FOREWORD

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This report covers work performed during the period from April 1961 through April 1962.

The following staff members contributed to the development of this program and their assistance is gratefully acknowledged: Mr. C. A. Hauck, Mr. R. M. Davids, Mr. G. D. Jones, and Mr. W. R. McIntosh.

ABSTRACT

Metal reinforced refractory ceramic coating systems have been developed to successfully withstand temperatures in excess of 4000°F while providing insulative values for the supporting substructure. Eighty coating compositions were formulated and thermally evaluated in the plus 4000°F range.

Refractory coating of model nose cones and leading edges has been accomplished by utilizing a vibratory casting technique and the feasibility of this approach has been demonstrated. Twelve small scale leading edge models and six small scale nose cone models were coated in addition to one 500 square inch leading edge and one 500 square inch nose cone model. Thicknesses ranged from 0.3 to 0.75 inch.

Mechanical data and thermophysical properties of an advanced coating system were obtained.

An up-to-date bibliography of reinforced refractory ceramic systems and allied subjects is included.

This technical documentary report has been reviewed and is approved.

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CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS (Continued)

TABLES

I. INTRODUCTION

The tremendous advances which have been made in the field of aerospace vehicle and propulsion systems have created an urgent need for reliable hardware, with the inherent capability of existing in temperature regimes of plus 4000°F. Previous work (reported in Reference 1 under Contract AF 33(616)-5441) has illustrated the competence of a system composed of metal reinforced refractory ceramic coatings to fill such requirements.

The current work has been directed toward the optimization of these coating systems and the fabrication of model leading edges and nose cones for simulated environmental testing. The work reported under the subject contract has been divided into the following phases:

1. Welding of refractory metal reinforcement media to a substrate and subsequent attempts to provide sufficient oxidation protection to the refractory metal

2. The optimization of coating compositions

3. The selection and optimization of the application technique of vibratory casting

4. Fabrication and coating of nose cone and leading edge models

5. Compilation of thermophysical data, including differential thermal analysis and thermal expansion characteristics

6. A bibliography of the state of the art of ceramic coating systems for use in the temperature regions above 3000°F

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II. SUMMARY

A. Purpose

The purpose of this program was to develop and evaluate reinforced refractory insulating type ceramic coatings of the type potentially useful on re-entry vehicles. The objectives of this program were:

1. To conduct a literature search and prepare a bibliography of related references
2. To select and optimize suitable coatings for plus 4000°F service temperature
3. To optimize application techniques
4. To prepare model nose cones and leading edges for simulated environmental testing
5. To document the development in the form of 35 mm color slides

B. Conclusions

1. Reinforcement

The present state of the art precludes the use of tantalum or molybdenum alloy reinforcement on N-155 structural substrate. Although they can be welded to the substrate satisfactorily, all attempts to protect these refractory metal reinforcement media resulted in unsuccessful systems.

Type 321 stainless steel reinforcement media can operate without requiring antioxidation coatings and without thermal failure when suitably submerged in the refractory ceramic coating.

2. Coatings

Practical reinforced refractory coating systems for long time use at plus 4000°F have been demonstrated.

3. Compositions

Refractory grains such as calcia-stabilized zirconia have been bonded into monolithic coatings utilizing fluorine-containing acids, amongst which hydrofluosilicic, monofluorophosphoric, and hydrofluosulfonic acids gave outstanding results.

4. Coating Techniques

Vibratory casting of thixotropic compositions has been demonstrated as a very successful technique of emplacing the refractory ceramic coating compositions.

For minor patching and touch-up requirements, troweling application of the coating composition is permissible.

5. Emittance Modifiers

The addition of metallic oxides to the basic coating compositions for the purpose of increasing the coating emittance at elevated temperatures has resulted in moderate gains in emittance values and, unfortunately, in drastic losses of structural integrity for the coatings.

III. WELDING OF REFRACTORY METAL REINFORCING TO N-155 ALLOY SUBSTRATE

Tantalum and 0.5% titanium-molybdenum alloy were selected as reinforcing media for N-155 substrate structure. These refractory metals were obtained in the form of ribbon, 0.125-inch wide by 0.010-inch thick. The ribbon had been rolled from wire so that rounded edges were provided. These ribbons were then passed through mated gears which formed a continuous corrugated strip as shown in Figure 1. Different sets of mated gears provided corrugated strip which measured a nominal 5/32, 5/16, and 1/2 inch, peak-to-peak.

The corrugated tantalum reinforcement was spot welded at each node to 0.040-inch thick N-155 alloy substrate with no apparent embrittlement of the reinforcing media. A Stryco Welder, Type 4559 XUD, was used for this phase of the work. The following welder settings were typical:

Heat percent - - - - - - - 52

Weld time cycles - - - - 2

The 0.5% titanium-molybdenum alloy ribbon was quite brittle as received. It was quite difficult to form a continuous corrugated ribbon because of the inherent brittleness, and the brittleness increased markedly during the spot welding operation.

Because of these difficulties, 0.5% titanium-molybdenum alloy was discarded as a reinforcing medium. No attempt was made to find the reason for the brittleness.

IV. OXIDATION-PROTECTIVE COATINGS FOR TANTALUM AND 0.5% TITANIUM-MOLYBDENUM REINFORCING MEDIA

As previously noted, tantalum and 0.5% titanium-molybdenum alloys were selected as the reinforcing media for N-155 substrate structure. In an effort to evaluate oxidation-resistant coatings from outside vendors, three flat tensile specimens of 0.5% titanium-molybdenum alloy were sent to American Machine & Foundry to receive their siliconized coating for refractory metals. Samples of tantalum and 0.5% titanium-molybdenum reinforced N-155 were also sent to Boeing in Seattle for siliconizing.

The three flat tensile specimens of 0.5% titanium-molybdenum which were sent to American Machine & Foundry to receive their siliconized antioxidation coating-were returned to Marquardt for evaluation. The test samples were resistance heated to 3000°F and held there for 30 minutes. Up to 2300°F, some small amounts of smoke were noted. This ceased when the temperature rose above 2300°F. No further smoking appeared. Some edge cracks were noted after cooling. The coating appeared glassy with a checkerwork of fine crazing. There was no apparent deterioration of the specimens.

Even though the results of coating of 0.5% titanium-molybdenum appeared promising, the material was discarded because of its brittleness, as discussed more fully in the preceding section.

The Boeing Company reported attack on nickel bearing alloys in their fluidized-bed siliconizing process. They therefore declined to siliconize the tantalum and 0.5% titanium-molybdenum reinforced N-155 test specimens which Marquardt sent them for processing.

The problems at this point were as follows: If the refractory metals were protected against oxidation by a diffusion coating such as American Machine & Foundry's disilicide, it was not possible to spot weld these coated metals to the N-155 substrate. According to Boeing's report if the reinforcing media were first spot welded to the N-155 substrate, subsequent disilicide coating would cause intergranular corrosion and low melting eutectic compounds in the substructure. Because of these problems, emphasis had to be shifted to the development of a dip type coating for tantalum that could be applied subsequent to the spot weld operation. The dip type coating systems which were evaluated are listed in Table I. A discussion of the evaluation of these compositions follows.

The tantalum reinforcing media was spot welded to the substrate as noted above. The coating compositions were mixed to a dipping consistency and the entire assembly was then dip coated. The coated assembly was air dried. Following the drying cycle, excess coating was removed from the back side of the substrate. Where required, a low temperature oven cure was employed.

The coated assembly was then encapsulated in a zirconia insulative body (TherMarq ZPF-100) and cured at 300°F for 2 hours to set up the chemical bond of the body.

TABLE I

ANTIOXIDANT COATINGS FOR TANTALUM REINFORCEMENT MEDIA

Coating Number	Composition*	Cure Temperature
D-1	Sodium silicate (S-35 brand) + water	200°F
D-2	Potassium silicate (Kasil) + water	200°F
D-3	Pyro-Chrome	300°F
D-4	CP-44	300°F
D-5	Alkaphos C	200°F
D-6	Aluminum powder (-325 mesh) + Brolite	ambient
D-7	Chromium powder (-325 mesh) + Nicrobraz liquid	ambient
D-8	Columbium powder (-325 mesh) + Nicrobraz liquid	ambient
D-9	Vanadium powder (-325 mesh) + Nicrobraz liquid	ambient
D-10	Nickel powder (-325 mesh) + Nicrobraz liquid	ambient
D-11	Nichrome powder (-325 mesh) + Nicrobraz liquid	ambient
D-12	Electroless nickel plate	--
D-13	Silver paint	ambient
D-14	Aluminum paint	ambient
D-15	Alumina paint	600°F
D-16	Phosphatherm	200°F
D-17	Aluminum powder (-325 mesh) + Nicrobraz liquid	ambient
D-18	Zirconia paint	300°F

*NOTE: All compositions were mixed to a slurry of dipping consistency.

