
	At Room Temp	After 6-Hour Water Boil	At -423°F	At Room Temp	After 6-Hour Water Boil	At -423°F	Resin Content wt%	Specific Gravity	Water Absorption wt%
None	0.567	No test	13.2	100	-	2300	9.75	2.20	0.2
None	-	-	-	-	-	-	-	-	-
None	3.14	-	9.00	100	-	287	11.1	2.2	0.3
None	9.19	-	26.6	100	-	289	11.8	2.18	0.12
-	9.95	9.26	20.5	100	93.2	206	11.4	2.21	0.11
-	10.2	9.55	23.0	100	93.1	225	11.4	2.22	0.12
None	3.23	2.76	8.68	100	85.8	-	7.07	1.91	-
4.8*	Specimens cracked during cutting			-	-	-	10.9	-	-
4.8**	4.41	No test	7.80	100	-	177	11.0	-	9.4
None	2.72	2.81	1.97	100	103.0	73	11.6	1.99	3.28
None	Ring damaged	-	-	-	-	-	-	-	-
None	10.6	-	23.9	100	-	227	12.3	2.21	0.13
None	10.6	-	19.1	100	-	-	14.2	2.17	0.20
None	Rings unsatisfactory on inspection			-	-	-	-	1.99	3.2
None	1.47	1.60	2.56	100	108	173	-	2.06	3.2
None	2.54	2.33	4.77	100	91.5	187	10.4	2.18	0.85
None	4.90	3.27	9.58	100	66.6	196	10.7	2.18	0.62
None	No test	No test	3.59	-	-	-	-	-	-

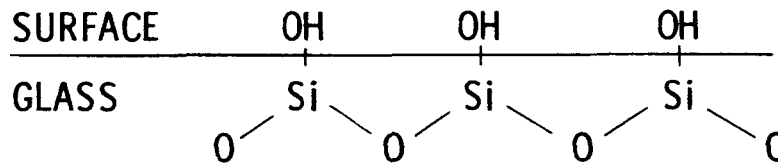
Table 11, Sheet 2



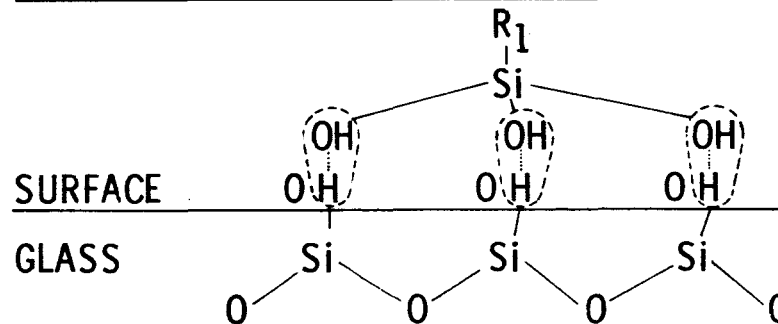
STEP I. THE COUPLING AGENT IS HYDROLYZED AS FOLLOWS:



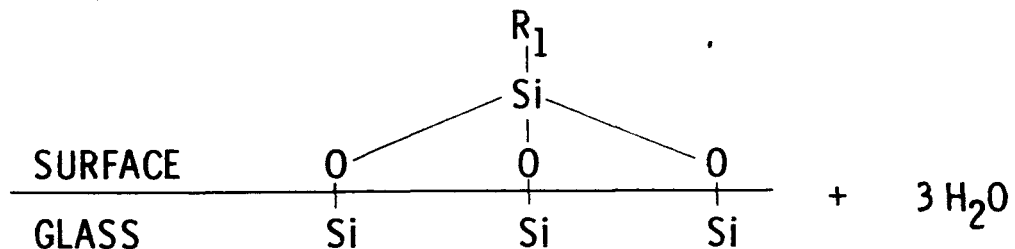
THE GLASS FIBER HAS AVAILABLE HYDROXYLS ON THE SURFACE REPRESENTED AS FOLLOWS:



STEP II. THE HYDROLYZED COUPLING AGENT CAN THEN REACT WITH SILANOL GROUPS ON THE GLASS SURFACE:

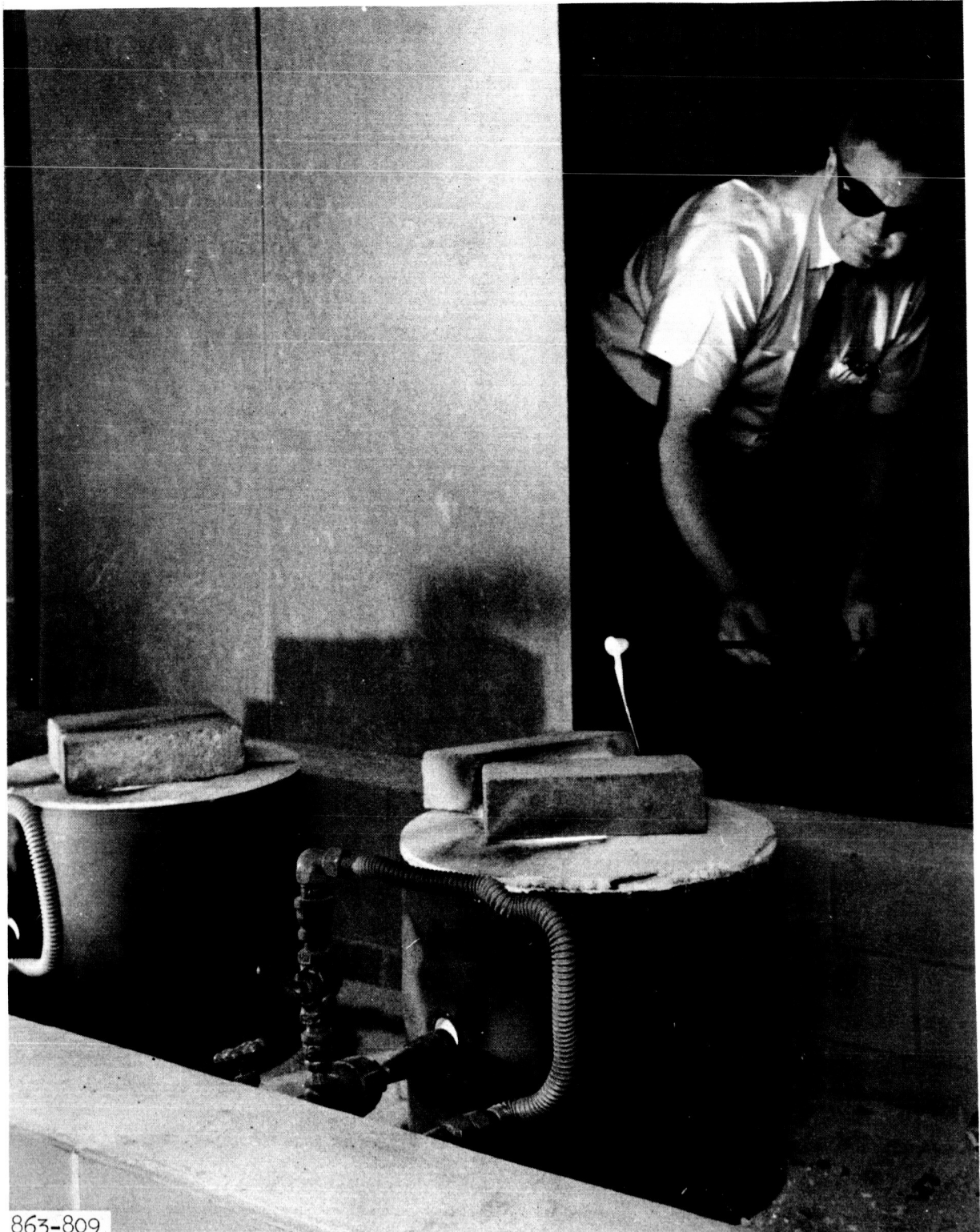


STEP III. THE CONDENSATION REACTION RESULTS IN THE FOLLOWING:



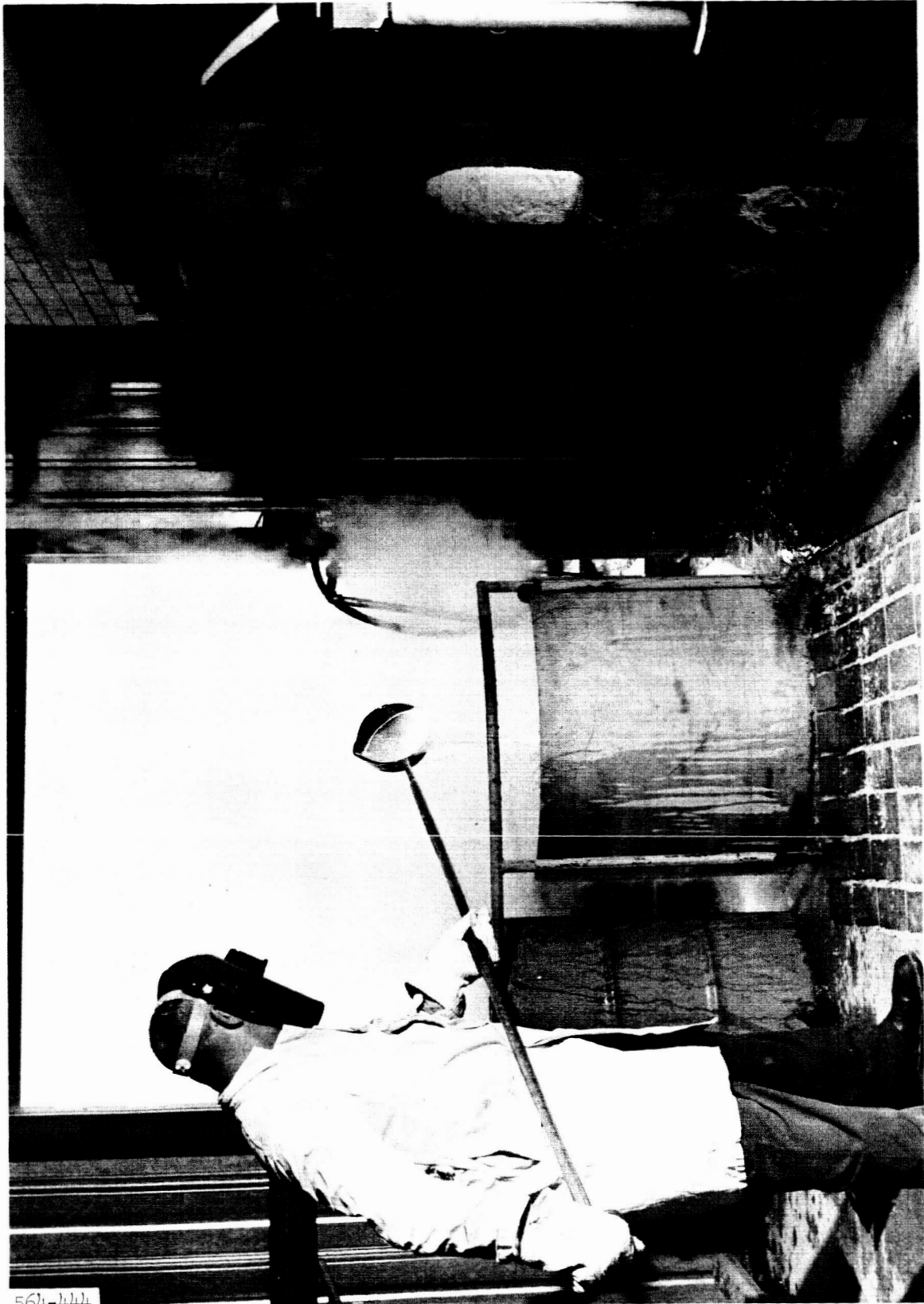
Possible Mechanism for Coupling-Agent Reaction with Glass-Filament Surface