The cured samples were then tested using the thermal drop test apparatus shown in Figure 2. Table II contains the data gathered from this evaluation.

The best protection was afforded by Composition D-7 which consisted of -325 mesh chromium powder suspended in Nicrobraz liquid.

More complex formulations for the oxidation protection of tantalum are shown in Table III.

Attempts to coat the refractory metal reinforcement, as spot welded to the substructure, using dip or paint type coatings were unsuccessful. Such coatings only partially protected the reinforcement from oxidation or they caused severe embrittlement after exposure to elevated temperatures.

In view of the poor results obtained in trying to provide oxidation protection for tantalum, another look was taken at the feasibility of utilizing type 321 stainless steel as the reinforcing media. This material requires no special oxidation protection when submerged in the refractory ceramic coating. When the apexes of the nodes were submerged about 0.150 inch below the ceramic hot face at 4000°F, the reinforcement remained intact.

At this point, the decision to use Type 321 stainless steel reinforcement rather than tantalum was made.

TABLE II

RESULTS OF THERMAL DROP TESTING OF ANTIOXIDANT COATINGS FOR TANTALUM ENCAPSULATED IN TherMarq ZPF-100

Sample* Number	Run No.	Run Time (min)	Coating Number	Description of Coating	Temperature (°F) Front Optical	Front Corrected	Rear T/C	Visual Evaluation of Tantalum after Removal of TherMarq ZPF-100
1	1	5	D-1	Na_2SiO_4	4000	--	1550	Top of reinforcement gone.
	2	10			4000	--	1460	
2	1	5	D-13	Ag Paint	4000	--	1700	Reinforcement completely gone.
	2	10			4000	--	1505	
3	1	4	D-3	Pyro-Chrome	4000	--	--	Reinforcement intact but oxidized.
	2	8			4000	--	--	
	3	3			4000	--	--	
4	1	6	D-4	CP-44	4000	--	--	Reinforcement intact but oxidized.
	2	4			4000	--	--	
5	1	6	D-2	Kasil	4000	--	--	Severe oxidation.
	2	5			4000	--	--	
6	1	6	D-5	Alkophos C	4000	--	--	Reinforcement oxidized.
	2	4			4000	--	--	
7	1	5	D-6	Al powder	4000	--	--	Reinforcement intact.
	2	10			4000	--	--	
8	1	5	D-7	Cr powder	4000	--	--	Reinforcement not oxidized.
	2	10			4000	--	--	
9	1	5	D-8	Cb powder	4000	--	--	Reinforcement badly oxidized.
	2	10			4000	--	--	
10	1	4	D-9	V powder	4000	--	--	Badly oxidized.
	2	8			4000	--	--	
11	1	5	D-10	Ni powder	4000	--	--	Severely oxidized.
	2	4			4000	--	--	

TABLE II (Continued)

Sample* Number	Run No.	Run Time (min)	Coating Number	Description of Coating	Temperature (°F) Front Optical	Front Corrected	Rear T/C	Visual Evaluation of Tantalum after Removal of TherMarq ZPF-100
12	1	5	D-11	Nichrome powder	4000	--	--	Reinforcement slightly oxidized.
	2	10			4000	--	--	
13	1	5	D-12	Electroless Ni	4000	--	--	Oxidized.
	2	10			4000	--	--	
14	1	5	D-14	Al paint	4000	--	--	Reinforcement badly oxidized.
	2	10			4000	--	--	
15	1	5	D-7	Cr powder	3760	4210	1640	No oxidation evident.
	2	10			3800	--	--	
16	1	7	D-15	Al_2O_3 paint	4020	--	--	Some oxidation.
	2	8			4000	--	--	
17	1	5	D-1	Na_2SiO_4	3740	4190	--	Some oxidation.
	2	10			3740	4190	--	
18	1	5	D-7	Cr powder	4000	4490	--	No oxidation.
	2	10			4000	4490	--	
19	1	5	D-16	Phosphatherm	3680	4120	--	Slight oxidation.
	2	10			3680	4120	--	
20	1	15	D-17	Al powder	3800	4260	--	Slight oxidation.
21	1	5	D-15	Al_2O_3 paint	3680	4120	--	Oxidation evident.
	2	10			3680	4120	--	
22	1	5	D-18	ZrO_2 paint	4000	--	1480	Excessive oxidation.
	2	5			4000	--	1470	
	3	5			4000	--	1485	

* Samples Nos. 1 through 14: The top of tantalum reinforcing was a nominal 1/16 inch below the surface of the body. Samples Nos. 15 through 22: This distance was 1/8 inch.

TABLE III

FORMULATION OF OXIDATION PROTECTIVE COATINGS FOR TANTALUM REINFORCEMENT MEDIA

Composition	Parts by Weight									
	1	2	3	4	5	6	7	8	9	10
Cr_2O_3	50	10	45	45	--	--	--	--	--	--
Colloidal Al_2O_3	--	40	5	5	--	--	--	--	--	--
Colloidal ZrO_2	--	--	--	--	--	--	--	76	90	27
ZrO_2 (-325 m)	--	--	--	--	--	--	--	18	6.5	20
$NH_4H_2PO_4$	4.5	4.5	4.5	--	--	--	--	--	--	--
H_2SiF_6	25	25	10	4.5	--	--	--	--	--	--
H_2PO_3F	--	--	--	--	--	--	--	--	--	1.0
Chrome metal	--	--	--	5	--	--	--	--	--	--
Tin flake	--	--	--	--	50(a)	50(b)	50(c)	--	--	--
Aluminum flake	--	--	--	--	50	50	50	--	--	--
Poly vinyl chloride	--	--	--	--	--	--	--	6	--	--
Kasil No. 1	--	--	--	--	--	--	--	--	3.5	--
Gum Tragacanth	--	--	--	--	--	--	--	--	--	0.2
Nicrobraz	--	--	--	--	--	--	qs	--	--	--
H_2O	--	--	qs	qs	--	--	--	--	--	--

Notes: (a) - In air-oxidized
(b) - Covered with graphite-oxidized
(c) - Cured in vacuum at 400°F - no adherence after firing

Samples 1, 3, and 4 afforded no oxidation protection during firing. Sample 2 was too lumpy and it therefore was not evaluated. No adherence was obtained with Samples 8 to 10.

V. BODY STUDIES

A. Composition Formulae

All composition formulae are given in Appendix III of this report.

B. Binders

Previous work (Reported in Reference 4) had clearly indicated the improvement of binders when fluorophosphoric acid was substituted for phosphoric acid. The incorporation of a fluorine radical was deemed significant. Work done at the Boeing Airplane Company (Reference 2) suggests the use of sulfuric acid as a binding agent for zirconia.

Therefore, to check the validity of the assumption regarding fluorine radicals, the compositions designated as TherMarq ZFS-101 to ZFS-106, inclusive were compounded. Compositions TherMarq ZFS-101 and ZFS-102, compounded directly from fluosulphonic acid, were quite difficult to handle. The acid fumed and was noxious. The compositions were of a mortar-like consistency which did not flow, resulting in difficult application. The curing cycle follows:

Time	Condition	Result
3 hours	Air dry	Soft
1 hour	250°F	Reasonably hard
1 hour	300°F	Hard, but steel will scratch
1 hour	450°F	Hard, not scratched by steel

The noted curing cycle resulted in an extremely hard body for TherMarq ZFS-101 and ZFS-102, but bloating was evident.

TherMarq ZFS-103 was prepared as follows: H_2SO_4 was added to water, then the solution was added to HF, blended ZrO_2 grains were then added to the resultant solution. This method of compounding the formulation eliminated the violent reaction and most of the fumes noted above. The formulation molded easily and exhibited evidence of thixotropy.

The TherMarq ZFS-104 composition was applied to a reinforced panel and exposed to the Thermal Drop Test Apparatus. TherMarq ZFS-104 was essentially the same as TherMarq ZFS-101, but it contained less water. The sample withstood a corrected front face temperature of 4340°F for five minutes. There was no glazing or cracking of the surface. Aside from the difficulty in preparation, this composition was satisfactory.

The TherMarq ZFS-105 composition utilized both fluosulphonic acid and monofluorophosphoric acid. The composition was more of a slurry than mortar consistency. Four hours of air drying did not result in much "set". Twenty-four hours of air drying were required for this composition to set sufficiently for

handling. Further work on this composition was discontinued because of its poor setting characteristic.

TherMarq ZFS-106 was an effort to compound a zirconia body without the direct use of acids. The body did not hold up under thermal testing and this approach was discontinued.

The TherMarq ZPF-100 body, utilizing monofluorophosphoric acid, was further investigated using lithium zirconate and chromium metal powder. There was also an investigation of grain size of the fused zirconia. Results of thermal drop tests of these bodies are tabulated in Table VIII.

As an evaluation of the curing temperature, two TherMarq ZPF-100 bodies were prepared and cured at 300°F and 450°F, respectively. These bodies were exposed to ambient atmosphere conditions and their weights were periodically recorded. The weight changes shown in Table IV indicate that the higher curing temperature definitely slows down water absorption by the TherMarq ZPF-100 body.

TABLE IV

WATER ABSORPTION CHARACTERISTICS OF TherMarq ZPF-100 AT TWO CURE TEMPERATURES

Elapsed Time (hrs)	TherMarq ZPF-100 Cured at 300°F			TherMarq ZPF-100 Cured at 450°F		
	Wt. (grams)	Wt. Gain Cum.	% Gain	Wt. (grams)	Wt. Gain Cum.	% Gain
As cured	61.91	--	--	56.97	--	--
18	62.15	0.24	--	--	--	--
24	62.17	0.26	--	--	--	--
42	62.30	0.39	+0.63	57.04	+0.07	+0.12
48	62.31	0.40	--	57.04	--	--
66	62.32	0.41	+0.66	57.06	0.09	+0.16
90	62.32	--	--	57.07	0.10	--
162	62.32	--	--	57.07	--	--

All subsequent formulations were cured at 450°F, based on the data shown in Table IV.

Hydrofluosilicic acid was next investigated as a binding agent for zirconia bodies. Compositions formulated with this binder were highly thixotropic and exhibited longer working times than either the monofluorophosphoric or hydrofluosulfonic acids. Formulations compounded with H_2SiF_6 also stood up well under thermal testing. For these reasons, hydrofluosilicic acid was chosen as the best bonding agent.

C. Formulations

Various approaches were taken to improve the characteristics of the basic hydrofluosilicic-zirconia body, TherMarq ZSF-101. The modifying action of dif-

ferent ammonium salts on the composition was noted, as well as the effect of changes in water concentration. The composition was formulated using hydrofluosilicic acids of varying concentration obtained from several different commercial sources. The concentration of acid in the formulation itself was varied. Refractory oxides and coloring agents were added to or substituted in the formulation in attempts to increase emittance. A discussion of the technique for evaluating emittance is contained in Reference 3. Test coupons were cast as shown in Figure 3.

1. Salts and/or Metal Additions

The effects of salts and/or metal additions are demonstrated in TherMarq ZSF-101 through TherMarq ZSF-109.

These compositions showed the effect of various anions on the binding action of the acid. TherMarq ZSF-101 was a molar substitution of H_2SiF_6 for H_2PO_3F in the basic TherMarq ZPF-100 body. Compositions TherMarq ZSF-102 and -103 omitted the $NH_4H_2PO_4$ and had less working time and fluidity than ZSF-101. TherMarq ZSF-104 was formulated with zirconium metal to increase the emittance of the body. This composition mixed readily. However, approximately one minute of mixing time resulted in the evolution of an odorless, colorless gas as evidenced by foaming of the mix. After trowelling into a 1/4 by 2 by 3-inch cavity, further evidence of gas evolution was shown by lifting of the panel out of the cavity. The coating was cured at 450°F and resulted in a hard, dense body of a light mottled gray color. Later exposure to the Thermal Drop Test Apparatus resulted in violent breaking up of the body.

Compositions ZSF-105 through -109 also released volatiles in sufficient amounts to cause bloating.

Compositions TherMarq ZSF-105 through -109 contained additives designed to improve the workable life of the coating. The ammonium carbonate (TherMarq ZSF-105) reacted with the hydrofluosilicic acid and liberated carbon dioxide. There was a slight bond formation but the resultant body was very crumbly.

Compositions TherMarq ZSF-105 and ZSF-108 contained ammonium fluoride which is highly hygroscopic. TherMarq ZSF-106 was a "wet" mix that worked fairly well. Doubling the amount of ammonium fluoride resulted in a very friable piece. This approach was discontinued.

Compositions TherMarq ZSF-107 and ZSF-109 contained ammonium chloride. The ammonium chloride appeared to be beneficial in slowing the acid action and resulted in workable bodies.

2. Hydrofluosilicic Acid from Various Vendors

Work on the optimization of the ZSF series was complicated by receipt of hydrofluosilicic acids in varying concentrations from several sources. Each of the acids was titrated with standard NaOH to the phenolphthalein end point. The percent acidity of each vendor's product was calculated. These results are tabulated in Table V.

TABLE V

ANALYSIS OF HYDROFLUOSILICIC ACID
FROM VARIOUS VENDORS

Vendor	% Acid
Baker & Adamson	31.0
Baker Chemical Company	32.5
Davison Chemical (1 lb sample)	35.1
Davison (bulk)	34.3
Harshaw (bulk)	30.9

Based on the varying concentration of the acid, TherMarq ZSF-101 was formulated as shown in Table VI.

TABLE VI

FORMULATION OF TherMarq ZSF-101 USING DIFFERENT HYDROFLUOSILICIC ACIDS

Constituent	Parts by Weight				
	B & A	Baker	Davison	Davison (bulk)	Harshaw (bulk)
ZrO_2 -30F (Norton H)	40	40	40	40	40
ZrO_2 -325F (Norton I)	30	30	30	30	30
$NH_4H_2PO_4$	1	1	1	1	1
H_2SiF_6	7.0	6.7	6.2	6.2	7.0
H_2O	--	--	qs	qs	--

No difference was noted when TherMarq ZSF-101 was made up with the above acids in the quantities noted with H_2O as required. The Davison acid was used to determine the maximum and minimum useful acid concentration.

3. Acid Concentration

The effects of acid concentration, substitution of refractories, modifying effect of $NH_4H_2PO_4$, and weight reduction were evaluated in TherMarq ZSF-124 through -130 and -132 through -139.

TherMarq ZSF-125 was overly fluid, and set slowly. This composition, therefore, was designated as having the upper acid concentration. Approximately 2 hours were required for TherMarq ZSF-125 to set at room temperature in comparison with TherMarq ZSF-101 which set in 10 minutes under the same condition. The TherMarq ZSF-125 coupon blistered badly after thermal testing.

The acid concentration was then reduced in an effort to determine the minimum quantity of acid which still resulted in a bond. TherMarq ZSF-126 resulted in a very weak coupon and was therefore not thermally evaluated. Compo-

sitions TherMarq ZSF-127 through -130 were intermediate to TherMarq ZSF-125 and ZSF-126.

Water was added dropwise as the acid was further decreased. A visual attempt was made in each case to maintain a consistency similar to previous mixes. TherMarqs ZSF-127, -128, and -129, on air drying, set in a similar short time interval. TherMarq ZSF-130 set more slowly with little green strength, and 200°F curing was required to develop a better bond equivalent to the preceding mixes at room temperature. However, the coupon did not endure well during testing. It was therefore inferred that TherMarq ZSF-130 represented the lower limit of acid concentration. Thermal evaluation of these mixes is shown in Table XI and depicted in Figure 3.

Samples of TherMarq ZSF-132 through -139 developed blisters and small cracks during exposure to 4000°F (uncorrected)*. Increasing the percentage of $NH_4H_2PO_4$, as in TherMarq ZSF-136 through -139, resulted in visible volatiles being given off during curing and firing. A one gram addition (1.43%) of $NH_4H_2PO_4$ to 70 grams of ZrO_2 was sufficient to prolong the working time of the mixture without creating visible volatiles.

Increasing the percentage of acid, as in TherMarq ZSF-132 through -135, indicated the effective acid range to be 6 to 7 grams per 70 grams of zirconia. TherMarq ZSF-132 was friable after firing. TherMarq ZSF-135 appeared slightly "soupy" during casting.

These compositions are shown after 4000°F exposure in Figure 4.