Figure 1



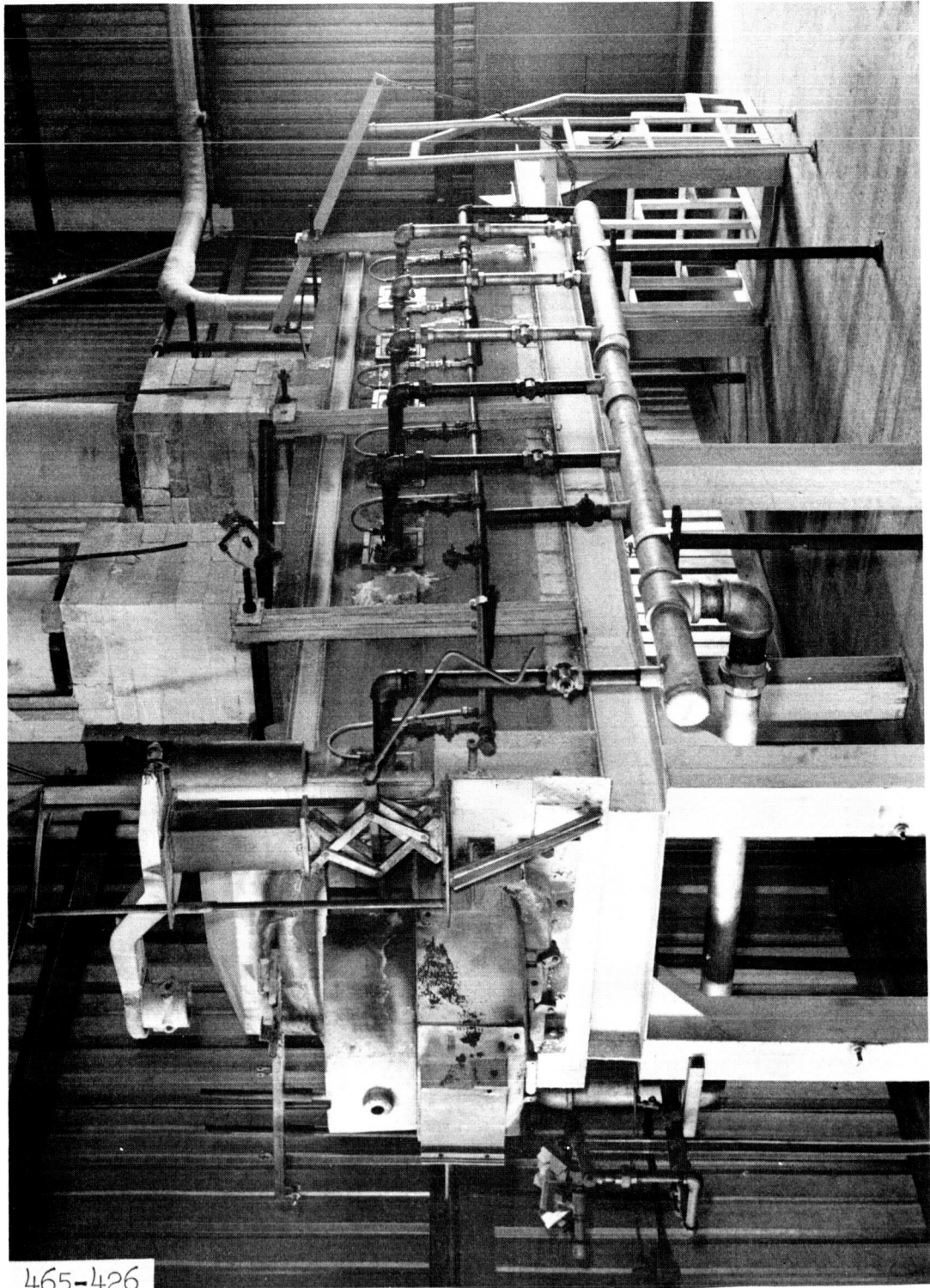
Laboratory Glass-Melting Furnaces, 1 lb Capacity

Figure 2



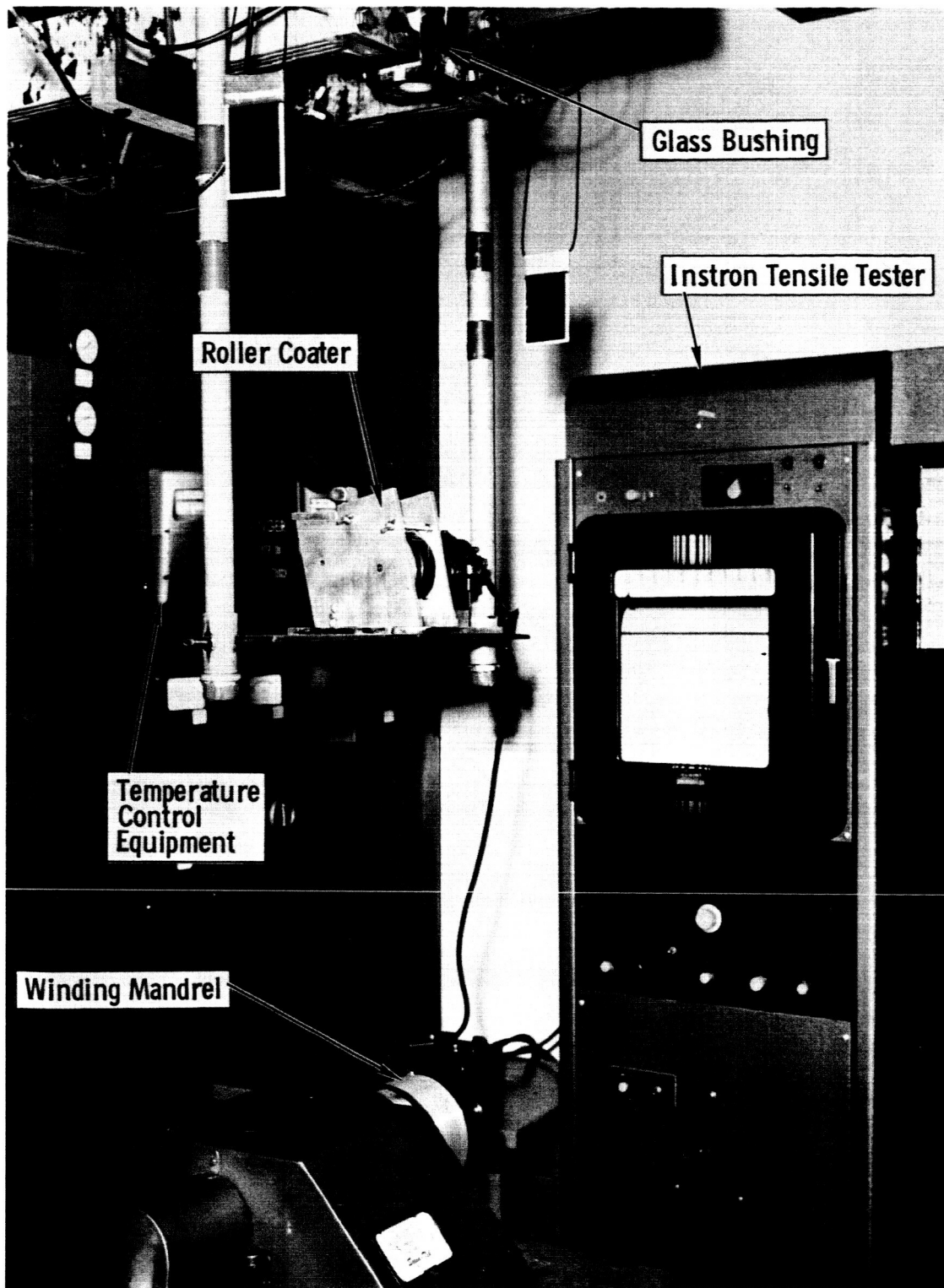
Glass-Melting Furnace, 2000 lb Capacity

Figure 3



Marble Furnace

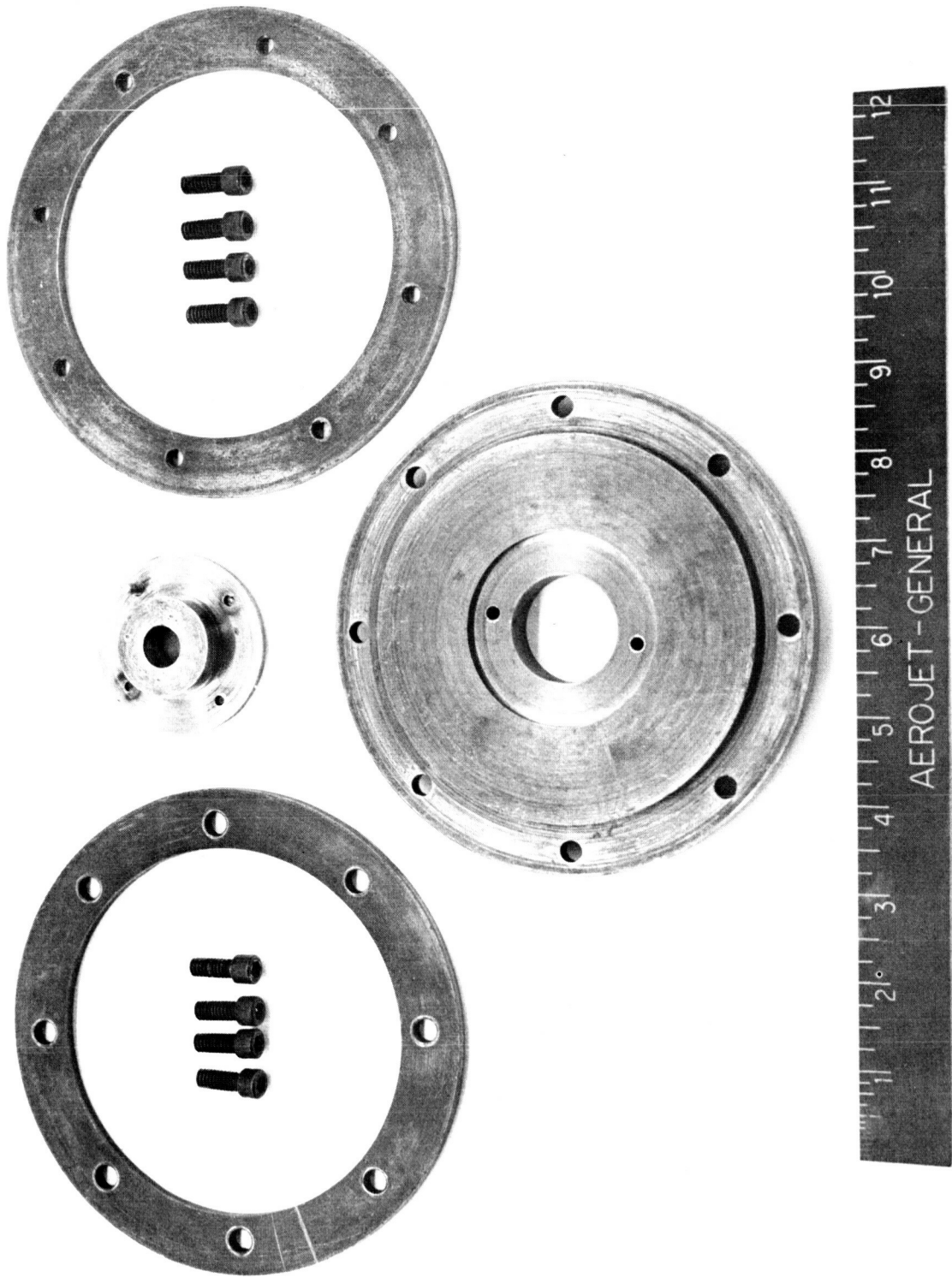
Figure 4



Monofilament-Fiber Furnace with Filament-Coating
and Ring-Winding Equipment

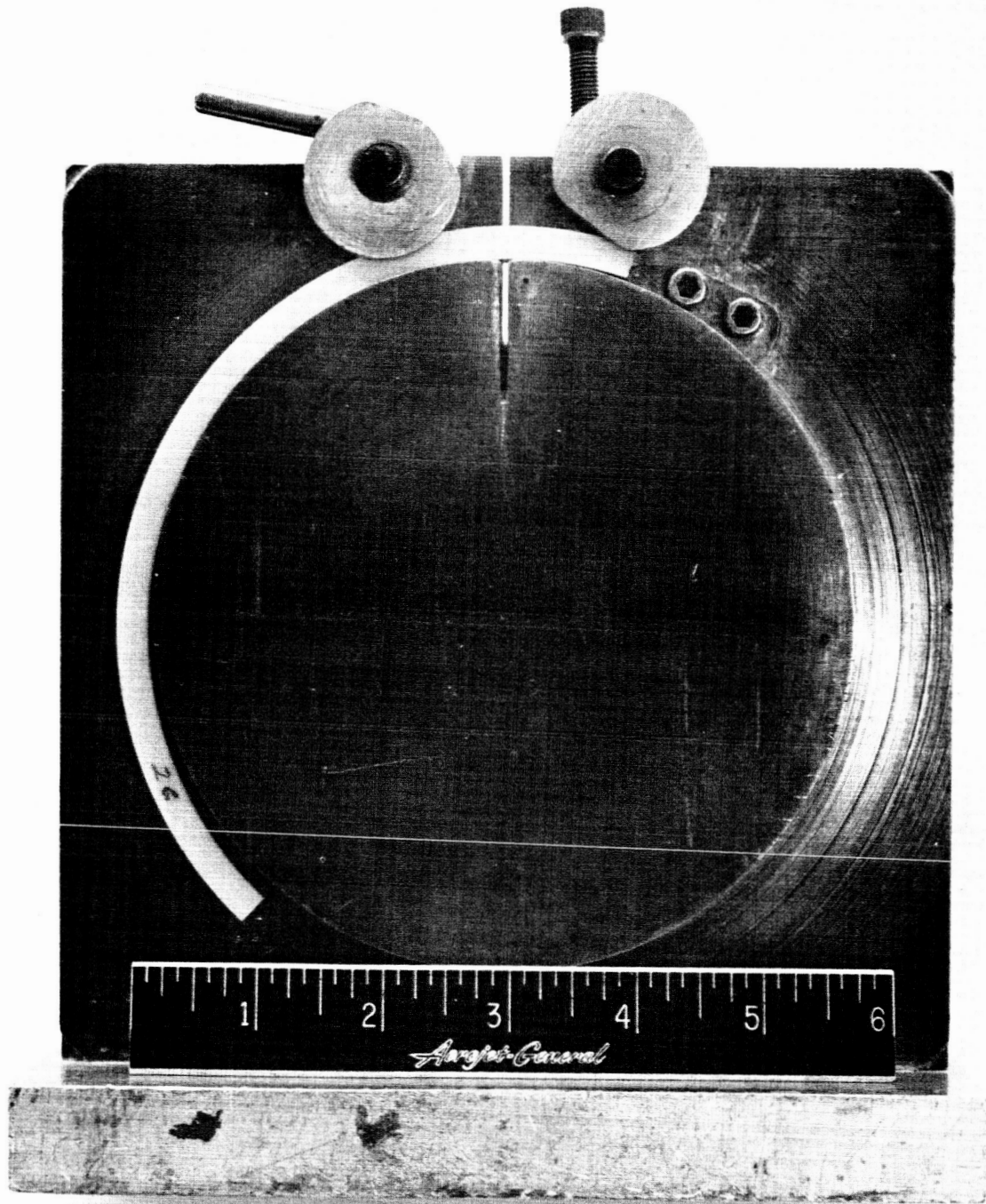
Figure 5

1065-009



NOL-Ring Fabrication Fixture, Disassembled

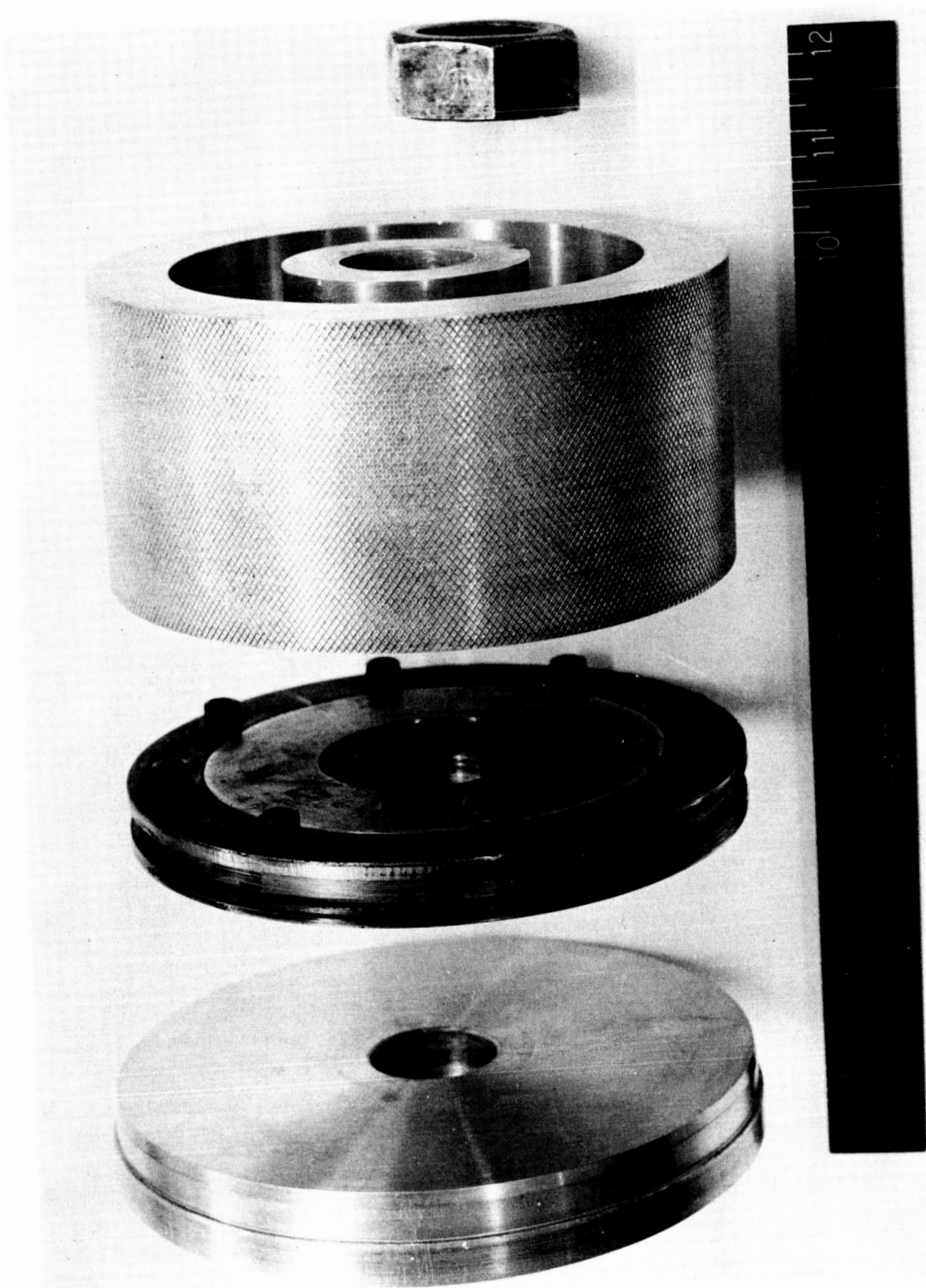
Figure 6



1065-007

NOL-Ring Cutting Fixture

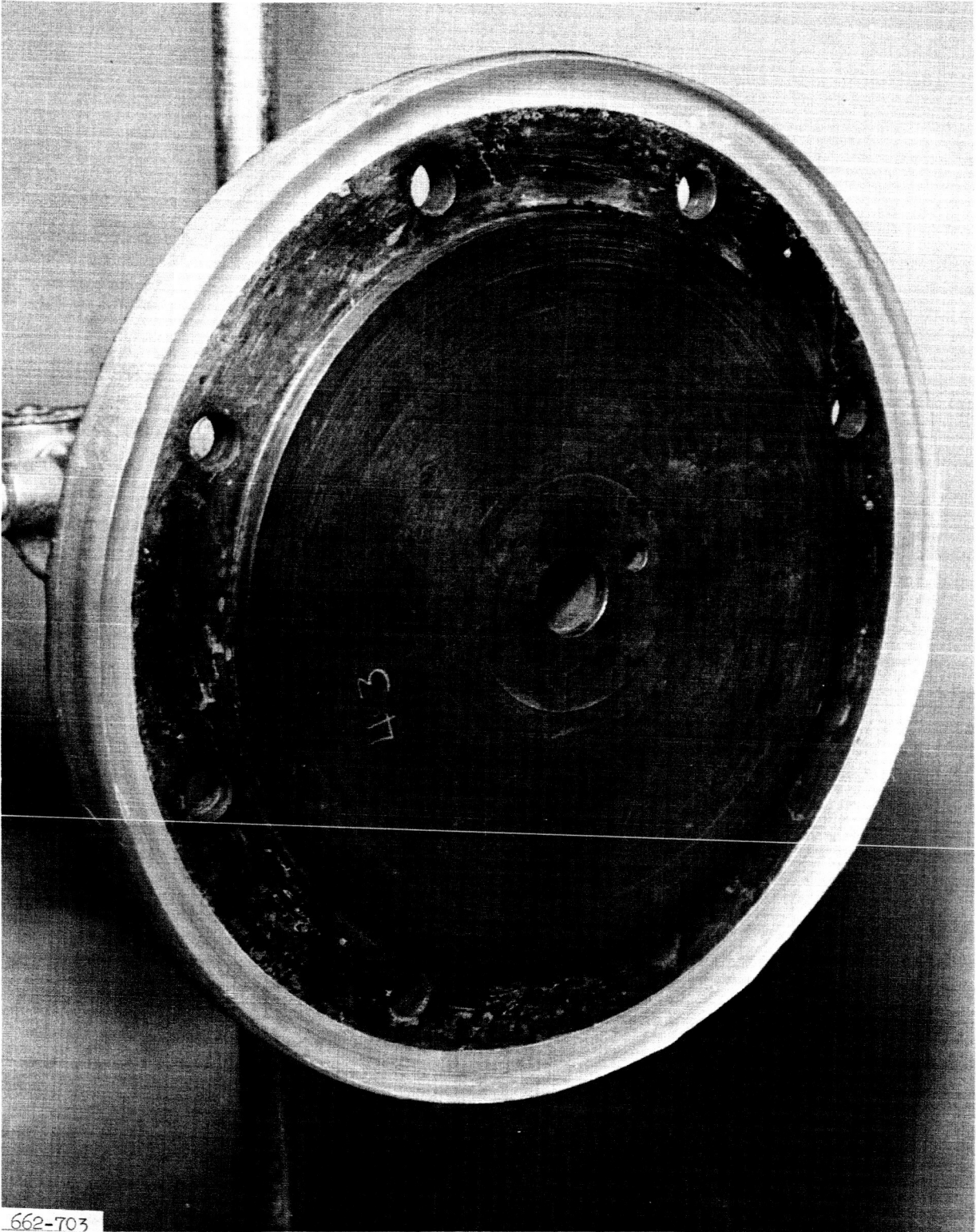
Figure 7



Starting and NOL-Fabrication Fixtures

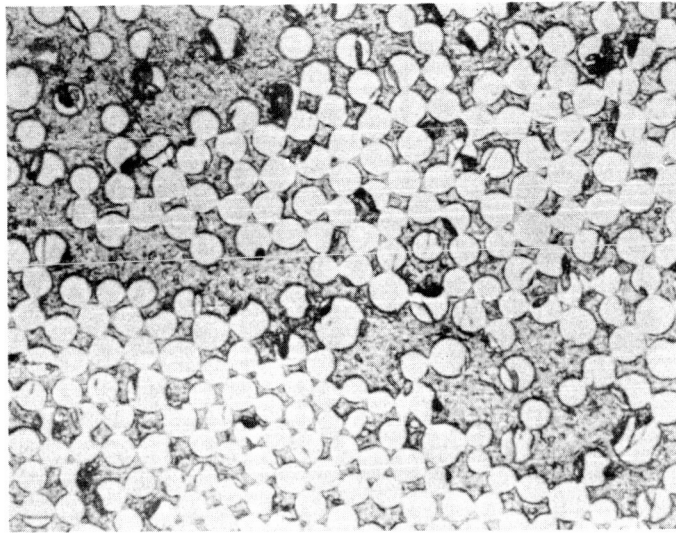
1065-008

Figure 8



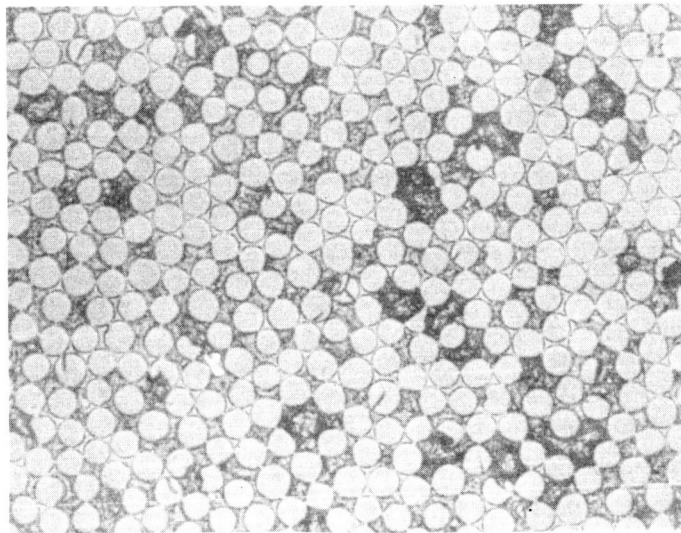
NOL Ring on Ring Fixture

Figure 9



560X

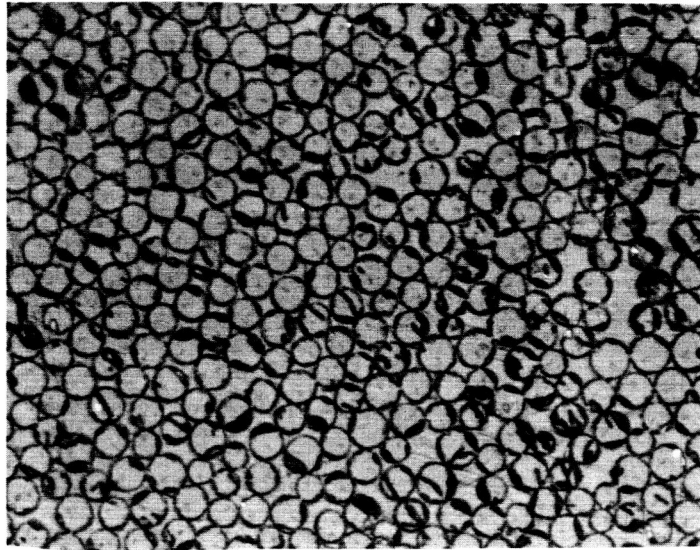
- A. Fabricated of Owens Corning, S-994, 20-end, prepreg roving with HTS finish and 787 resin system; void area existed throughout specimen.