TherMarq ZSF-131 is basically the same composition as ZSF-124 but the differences turned out to be quite important. At the time this mix was formulated, proper raw materials were not on hand and the following substitutions were made:

TABLE VII

COMPARISON OF ZIRCONIA GRAINS

Constituent	ZSF-101	ZSF-124	ZSF-131
ZrO_2 -30F (Norton H)	40	40	--
ZrO_2 -36F (Norton H)	--	--	40
ZrO_2 -325F (Norton I)	30	30	--
ZrO_2 -325F (Zircoa B)	--	--	30
$NH_4H_2PO_4$	1	1	1
H_2SiF_6 (Davison)	6.2	7	7

To pinpoint further the effective range of acid concentration, compositions ZSF-124 through -130 were subjected to thermal evaluation by torch testing. These results are shown in Table XI.

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* Ray-O-Tube out of service.

During thermal drop testing, it was noted that the temperature of the back face of test coupons never exceeded 2230°F. In an attempt to reduce the weight of the insulative coating, TherMarq ZSF-114 was formulated. This composition was a standard ZSF-101 mix with a 1/16-inch layer of Fiberfrax placed between the ZrO_2 and the substrate. The thermal drop was not noticeably improved, and the effect on adherence of the coating to the substrate was detrimental.

4. Synergism

During previous experimental work, the phenomenon of "synergism" had been anticipated and noted. According to Webster, synergism is defined as "the cooperative action of discrete agencies such that the total effect is greater than the sum of the effects when the agency is taken independently." Compositions TherMarq ZSF-140 through -147 were formulated to evaluate synergistic effects.

TherMarq ZSF-144 and -145 were the wettest compositions of the series. TherMarq ZSF-146 and -147 required water addition. The addition of $(NH_4)_2\ SiF_6$ to TherMarq ZSF-140 to -142, -145, and -146 seemed to dry out these compositions. A very pungent odor was apparent when H_2PO_3F was used in conjunction with H_2SiF_6 as in TherMarq ZSF-142 through -147.

The fired properties of TherMarq ZSF-144 and -145 were comparable to those of TherMarq ZSF-141. Since 14.3 percent less acid was used to bond TherMarq ZSF-144 and -145, it can be definitely concluded that this was the result of synergism. Visual evidence of this phenomenon is shown in Figure 5.

5. Emittance Additives

Coloring agents and refractory oxides were added to the basic formulation to raise the emittance of the body. TherMarq ZSF-110 through -113, -115 through -123, and -148 through -165 depict this phase of the work. Results are tabulated in Tables IX, X, XII, XIII, and XIV and illustrated in Figures 6 and 7.

The consistencies of these compositions were essentially the same with exception of TherMarq ZSF-113 and -162. These compositions required considerable additional water because of the presence of $SrZrO_3$. Thermal evaluation data appear in Tables IX and XIII.

TherMarq formulations ZSF-140 through -147, which were shown to be synergistic, were repeated with the partial substitution of chromia for zirconia fines in an effort to raise the emittance. Two wetting agents were also evaluated in this series. These formulations were designated TherMarq ZSF-148 through -155.

All of these formulations were too dry, and therefore required the addition of water to achieve coating consistency. The addition of the wetting agents did not appear significant. All of the compositions were light green in color. Emittance values and thermal evaluations are tabulated in Table XII.

TherMarq ZSF-164 and -165 were formulated to evaluate the substitution of cobalt oxide for zirconia fines.

These composites were later subjected to the thermal drop test torch along with a control sample of TherMarq ZSF-101. Thermal results are shown in Table XIV.

D. Thermal Evaluation

The thermal drop test was used to evaluate all coupons that exhibited any cohesiveness after curing.

Since the Ray-O-Tube was not always in operation, some data are included for which no emittance values are shown.

TherMarq ZSF-104 withstood a corrected front face temperature of 4340°F for 5 minutes when exposed to the thermal drop test.

Thermal histories of formulations based on monofluorophosphoric acid are tabulated in Table VIII.

TABLE VIII

RESULTS OF THERMAL DROP TESTING OF MODIFIED TherMarq ZPF-100 BODIES

TherMarq Number	Coating Thickness	Time (min)	Ray-O-Tube (°F)		Thermal Drop (°F/0.001 in.)	Remarks
			Front	Back		
ZPF-101	0.284	5	3650°	1300°	8.3°	No cracks - slight glaze
ZPF-102	0.303	5	3695°	1325°	7.8°	No cracks - slight glaze
ZPF-103	0.295	5	3650°	1250°	8.1°	No cracks - slight glaze

TherMarq ZPF-104 through -108 were exposed to the thermal drop test torch for a 15-minute cycle at temperatures of approximately 3700°F, uncorrected on the optical pyrometer. The bodies looked quite good in all cases. Small cracks formed, but these did not appear to penetrate the body thickness.

The thermal tolerances for some of the early high emittance coatings are shown in Table IX.

TABLE IX

THERMAL DROP TESTING OF TherMarq ZSF-110 THROUGH -113

TherMarq Number	Color Before Test	Run Time (min)	Optical Front Face Temperature* (°F)	Remarks
ZSF-110	Brown	5	3880°	Eroded and turned gray
ZSF-111	Green	5	4000° to 4100°	Glazed, no color change, looked good
ZSF-112	Pale blue-green	5	3930°	Cracked and blistered
ZSF-113	Ivory	5	4000° to 4250°	Glazed, looked good

* Ray-O-Tube unavailable.

The comparison shown in Table IX was visual. Later composites of similar formulations of the TherMarq ZSF series (ZSF-119 and ZSF-155) showed the emittance to be in the 0.46 to 0.66 range. Measured emittance values of TherMarq ZSF-115 to -123 are compared with that of TherMarq ZSF-101 in Table X.

TABLE X

MEASURED EMITTANCE VALUES OF TherMarq ZSF-115 THROUGH -123
AS COMPARED TO TherMarq ZSF-101

TherMarq Number	Temperature (Corrected) (°F)	Emittance	Remarks
ZSF-101	4257°	0.45	Slight cracks
ZSF-115	3960°	0.75	Slight surface peeling - looked good
ZSF-116	3950°	0.65	Slight glaze, very small cracks, looked good
ZSF-117	4060°	0.52	Blistered
ZSF-118	--	--	Specimen friable - not tested
ZSF-119	3803°	0.66	Peeling, small holes, and cracks
ZSF-120	4120°	0.77	Blistered and cracked
ZSF-121	4200°	0.68	Blistered and cracked
ZSF-122	4118°	0.78	Blistered and cracked
ZSF-123	4155°	0.77	Blistered and cracked

TherMarq formulations ZSF-115 and ZSF-116 emerged as the most promising compositions, having both high emittance and relatively good surface characteristics. Since the remaining coupons all blistered, cracked, and peeled, the resultant rough surfaces may have been responsible for the high emittances exhibited by these coupons in addition to the effect of the coloring agents.

The thermal evaluation of TherMarq ZSF-124 through -130 is shown in Table XI. This series of mixes was used to evaluate mechanical strength (tabulated in Tables XVI through XVIII, Section VII).

TherMarq ZSF-132 through -139 were a series of coatings which incorporated increasing amounts of binder or $NH_4H_2PO_4$ in their formulation. They are shown after testing in Figure 3. Visible volatiles were given off during exposure to 4000°F (uncorrected) and all fired coupons developed blisters and small cracks.

TherMarq ZSF-140 through -147 were used to evaluate the phenomenon of synergism. Their appearances after exposure to a temperature of 4000°F is shown in Figure 5.

After exposure to the thermal drop test torch for fifteen minutes at 3900°F*, TherMarq ZSF-141, -144, and -145 had few blisters and still looked good. All other composites were blistered and cracked. Since TherMarq ZSF-144 and -145

- - - - - - - - - - -

* Estimated

contained less combined acids than the binder used in ZSF-141, evidence of synergism was again concluded after thermal evaluation. Visual evidence of this result is shown in Figure 5.

TABLE XI

THERMAL EVALUATION OF TherMarq ZSF-124 THROUGH -130

TherMarq Number	Run Time (min)	Optical Front Face Temperature* (°F)	Remarks
ZSF-124	5	4000°	Very slight glaze--appeared dense
ZSF-125	5	4000°	Badly blistered in 20 seconds; then rerun for 5 minutes--cracked and glazed
ZSF-126	--	--	Not run because of poor green cohesiveness
ZSF-127	5	4000°	Slight glaze--appeared porous
ZSF-128	5	4000°	Glazed--appeared porous
ZSF-129	5	4000°	Very glazed--appeared porous
ZSF-130	5	4000°	Very, very glazed--appeared porous and decrepitated

* Uncorrected because Ray-O-Tubes were not available for this test.