500X

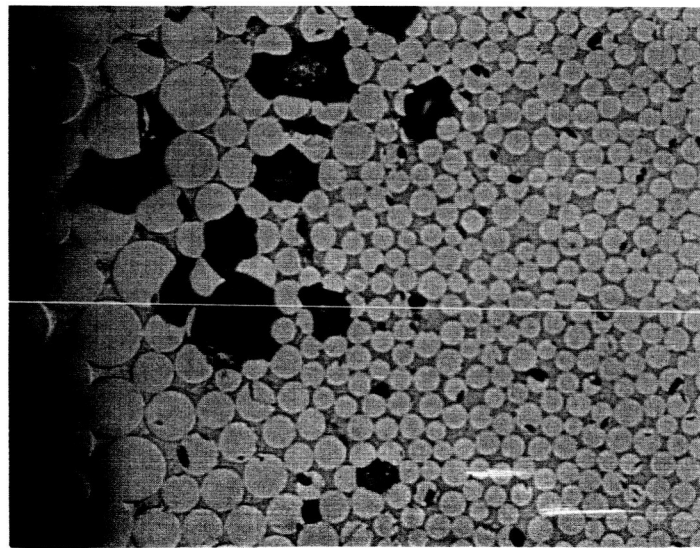
- B. Wound with 4H-1 glass at 10,000 fpm, having uniform fiber diameters and relatively void-free structure.

Cross Sections of NOL Rings, Photomicrographs



500X

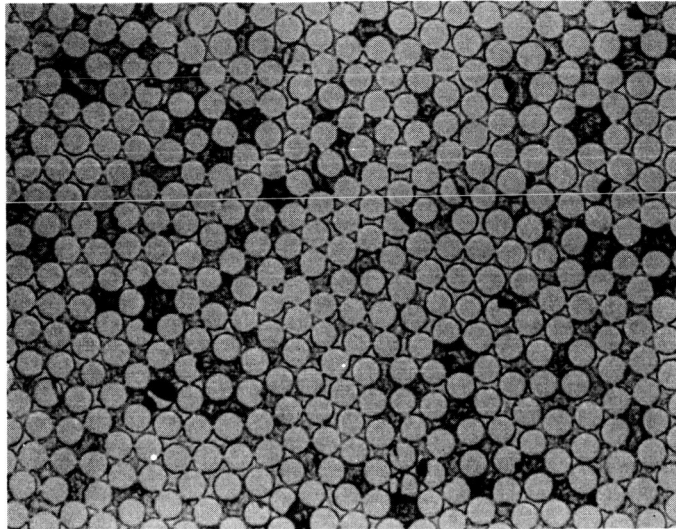
- A. Wound with 4H-1 glass at 8000 fpm. Dense composite laminate having uniform filament diameters and void-free structure.



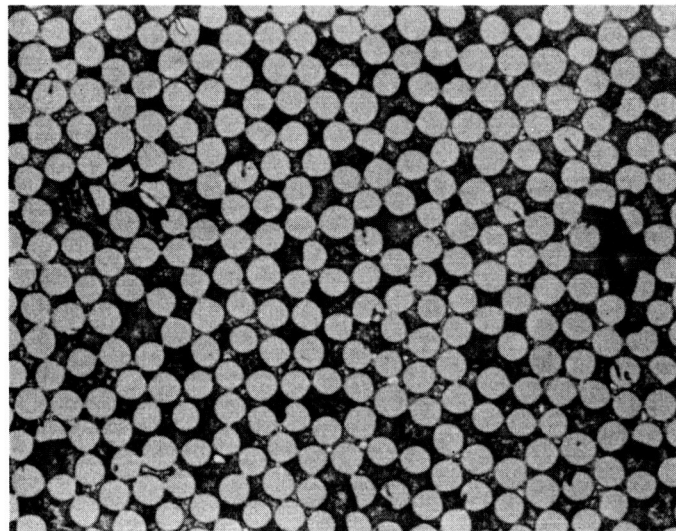
400X

- B. Large-diameter fibers resulted from winding in NOL-ring mandrel before the desired winding speed was attained (when the filaments had a uniform diameter, as shown).

Cross Sections of NOL Rings, Photomicrographs

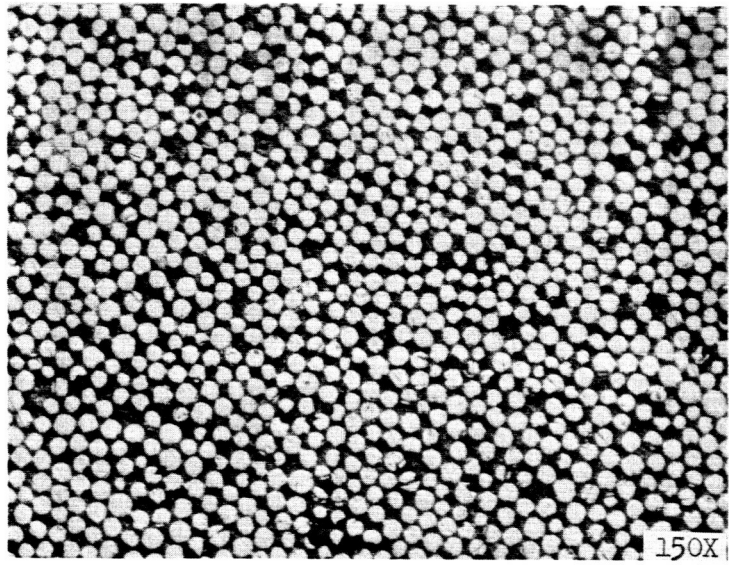


500X

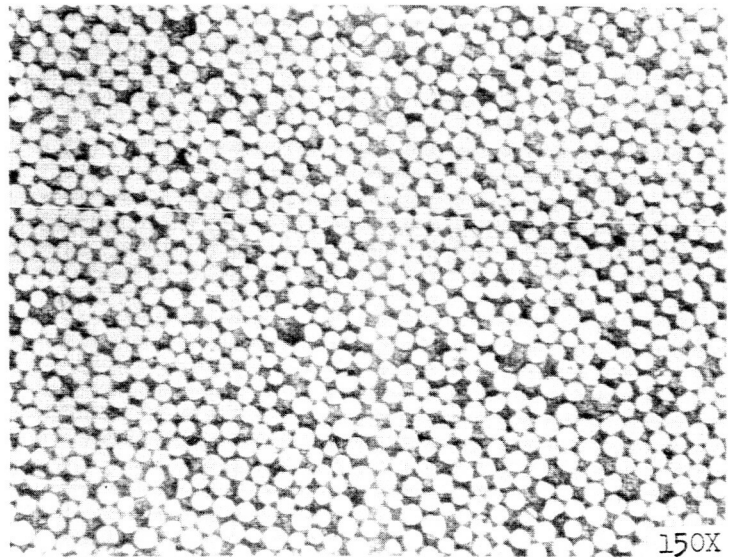


500X

NOL-Ring Fabrication Study, Monofilament Packing (Photomicrographs)