TherMarq ZSF-148 through -155 contained partial substitutions of chrome oxide for zirconia fines. Thermal test data for this series are shown in Table XII.

TABLE XII

THERMAL EVALUATION OF TherMarq ZSF-148 THROUGH -155

	TherMarq ZSF-Number							
	148	149	150	151	152	153	154	155
Optical pyrometer (°F)	3580	3510	3560	3000	3530	3460	3490	3850
Ray-O-Tube (°F)	3350	3325	3410	2550	3140	3130	3150	3500
True temperature (°F)	3880	3700	3730	3360	3930	3830	3850	4250
Emittance	0.56	0.67	0.71	0.35	0.42	0.45	0.48	0.46
Time (minutes)	5	5	5	5	5	5	5	5

The use of chrome oxide in these compositions raised the emittance. In all cases, the fired color was green to light gray with attendant blisters and cracks. A white powder was also deposited on the periphery of specimens ZSF-148 to -154. TherMarq ZSF-155 did not have this white precipitate. Since $(NH_4)_2SiF_6$ was omitted from this composition, it may be concluded that its presence in TherMarq ZSF-148 to -154 is the cause of the white precipitate which was noted. It is believed that the difference in expansion rates of Cr_2O_3 and ZrO_2 was the

cause of the cracks and blisters noted. These composites are shown in Figure 6 as they appeared after exposure to a temperature of 4000°F.

Thermal results of a series containing additives other than chrome oxide are tabulated in Table XIII.

TABLE XIII

THERMAL EVALUATION OF TherMarq ZSF-155 THROUGH -163

	TherMarq ZSF-Number								
	155	156	157	158	159	160	161	162	163
Thickness (inches)	0.291	0.276	0.262	0.291	0.292	0.287	0.303	0.284	0.285
Optical pyrometer (°F)	3150	3440	3025	3410	3410	3200	3220	3190	3280
Ray-O-Tube (°F)	2450	3000	2450	2825	2850	2420	2500	2500	2500
Thermocouple (°F)	1870	1740	1720	1860	1965	1810	1930	1770	1830
Time (minutes)	10	10	10	10	10	10	10	10	10
Emittance	0.35	0.36	0.55	0.26	0.27	0.38	0.42	0.45	0.37
True temperature (°F)	4180	3900	3530	4010	3970	3680	3980	3890	4170
Thermal drop (°F/mil)	7.9	7.8	6.9	7.4	6.9	6.5	6.8	7.5	8.2
Color (Fired)	Gray-green	Speckled gray	Gray	Yellow-white	Yellow-white	Yellow-white	Yellow-white	Yellow-white	Buff

TherMarq ZSF-162 and -163 had large cracks but no evidence of glaze or blisters. TherMarq ZSF-155, -157, -160, and -161 exhibited smaller cracks with no blisters or glazed spots. The remaining mixes, TherMarq ZSF-156, -158, and -159, were all blistered and cracked. TherMarq ZSF-157, which contained Co_2O_3 exhibited the highest emittance. Other mixes, based on cobalt oxide, are tabulated in Table XIV. The appearances of TherMarq ZSF-155 through -163 after exposure to a temperature of 4000°F are shown in Figure 7.

All specimens were cracked to some degree with the severity of the cracking directly related to the increasing percentage of cobalt oxide. The small gain in emittance hardly appeared worth the sacrifice in structural characteristics of the coating. The appearance of the specimens after exposure to a temperature of 4000°F is shown in Figure 8.

TABLE XIV

THERMAL EVALUATION OF TherMarq ZSF-164 AND ZSF-165 CONTAINING COBALT OXIDE AND COMPARISON WITH CONTROL SAMPLE TherMarq ZSF-101

	ZSF-101	ZSF-164	ZSF-165
Thickness (inches)	0.285	0.288	0.279
Optical pyrometer (°F)	3350	3220	3250
Ray-O-Tube (°F)	2610	2650	2675
Thermocouple (°F)	1800	1840	1900
Time (minutes)	10	10	10
True temperature (°F)	4200	3760	3820
Emittance	0.41	0.53	0.53
Thermal drop (°F/mil)	8.4	6.7	6.9
Color (Fired)	Yellow-white	Gray	Gray

VI. SIMULATED APPLICATION THERMAL STUDIES

Logical applications for reinforced refractory coatings include nose caps and leading edges. In both applications, the substrate back faces are submerged so that rejection of heat by radiation and convection is severely limited. The following experiment was conducted to simulate this condition and to obtain some comparative data.

A rectangular cavity with an annular ledge was carved into an alumina insulating brick in such a manner that a 2 by 3-inch reinforced refractory coupon could be placed into the ledge to close the cavity. The refractory face of the coupon was flush with the face of the brick, while the N-155 substrate of the coupon faced the rear of the cavity in the brick. Thermocouple leads were introduced through small diameter holes in the sides of the brick at an angle with the back of the coupon. The thermocouple was welded to the N-155 material in the usual fashion at a site opposing the area on the coating which received the thermal drop test flame.

Thermal drop tests were conducted to steady state conditions. A series of specimens of TherMarqs ZSF-101 and ZPF-100 were made each with nominal thickness of 1/4, 1/2, and 3/4 inch. These samples were then thermal drop tested both in air and encased in brick. The results are tabulated in Table XV.

It is quite apparent from Table XV that in all cases the thermal drop efficiency deteriorates quite rapidly in thicknesses over 1/4 inch. TherMarq ZSF-101 appears to have a slight edge over ZPF-100 in thicker sections. There is also less tendency to glaze and crack.

TABLE XV

COMPARATIVE THERMAL DROP DATA FOR TherMarq ZSF-101 AND ZPF-100

	TherMarq Number			
	ZSF-101	ZSF-101	ZPF-100	ZPF-100
Run condition	In brick	In air	In brick	In air
Time (minutes)	9.5	12	10	10
Thickness (inches)	0.217	0.257	0.246	0.237
Front face temperature (°F)	3130°	2820°	3750°	2880°
Front face (corrected) (°F)	3490°	3140°	4200°	3205°
Back face temperature (°F)	2020°	1200°	2230°	1205°
Thermal drop (°F/mil)	6.8°	7.5°	8.0°	8.4°
Run Condition	In brick	In air	In brick	In air
Time (minutes)	16	11.5	21.5	16.5
Thickness (inches)	0.542	0.490	0.493	0.488
Front face temperature (°F)	2770°	2940°	3210°	2920°
Front face (corrected) (°F)	3080°	3270°	3580°	3250°
Back face temperature (°F)	1410°	1120°	1720°	1210°
Thermal drop (°F/mil)	3.1°	4.4°	3.8°	4.2°
Run condition	In brick	In air	In brick	In air
Time (minutes)	25	30	25	21.5
Thickness (inches)	0.758	0.788	0.722	0.723
Front face temperature (°F)	2680°	2950°	2550°	2900°
Front face (corrected) (°F)	2980°	3285°	2830°	3230°
Back face temperature (°F)	1270°	760°	1270°	940°
Thermal drop (°F/mil)	2.3°	3.2°	2.2°	3.1°

VII. MECHANICAL PROPERTIES

A. Impact Strength

TherMarq compositions ZSF-124 through -130 were checked for resistance to impact using a falling ball technique. A ball was held by an electromagnet at a prescribed height above the specimen so that only potential energy was transmitted on impact. Sections of these coupons were first qualitatively checked by repeatedly dropping a steel ball bearing from a 2-foot distance. The parts were tested to destruction. Impact strength data are tabulated in Tables XVI through XVIII.

TABLE XVI

QUALITATIVE COMPARISON OF IMPACT STRENGTHS OF TherMarq ZSF-124 THROUGH -130

TherMarq Number	Weight of Ball (gms)	Diameter of Ball (inches)	Number of Times Dropped	Remarks
ZSF-124	21.5	0.6875	5	Cracked
ZSF-125	21.5	0.6875	3	Cracked
ZSF-126	--	--	--	Not tested--no green strength
ZSF-127	21.5	0.6875	4	Cracked
ZSF-128	21.5	0.6875	3	Cracked
ZSF-129	21.5	0.6875	3	Cracked
ZSF-130	21.5	0.6875	1	OK
ZSF-130	95.0	0.905	1	Cracked

Other sections of coupons of TherMarq ZSF-124 through -130 were evaluated quantitatively by gradually raising the electromagnet and thereby increasing the potential energy of the ball to the breaking point of the specimen. The results are shown in Table XVII.