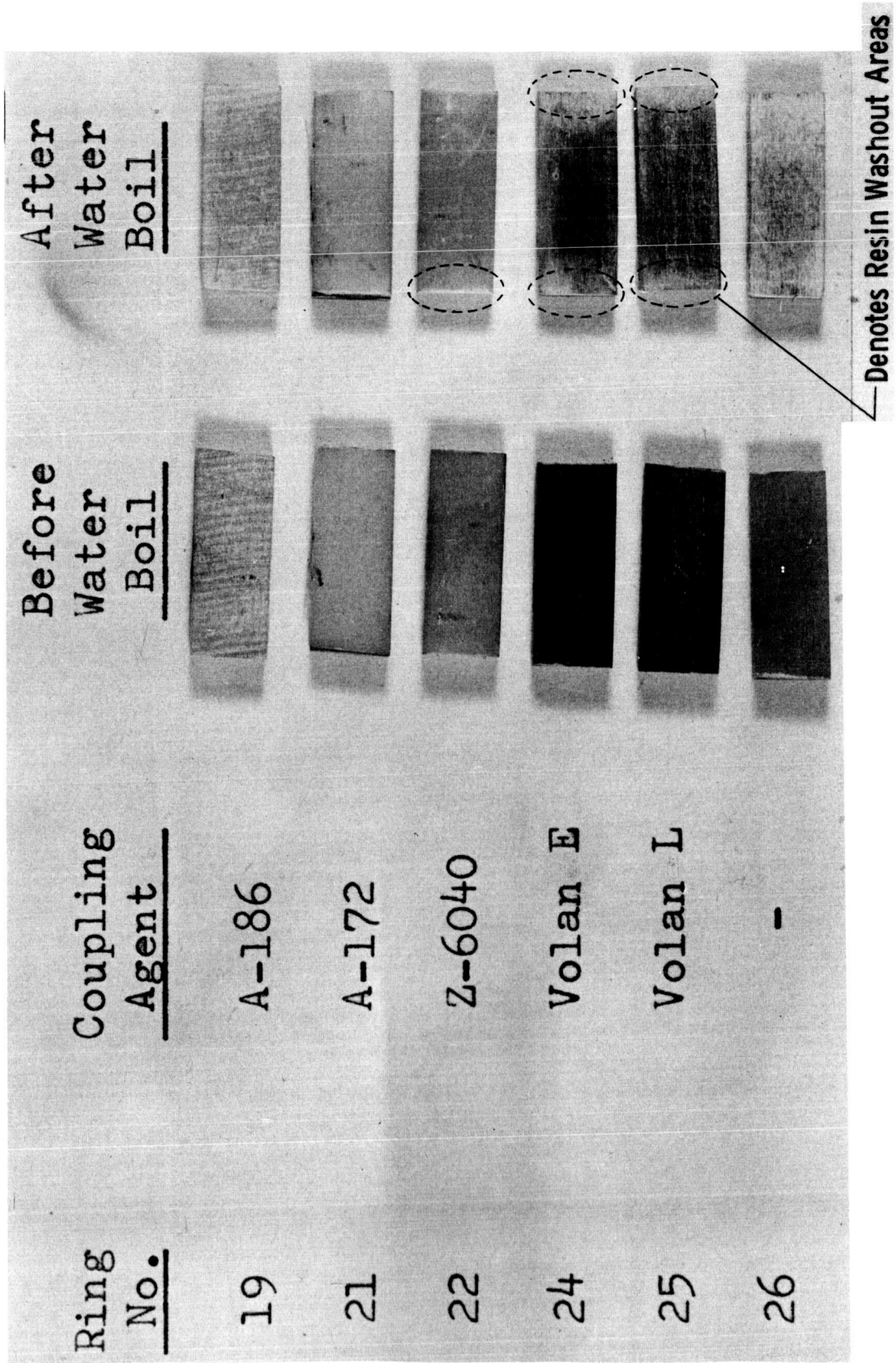
Before Water Boil



After Water Boil

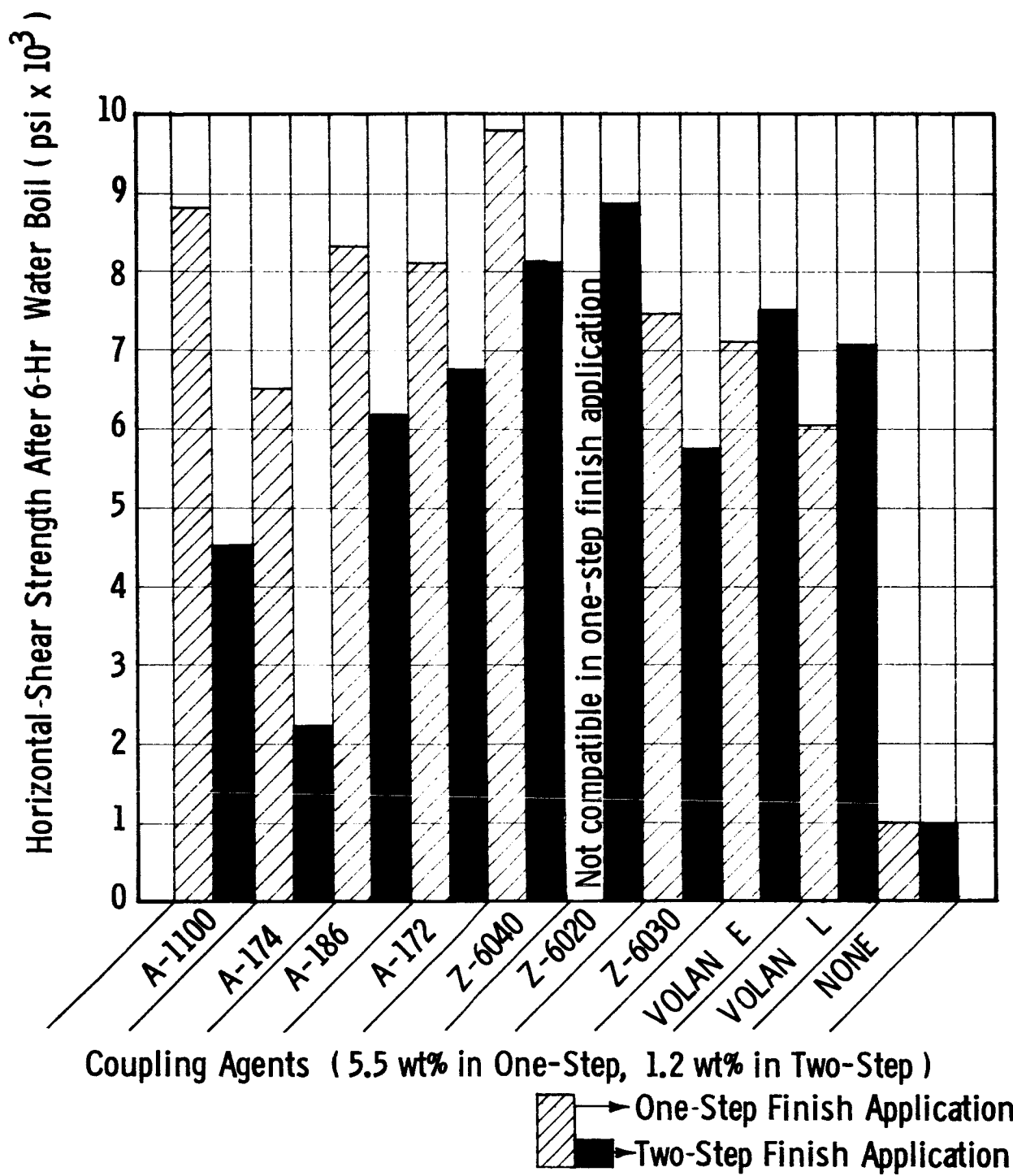
NOL-Ring Fabrication Study, Monofilament Packing (Photomicrographs)

Figure 13



Coupling-Agent Study, Before and After Water Boil

Figure 14

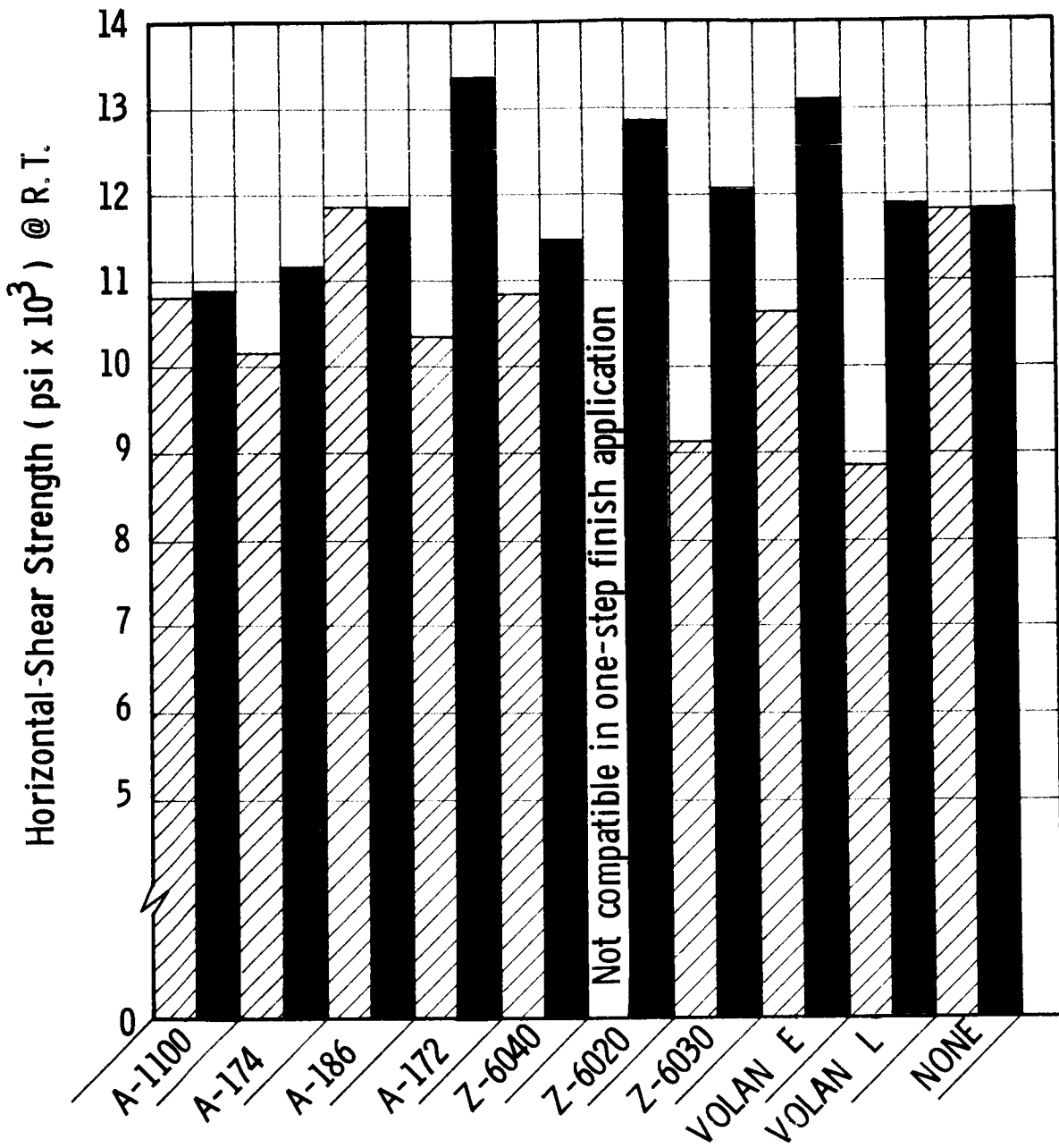


Coupling Agents (5.5 wt% in One-Step, 1.2 wt% in Two-Step)

One-Step Finish Application
 Two-Step Finish Application

Effect of Finish Application Containing Various Coupling Agents on Horizontal-Shear Strength After 6-Hour Water Boil

Figure 15

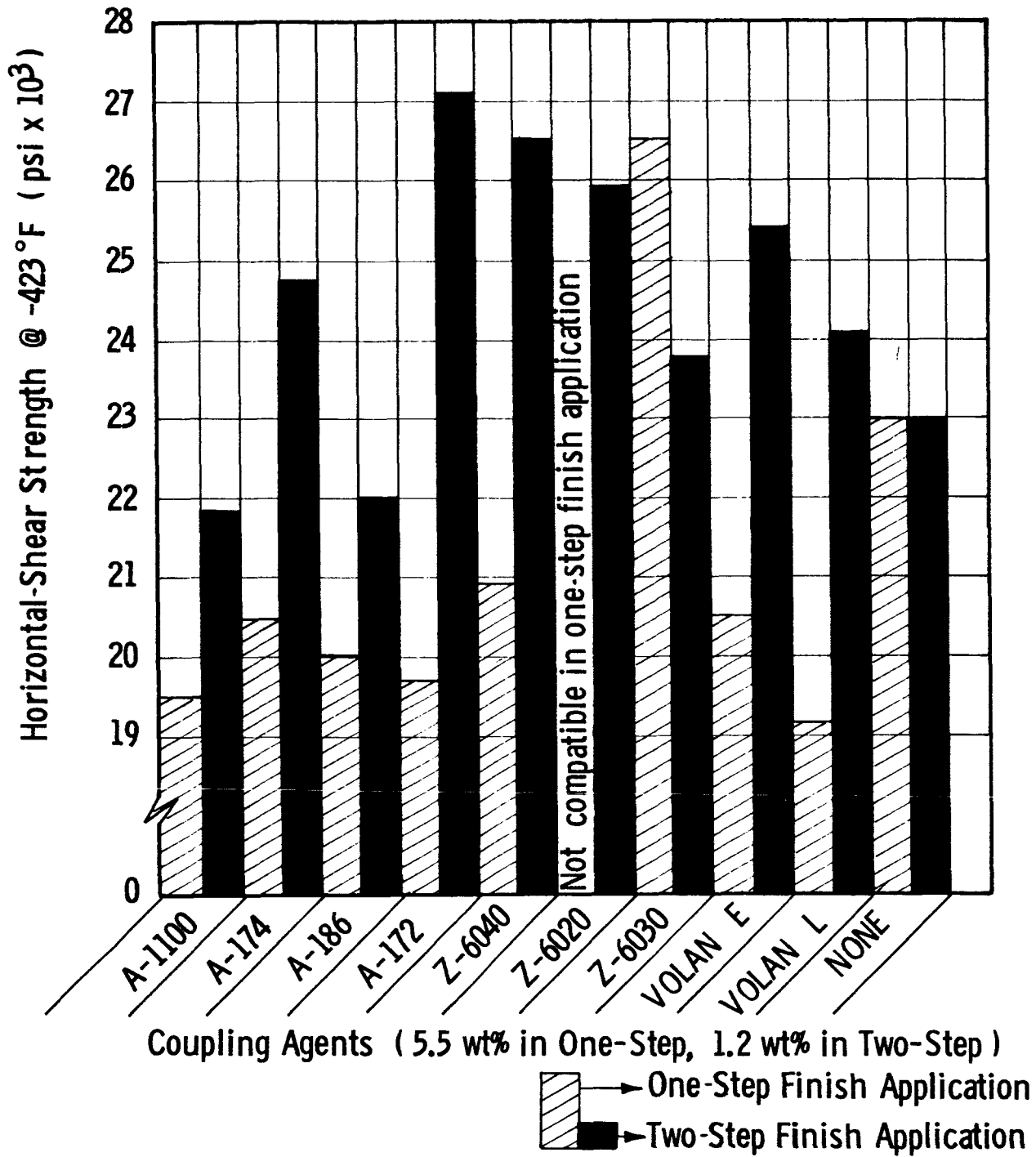


Coupling Agents (5.5 wt% in One-Step, 1.2 wt% in Two-Step)