TABLE XVII

QUANTITATIVE COMPARISON OF IMPACT STRENGTHS OF TherMarqs ZSF-124 THROUGH -130

Weight of Ball (gms)	Diameter of Ball (inches)	Distance (inches)	Potential Energy (inch-pounds)	TherMarq Numbers					
				ZSF-124	ZSF-125	ZSF-127	ZSF-128	ZSF-129	ZSF-130
3.2	0.375	4	0.028	No change	No change	No change	No change	No change	No change
3.2	0.375	10	0.071	No change	No change	No change	No change	No change	No change
3.2	0.375	16	0.113	No change	No change	No change	No change	Cracked	No change
3.2	0.375	22	0.156	No change	No change	Cracked	No change	Cracked	No change
3.2	0.375	28	0.199	No change	No change	Cracked	No change	Cracked	No change
3.2	0.375	34	0.240	No change	No change	Cracked	No change	Cracked	Cracked
3.2	0.375	40	0.284	No change	No change	Cracked	No change	Cracked	Chipped
3.2	0.375	46	0.327	No change	No change	Cracked	No change	Cracked	Broken
3.2	0.375	52	0.369	No change	Cracked	Cracked	No change	Broken	
3.2	0.375	58	0.412	No change	Cracked	Broken	Cracked		
21.5	0.6875	4	0.188	No change	Cracked		Cracked		
21.5	0.6875	10	0.470	No change	Cracked		Cracked		
21.5	0.6875	16	0.752	No change	Cracked		Broken		
21.5	0.6875	22	1.034	No change	Cracked				
21.5	0.6875	28	1.316	No change	Broken				
21.5	0.6875	34	1.612	Cracked					
21.5	0.6875	40	1.880	Cracked					
21.5	0.6875	46	2.162	Cracked					
21.5	0.6875	52	2.444	Cracked					
21.5	0.6875	58	2.726	Broken					

Impact strengths calculated from these data are shown in Table XVIII.

TABLE XVIII

ULTIMATE IMPACT STRENGTHS OF TherMarq ZSF-124 THROUGH -130

TherMarq Number	Impact Strength to Break (inch-pounds)	Impact Strength to Crack (inch-pounds)
ZSF-124	2.726	1.612
ZSF-125	1.316	0.369
ZSF-126	Not tested	Not tested
ZSF-127	0.412	0.156
ZSF-128	0.752	0.412
ZSF-129	0.369	0.113
ZSF-130	0.327	0.240

B. Modulus of Rupture

Test bars approximately 5 by 1 inch were molded for modulus of rupture tests. The bars were cured to 450°F and then broken in a Baldwin Physical Testing Machine using three point loading on a 4-inch span. The loading rate in all cases was 500 lbs/min. Modulus of rupture data for these compositions are shown in Table XIX.

TABLE XIX

MODULUS OF RUPTURE COMPARISON OF TherMarq ZSF-101, -124, & -131

TherMarq Number	Sample Number	Modulus of Rupture (psi)
ZSF-101	1	942
	2	949
	3	930
	Average	940
ZSF-124	1	515*
	2	1050
	Average	783
ZSF-131	1	708
	2	595
	3	770
	4	718
	Average	698

* Presumed anomolous reading, may have been due to incipient crack or nonuniform porosity.

Table XIX shows that TherMarq ZSF-101 and -124 are apparently stronger than the TherMarq ZSF-131.

VIII. THERMOPHYSICAL PROPERTIES

A. Thermal Expansion

The thermal expansion characteristics of the TherMarq ZSF-124 coating composition were determined using a Brinkman-Netzsch automatic recording dilatometer equipped with a sintered alumina sample holder and transmission rod. The apparatus is shown in Figure 9. The equipment was calibrated using a sample of single crystal alumina whose orientation and thermal expansion were precisely known.

Expansion runs were made with the TherMarq ZSF-124 composition in the air dried condition, after curing at 450°F, and after firing at 2700°F for 12 hours. A program controlled heating rate of 9°F/min was used for all determinations. The results of these determinations are shown graphically in Figure 10. The length changes indicated for the air dried and 450°F cured specimens were both reversible and irreversible. The length changes shown for the prefired specimen were totally reversible. The magnitude of the permanent shrinkage of the air dried and 450°F cured specimens when fired to 2700°F were 2.43 and 1.98 percent, respectively.

B. Differential Thermal Analysis (DTA)

The DTA equipment shown in Figure 11 was used to detect the presence of chemical or phase transformations in the TherMarq ZSF-124 coating composition. The DTA apparatus consisted of a vertical Pt-40% Rh wound tube furnace that could be raised or lowered for access to the sample holder. The sample holder was a sintered alumina block containing three centrally located cavities for the sample, the reference material, and the reference thermocouple. Reaction between the sample material and sample holder was prevented by encapsulating the sample in platinum foil before inserting into the sample holder cavity. Pt vs. Pt/13 Rh was used for both the reference and the differential thermocouples. The output of the couples was fed into a Brown X-Y recorder. An output of 40 millivolts produced a one-inch deflection on the DTA trace.

Results from numerous differential thermal analyses of TherMarq ZSF-124 at temperatures up to 2700°F and at various heating rates showed this formulation to be completely free of any chemical or phase transformation.

IX. VIBRATORY CASTING TECHNIQUES

Reinforced refractory ceramic coatings have been applied in the past as trowelled coatings. Vibratory casting is an excellent method of extending the application range of this type coating.

The H_2SiF_6 bonded ceramic coatings were highly thixotropic: a stiff, mortar-like consistency when at rest and quite fluid under vibratory loading. A vibratory table was constructed which consisted of a suitably suspended plate, activated by means of an "Airoviber" vibrator. Metal or modified plaster molds were used to form the parts. The coating material was placed inside the cavity and the induced vibration caused the material to flow and fill the cavity. An added advantage of this method is that the size of the part to be coated is limited only by the capacity of the vibrator.

X. MODEL NOSE CONES AND LEADING EDGES

Designs for model leading edges and nose cones of approximately 20 square inch and 500 square inch sizes were submitted to the ASD Project Engineer for approval before fabrication of the units was started.

Once approval had been obtained and the prototype substrates had been fabricated, molds were designed and fabricated of steel and Hydrocal plaster. The plaster was impregnated with 20% Elvax-fortified, paraffin wax as a parting agent. The molds were used in the vibratory casting of the small scale model nose cones and leading edges. The table was vibrated at a speed of 5400 vibrations per minute during the casting of the model nose cones and leading edges. These molds were designed with interchangeable inserts as shown in Figure 12. Figures 13 and 14 show the nose cone and leading edge molds before casting of the plaster support.

Type 321 stainless steel reinforcement 0.125 inch wide by 0.010 inch thick was spot welded to the substrates in preparation for refractory coating. The welding operation is shown in Figure 15 and Figures 16 and 17 are views of the small scale models with reinforcement completely attached.

The parting surface of each of the leading edge molds was stainless steel. When these surfaces were waxed, they afforded readily releasable areas. Because of the complexity of fabricating a metal mold for the nose cone, the parting surface of the mold was waxed plaster.

The refractory coating material (TherMarq ZSF-124) was mixed in the sigma bladed vacuum dough mixer shown in Figure 18. Ammonium hydroxide was used to neutralize and prevent acid vapors from entering the vacuum pump.

The small scale components were aligned in their proper molds, bolted to a vibratory table, and the casting operation was completed. Figure 19 shows the casting operation. No problems were encountered in releasing the leading edges from the molds. In the case of the nose cones, however, extremely poor parting characteristics resulted in a 50% yield when the parts were removed from the mold.

Figure 20 shows the completed small scale components after curing. Thermocouples were attached at the request of the ASD Project Engineer. Three basic curvatures of leading edge models were coated; two samples of each thickness were made. The cured weights of the specimens are shown in Table XX.

The general procedure in vibratory casting of the 500 square inch models was similar to that followed in the fabrication of the small scale components. The 500 square inch leading edge model substrate is shown in Figure 21. Stainless steel reinforcing ribbon 0.125 inch wide by 0.10 inch thick was spotwelded to the substrate in preparation for refractory coating. Approximately 3,000 spot welds were needed to attach the reinforcements to each model. The 500 square inch leading edge model with reinforcement attached is shown in Figure 22. A similar view of the 500 square inch nose cone model is shown in Figure 23.