 One-Step Finish Application
 Two-Step Finish Application

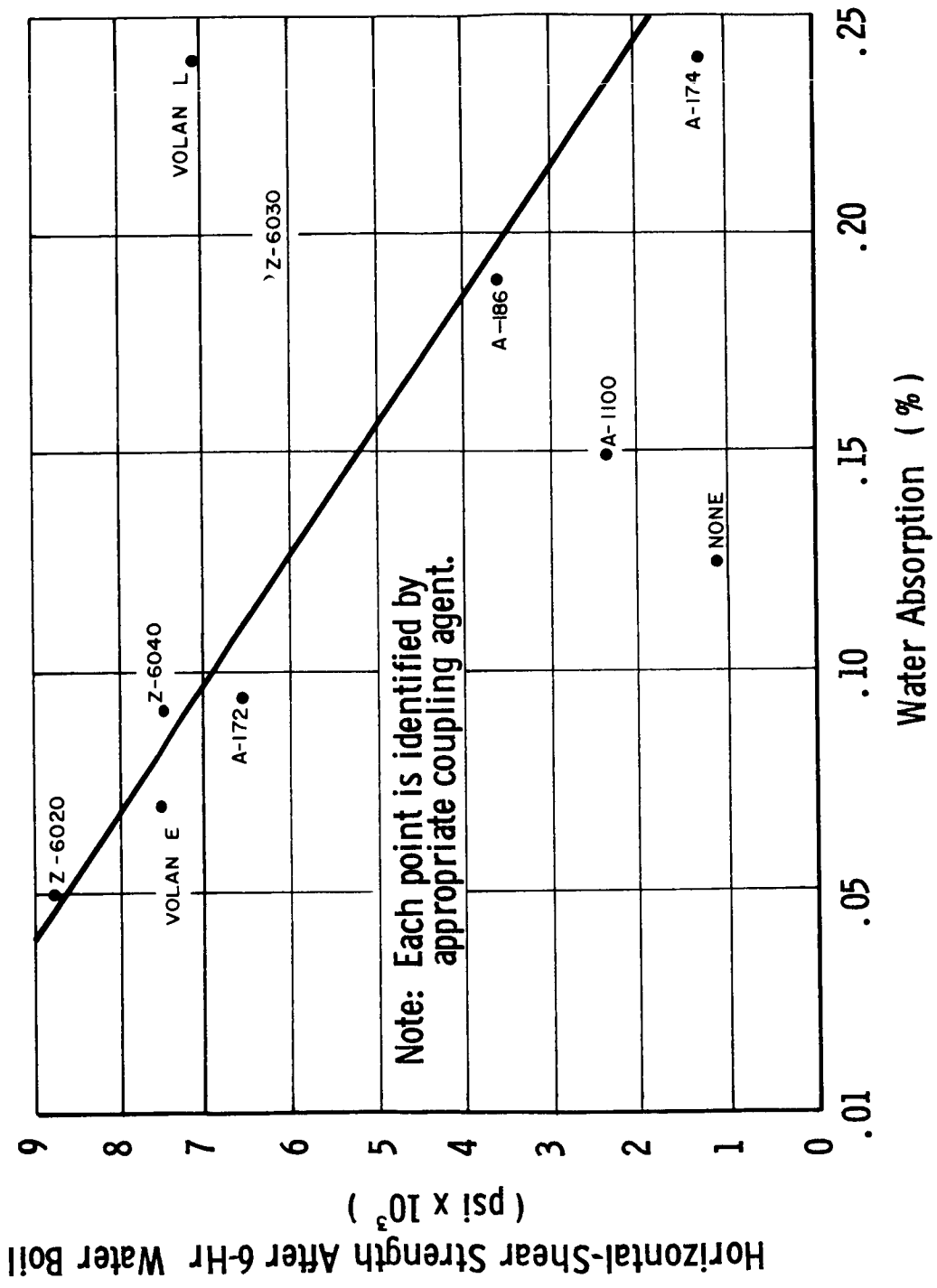
Effect of Finish Application Containing Various Coupling Agents on Ambient-Temperature Horizontal-Shear Strength

Figure 16



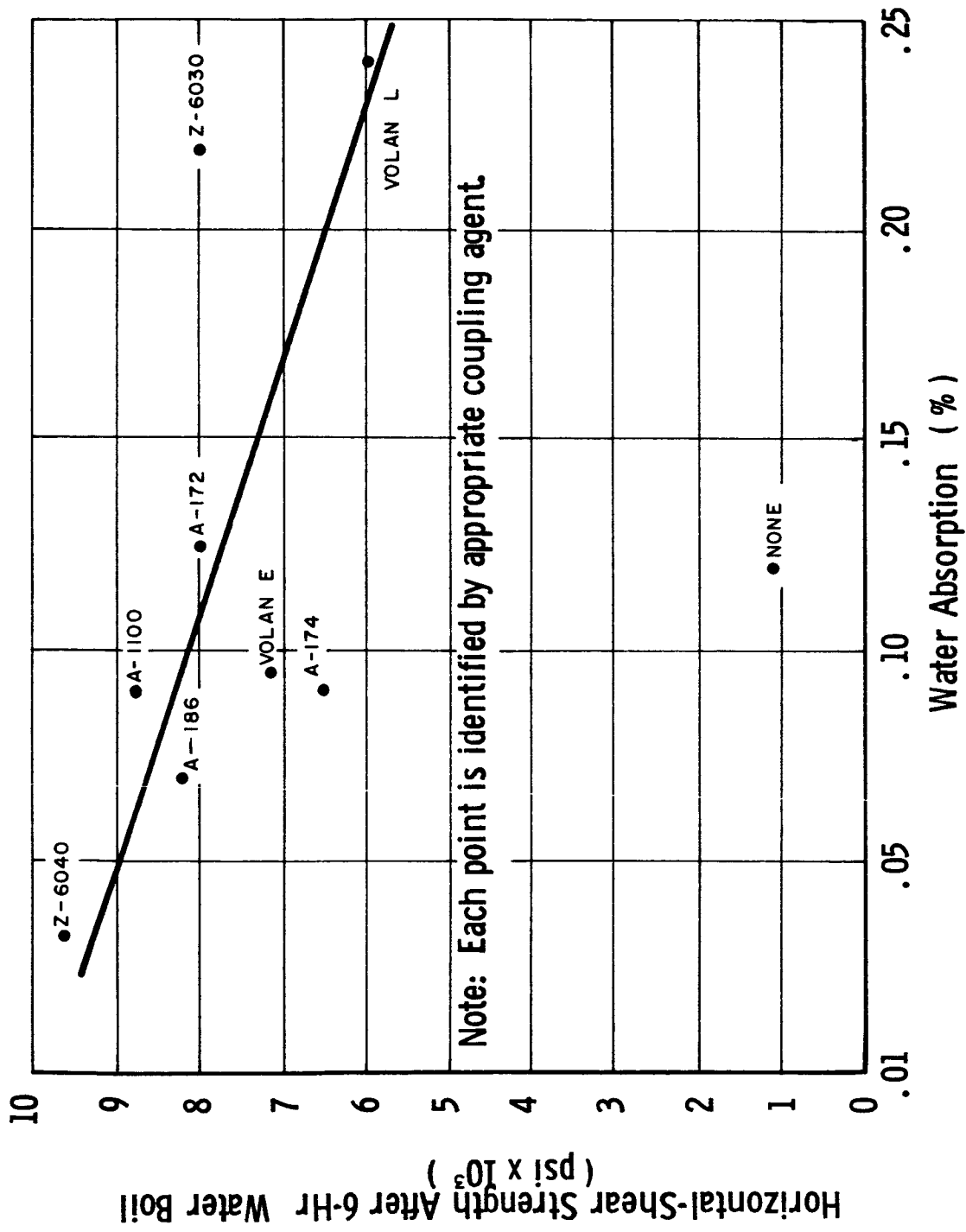
Effect of Finish Application Containing Various Coupling Agents on Horizontal-Shear Strength at -423°F

Figure 17



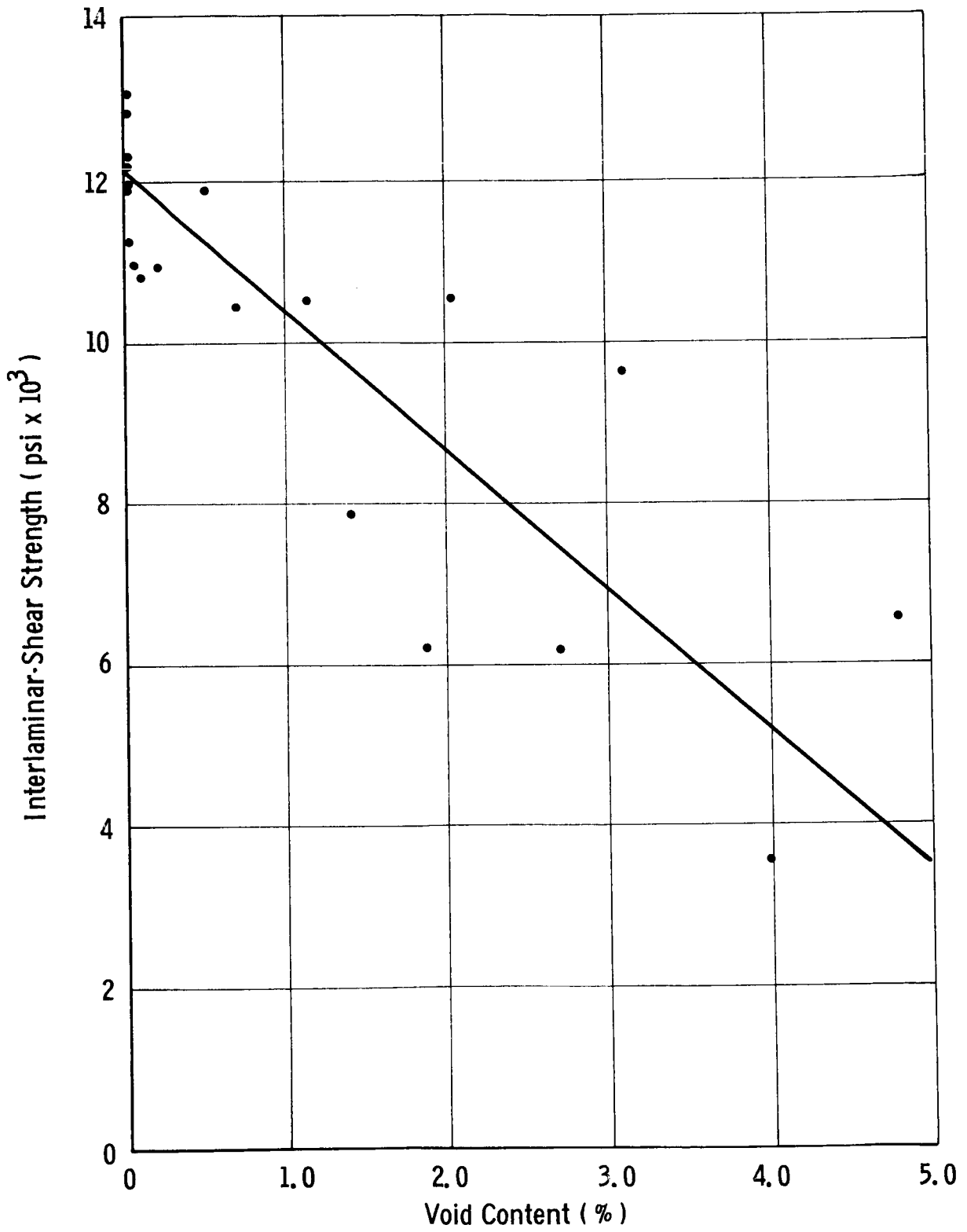
Water Absorption of Coupling Agents vs Interlaminar-Shear Strength After Water Boil (Two-Step Application)

Figure 18



Water Absorption of Coupling Agents vs Interlaminar-Shear Strength After Water Boil (One-Step Application)

Figure 19



Interlaminar-Shear Strength vs Void Content

Figure 20

APPENDIX

EVALUATION TECHNIQUES

I. VISCOSITY AT ROOM TEMPERATURE

A Brookfield viscometer (Model LVT), beaker, and thermometer are used in this procedure to determine the viscosity of resin-finish material at room temperature.

The test specimen consists of approximately 400 cc of catalyzed resin-finish system placed in the beaker and conditioned in a water bath until a temperature of $73 \pm 2^{\circ}\text{F}$ is reached.

The spindle of the viscometer is positioned in the container so that the upper surface of the sample is in the center of the shaft indentation and the spindle is in the center of the beaker. The viscometer is spun at 30 rpm, and a reading is recorded (together with the temperature) after every 20 revolutions. The viscosity is then determined directly from the Brookfield chart.

II. RESIN CONTENT

The procedure used to determine the resin content of organic plastics reinforced with glass fibers requires an analytical balance, a desiccator, a heat-resistant nonreactive crucible, and a muffle furnace with temperature controls.

The test specimen should weigh at least 1.5 g, and the edges should not be frayed. It is weighed on the analytical balance in the previously weighed ignition crucible, and is then heated for 30 ± 5 min in the muffle furnace, which has been stabilized at $1400 \pm 50^{\circ}\text{F}$. It is cooled to the ambient temperature in the desiccator and is reweighed to the nearest milligram.

The resin content (wt%) is calculated from

$$\text{Resin content} = \frac{\text{loss in weight}}{\text{original weight}} \times 100$$

III. HORIZONTAL-SHEAR TESTS, NOL-RING COMPOSITE

The parallel interlaminar-shear strengths of glass-resin composites at room and cryogenic temperatures are determined with the aid of a routing fixture, a cutting fixture, test fixtures, a cryostat (Figure A-1), and an Instron testing machine.

The test specimens (Figure A-2) are cut from a previously prepared NOL-ring composite and conform to ASTM Specification D2344-65T. They are measured with a suitable ball-type micrometer, reading to at least 0.001 in. for the width, thickness, and length; at least three readings are made per specimen. The specimens are tested at room temperature, at room temperature after a 6-hour water boil, and at -123°F. The crosshead speed is 0.05 in./min.

The horizontal-shear strength is calculated from

$$S_H = \frac{0.75 P_B}{b d}$$

where

S_H = horizontal-shear strength (psi)

P_B = breaking load (lb)

b = specimen width (in.)

d = specimen thickness (in.)

IV. TENSILE-STRENGTH TEST, NOL-RING COMPOSITE

A split-disk test fixture (Figure A-3) and an Instron testing machine are used to determine the tensile strength of glass/resin composites at room and cryogenic temperatures.

The test specimen is an NOL ring conforming to ASTM Specification D2291-64T, Type B. It is measured to eight equally spaced areas. A ring is simulated on a sheet of paper and the measurements are recorded. The specimen is mounted on the split disk and is installed in the testing machine. A cross-head speed of 0.10 in./min is used.

The composite tensile strength is calculated as follows:

$$\text{Composite tensile strength} = \frac{P_B}{2A}$$

where

A = cross section of ring (sq in.)

V. RESIN SOLIDS

Determination of the percentage of solids contained in a resin or resin system requires an analytical balance, an evaporating dish, an air-circulating oven with a temperature controller, and a desiccator.

The specimen consists of at least 10 g of the resinous material, catalyzed if required. It is weighed on the analytical balance in the previously

weighed dish and is placed in the oven (stabilized at the minimum recommended temperature) for the recommended time. It is then cooled to room temperature in the desiccator and is reweighed to the nearest milligram.

The resin solids (wt%) are calculated from

$$\text{Resin solids} = \frac{\text{loss in weight}}{\text{original weight}} \times 100$$

VI. SPECIFIC GRAVITY

This procedure determines specific gravity as the ratio of the weight of a given volume of material to that of an equal volume of water at the same temperature. The equipment includes an analytical balance, a piece of corrosion-resistant wire, a beaker of distilled water, and a thermometer.

The test specimen is a solid of any size or shape that can be conveniently prepared and tested. The corrosion-resistant wire is fastened to the hook on the pan support of the analytical balance, and the weight is recorded to the nearest 0.1 mg. The test specimen is attached to the wire (so that it is suspended about 1 in. above a beaker support) and is weighed to the nearest 0.1 mg. It is then immersed in the beaker and is weighed to the nearest 0.1 mg. After the specimen is removed from the wire, the weight of the wire in water is recorded.

The specific gravity of the specimen is calculated from

$$\text{Specific gravity} = \frac{k - p}{(k-p) - (b-c)} = \frac{a}{a - m}$$

where

k = weight of specimen plus wire in air (g)

p = weight of wire in air (g)

b = weight of specimen in water plus partly immersed wire (g)

c = weight of wire partly immersed in water (g)

a is the equivalent of k-p and represents the weight of the specimen in air (g)

m is the equivalent of b-c and represents the weight of the specimen in water (g)

VII. VOID CONTENT

The equipment used to determine the percentage of voids (air bubbles) in filament-wound-composite NOL rings includes an analytical balance, a corrosion-resistant wire, a beaker of distilled water, a thermometer, a desiccator, a heat-resistant crucible, and a muffle furnace with temperature controls.

The composite test specimen should be a representative NOL-ring section at least 1-1/4 in. long and weighing at least 1 g; the edges should not be frayed. It is weighed on the analytical balance and the specific gravity is determined as described above. The original or dry specimen weight determined during that procedure is used as the composite or original weight for resin-content determination with this specimen (see paragraph II).

The specific gravity of the matrix resin is determined (paragraph VI) from a previously cured, unfilled, and void-free resin block approximately 1/2 in. square. The specific gravity of glass reinforcements is determined from glass onions obtained during ring fabrication. The glass sample should weigh at least 1 g.

The void content (vol%) is determined from

$$\text{Void content} = \frac{\text{volume of voids}}{V_c} \times 100$$

where

$$\text{Volume of voids (cc)} = V_c - (V_R + V_g)$$

$$V_c = \text{volume of composite (cc)} = W_o / SG_c$$

$$V_R = \text{volume of resin (cc)} = W_R / SG_R$$

$$V_g = \text{volume of glass (cc)} = W_g / SG_g$$

$$W_o = \text{original composite weight in air (g)}$$

$$W_R = \text{resin weight (g)}$$

$$W_g = \text{glass weight (g)}$$

$$SG_c = \text{specific gravity of composite (g/cc)}$$

$$SG_R = \text{specific gravity of resin (g/cc)}$$

$$SG_g = \text{specific gravity of glass (g/cc)}$$

VIII. WATER ABSORPTION

An analytical balance, a hot plate, and a beaker of distilled water are used to determine the water absorption of glass-filament-wound composites that have been subjected to a 6-hour water boil.

The test specimens are weighed to the nearest milligram and are immersed in boiling distilled water for 6 hours. They are removed, blotted dry, and reweighed to the nearest milligram.

The increase in water absorption (wt%) is calculated from

$$\text{Water absorption} = \frac{\text{wet weight} - \text{original weight}}{\text{original weight}} \times 100$$

IX. WETTING

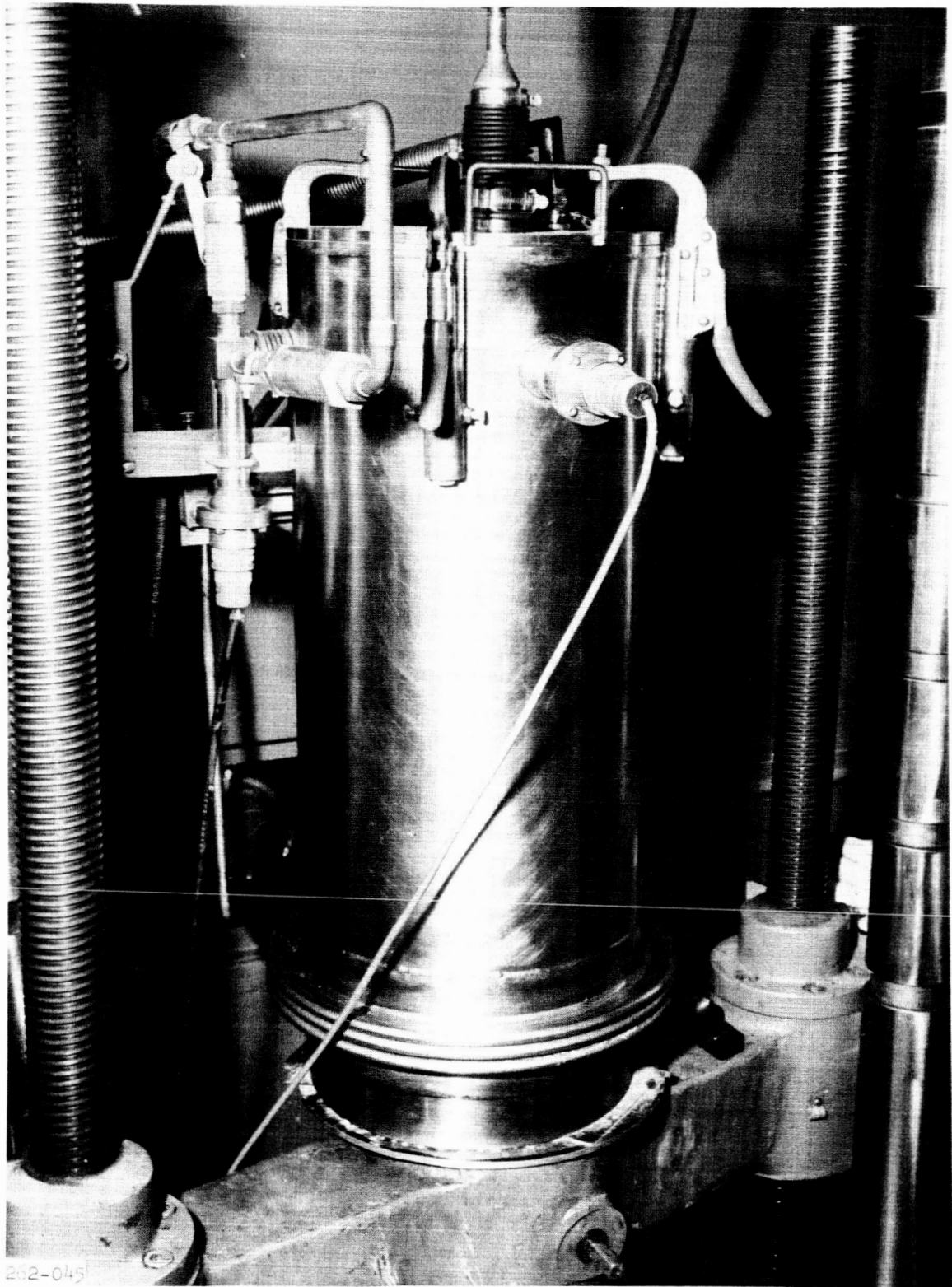
The contact angle between a finish or resin and a glass filament is determined with the aid of a Zeiss Ultraphot, a cardboard fiber mount, a protractor, a slide glass, a microdrop hypodermic needle, and a heat lamp.

The test specimen is a glass filament drawn from a monofilament bushing. It is mounted on the cardboard fiber holder and is positioned horizontally on the slide, with the fiber slightly above the slide surface. The specimen area is heated with the lamp to the same temperature as the finish and resin when they are being wound into an NOL ring.

One of the following techniques is used to apply the finish and/or resin to the filament: (a) A microdrop is lightly touched to the center of the filament after mounting and positioning on the slide, (b) a mounted filament is immersed in the coating material before placement on the slide, or (c) a fiber is coated during fiberization, is mounted on the fiber holder, and is placed on the slide.

Two capillary fronts then travel horizontally out from the microdrop along the suspended filament. After 60 sec, the fronts are photographed at a magnification of 500X with dark-field illumination. Figures A-4 and A-5 reproduce photomicrographs made during wetting studies.