TABLE XX

WEIGHTS OF REFRACTORY CAST ON SMALL SCALE COMPONENTS

Component	Part Number	Thickness of Refractory (inches)	Refractory Weight (grams)
Nose cone	703228-401	0.3	899
	703228-401	0.3	879
	703228-401	0.3	877
Nose cone	703228-401	0.5	1650
	703228-401	0.5	1615
	703228-401	0.5	1600
Leading edge	703228-403	0.3	1010
	703228-403	0.3	1080
Leading edge	703228-403	0.5	1810
	703228-403	0.5	1750
Leading edge	703228-403	0.75	2582
	703228-403	0.75	2670
Leading edge	703228-404	0.3	1073
	703228-404	0.3	1066
Leading edge	703228-404	0.5	1770
	703228-404	0.5	1741
Leading edge	703228-405	0.3	1150
	703228-405	0.3	1128

To avoid the necessity of fabricating a special male mandrel, the substrate for the nose cone was first temporarily coated with plaster and used as a mandrel upon which the female mold could be cast. Figure 24 shows the machining of this mandrel to the desired dimension. The finished mandrel, coated with shellac, is shown in Figure 25.

Because of the difficulties experienced in separating the small scale nose cones from their molds, a five-piece mold was designed for the 500 square inch nose cone model. This mold is shown in Figure 26. A fluorine-base parting agent--KEL-F--soft wax, Grade 40 was also obtained from E. I. DuPont, Inc. as a mold release coating.

The mold for the 500 square inch leading edge model was fabricated by bending a sheet of cold rolled steel to the desired dimension. This surface was then waxed in a similar fashion to the method used for the small scale leading edge molds.

Both large scale components were then aligned in their respective molds, they were bolted to a vibratory table, and the refractory casting operation was

accomplished. These components are shown prior to casting in Figures 27 and 28 and after casting in Figures 29 and 30.

No problems were experienced in releasing the 500 square inch leading edge model from its mold. The parting agent--KEL-F soft wax, Grade 40--used in the nose cone mold tended to adhere to the mold and the part rather than permit separation. Extensive patching of the part was therefore required. The weight of refractory used to coat the 500 square inch nose cone model was 10,201 grams, and that used to coat the 500 square inch leading edge mold was 10,276 grams. The refractory coating thickness was a nominal 0.3 inch in both cases. The finished components are shown in Figures 31 and 32.

XI. FUTURE WORK

Lack of time necessitated curtailment of development work in several areas which gave promise of beneficial results if pursued further. Other areas were not touched upon because they were outside the scope of the contract, although related thereto. In making recommendations for future work, both areas are included in the following items:

1. Reliable antioxidant coatings must be developed for refractory metal reinforcement media. Such coating must be applied without detrimentally affecting the substrate structure, or interfering with attachment welds.

2. Because the trend is to higher temperatures and more dynamic environments, the need for stronger and more refractory reinforced ceramic coatings to withstand the environments becomes apparent. Thoria and modified thoria coatings should be investigated for the plus 5000°F regime.

3. The applicability of vibratory casting has been demonstrated. However, the mold preparation and better parting agents require further investigation.

4. Synergism has been lightly touched upon. Further work on this phenomenon is indicated.

5. No satisfactory additive was found to raise the emittance of the coating without tending to destroy the coating. Alteration of the surface by staining, roughening, or combinations of these operations may yield the desired result. This should be investigated.

XII. ADDENDUM

The following work was not done under the subject contract but is a pertinent item of interest, since it concerns a large scale application of reinforced refractory coatings to a 2800°F Clean Air Heater under Contract AF 33(600)-37639.

A large heat exchanger approximately 14 feet high by 18 inches ID in four sections with eight pipe sections and elbows was coated with 1 5/8 inch thick reinforced TherMarq ZSF-124.

The reinforcement was corrugated Type 321 stainless steel 1/8-inch wide by 0.010 inch thick. Over 25,000 spot welds were used to fasten the reinforcement to the ID of the heat exchanger sections. Approximately one ton of coating material was installed by vibratory casting. Three sections of the heat exchanger with reinforcement attached are shown in Figures 33 through 35. Figure 36 shows the top dome section during the coating operation. Four views of sections of the heat exchanger after coating are shown in Figures 37 through 40. The secondary piping for the unit is shown in Figures 41 and 42, and Figure 43 shows the completely installed unit.

The completed unit will operate using vitiated air at 3100°F as the heating medium. Clean air will enter at 1500°F and will be heated to 2800°F. The normal operating pressure will be 220 psig.

XIII. REFERENCES

1. Marquardt Report 5802, "(Title -- Unclassified) Development and Evaluation of Insulating Type Ceramic Coatings During the Period 1 May, 1959 to 30 April, 1960", dated 30 April, 1960. UNCLASSIFIED.

2. WADD Technical Report 60-491, "Development of Reinforced Ceramic Materials Systems", (L. M. Stejskal, et al), dated 19 May, 1960.

3. Sklarew, S., "Reinforced Refractory Ceramic Coatings for Ramjet and Supersonic Aircraft Applications", published in Mechanical Properties of Engineering Ceramics, edited by W. W. Kriegel and H. Palmour III, 1961.

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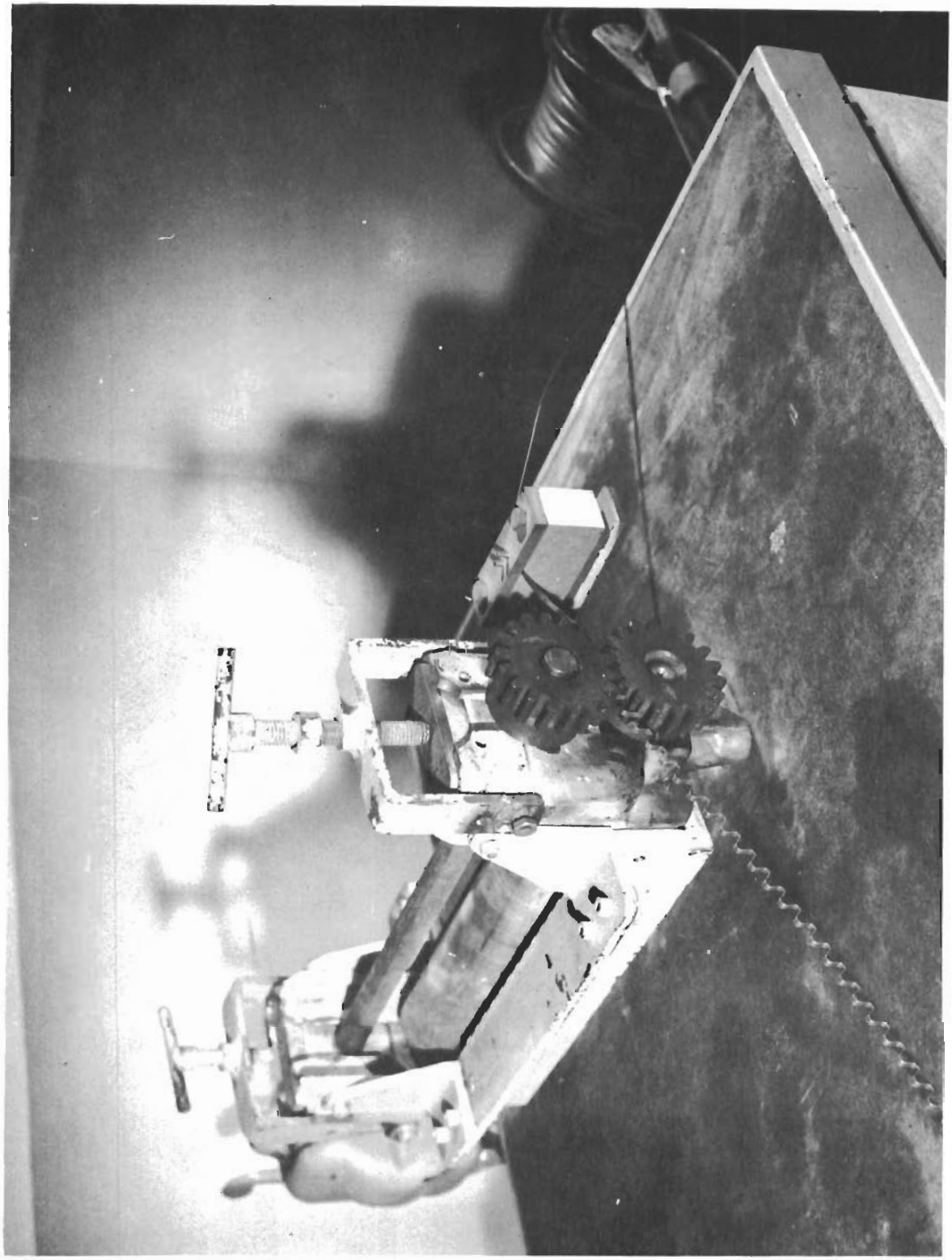