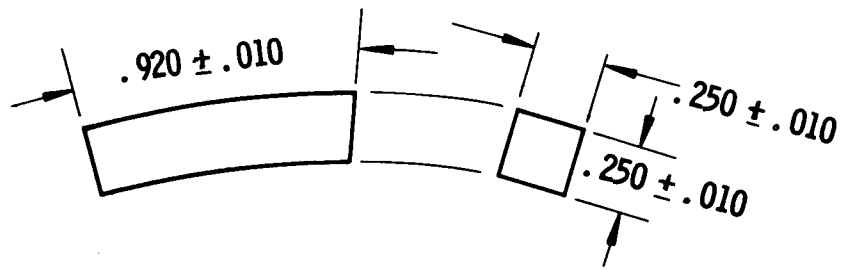
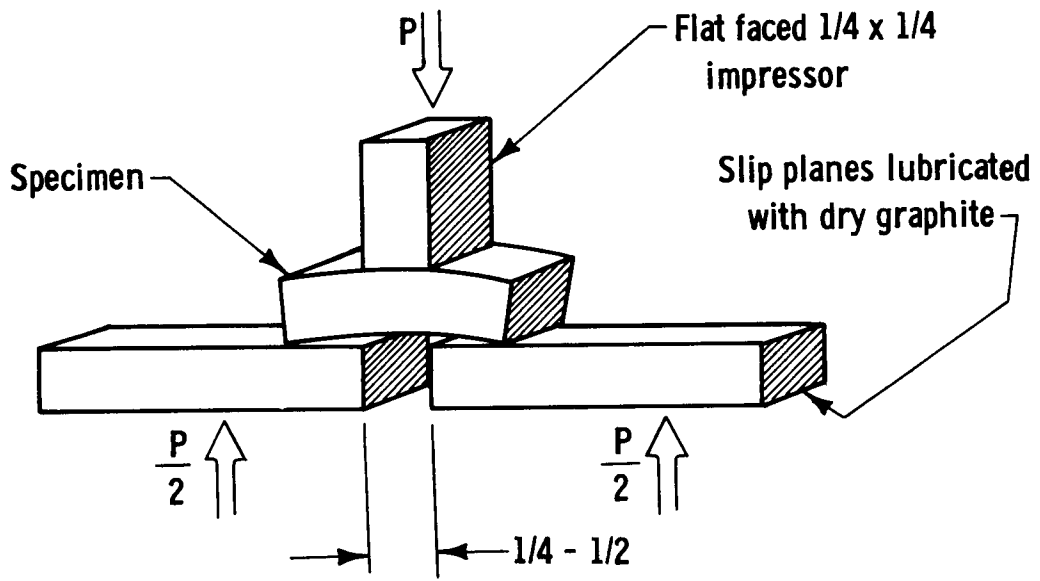
The contact angle of the finish or resin is determined by using a protractor to measure the angle at which the fluid contacts or wets the filament.



262-045

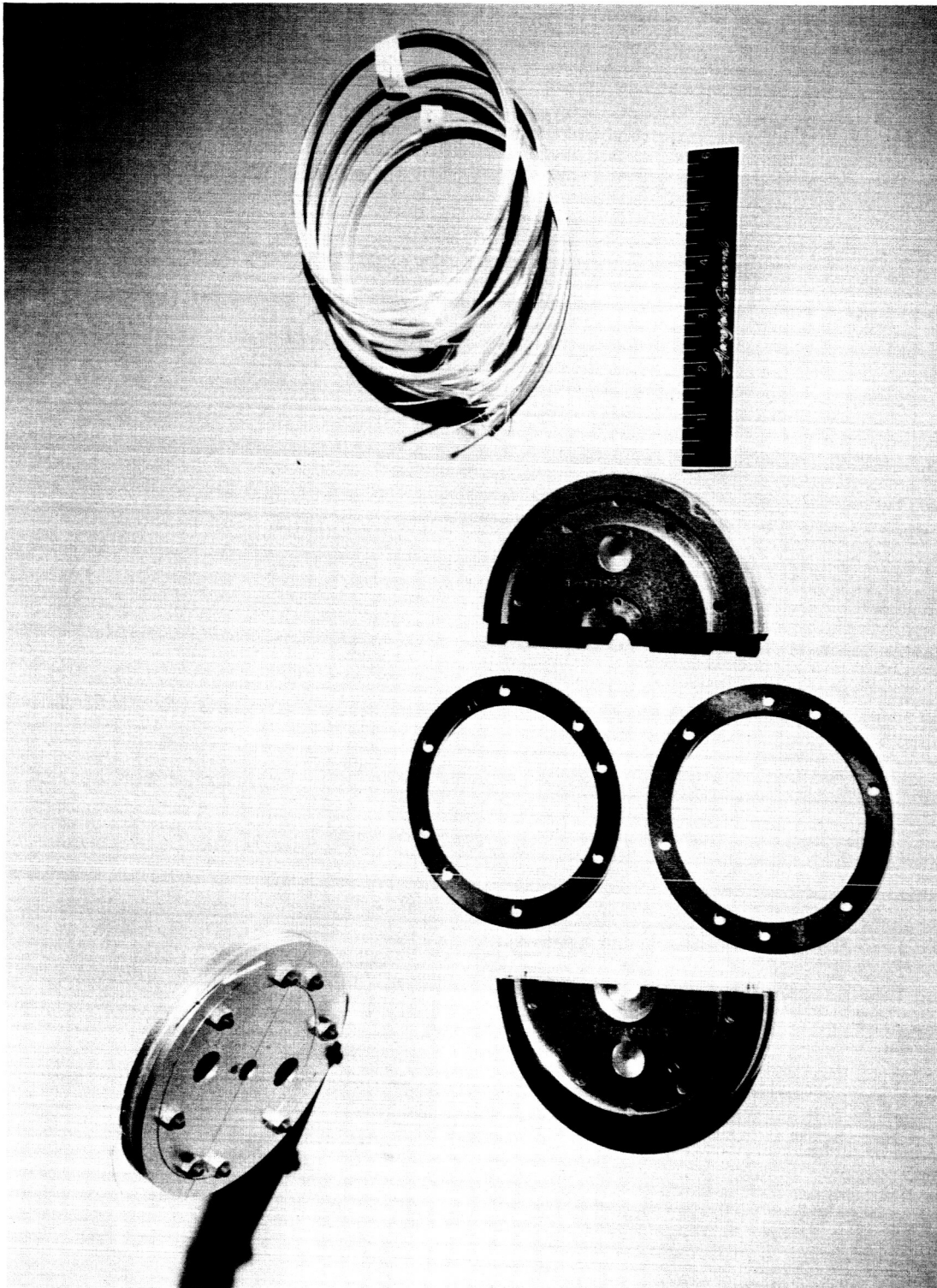
Cryostat for Tensile Testing at -423°F

Figure A-1



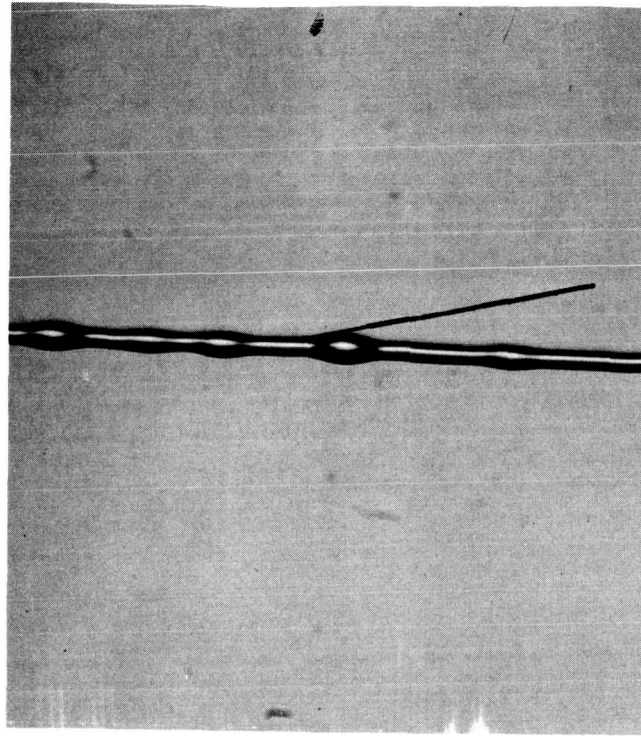
Horizontal-Shear-Strength Test Specimen

Figure A-2

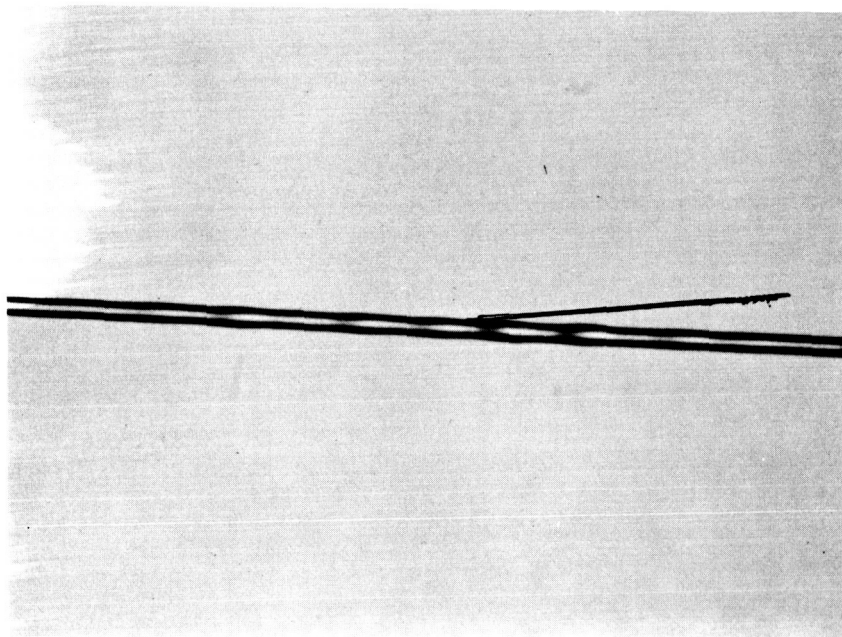


Ring Specimens

Figure A-3



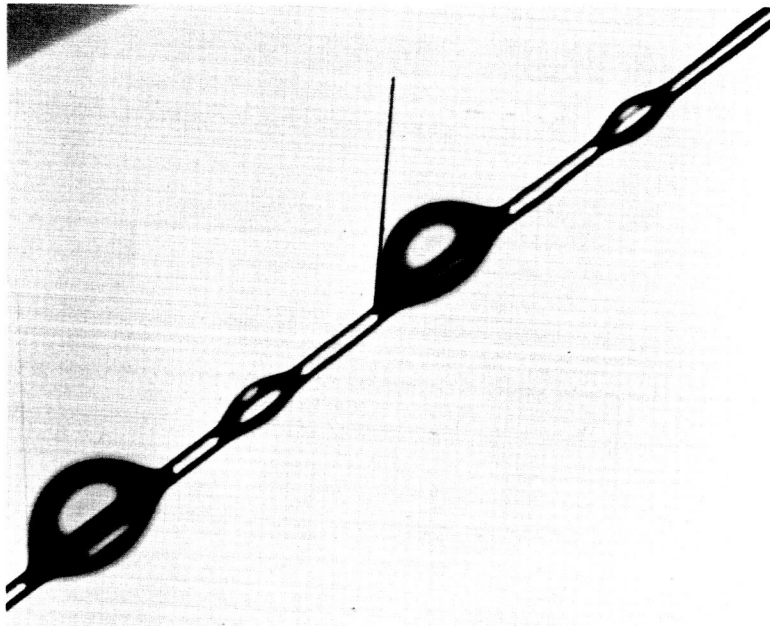
Contact Angle 15°



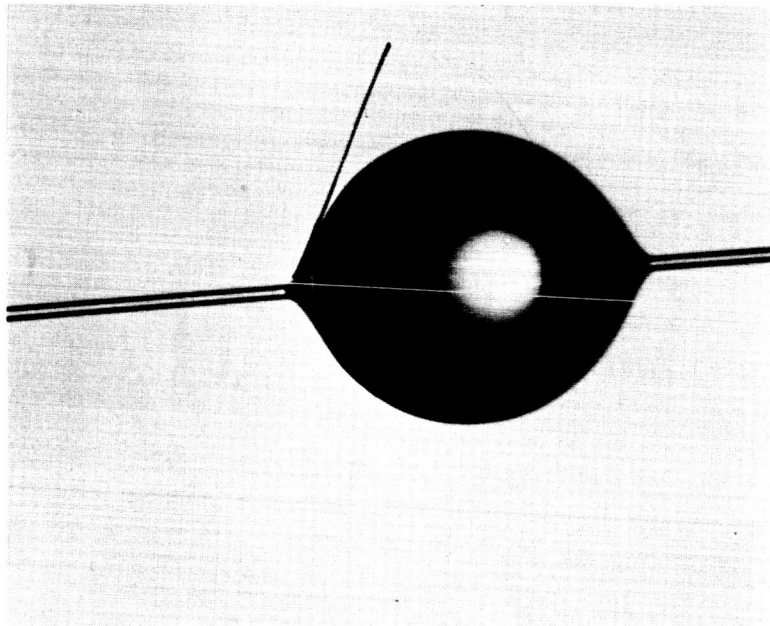
Contact Angle 8°

Contact Angles Obtained in Wetting Study
Epon 828/NMA Resin System Applied by Roller Coater

Figure A-4



ELS-3001 Resin, Contact Angle 48°



Epon 58-68R Resin, Contact Angle 64°

Contact Angles Obtained in Wetting Study
ELS-3001 and Epon 58-68R Resins Applied by Dipping

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