FIGURE 1. Forming Corrugated Reinforcement Strip

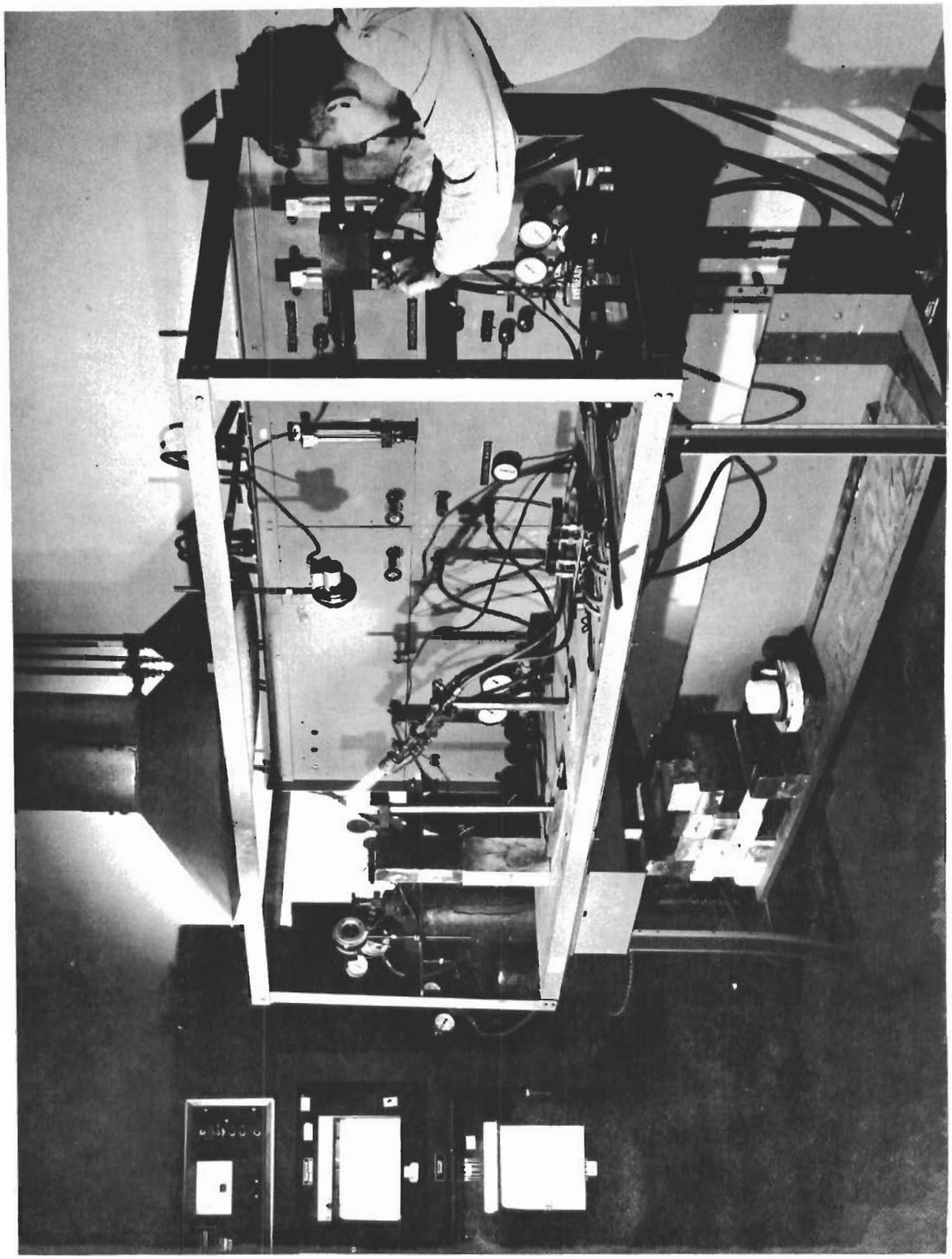

FIGURE 2. Setup for Thermal Drop Testing

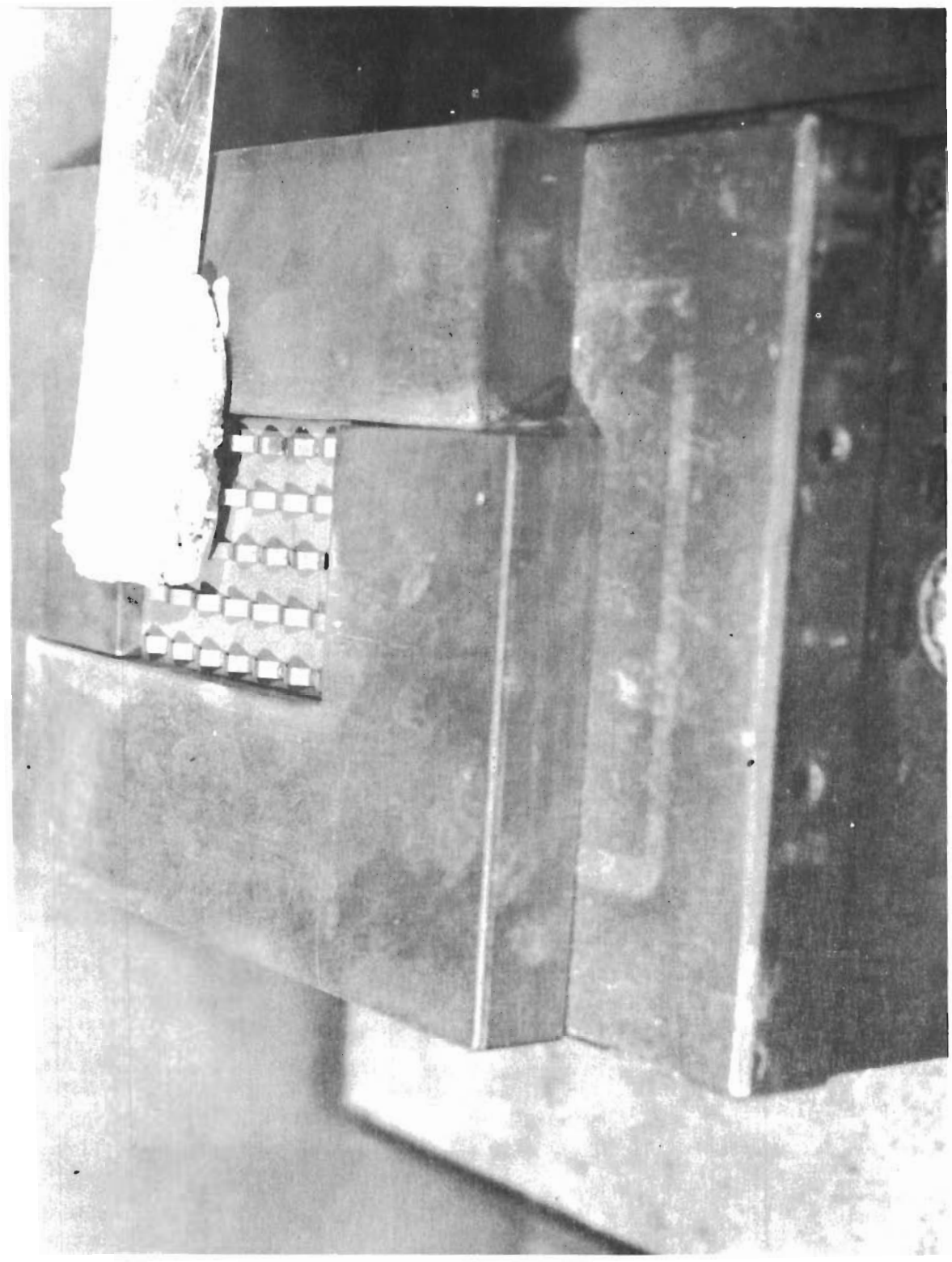

FIGURE 3. Casting of Coupons

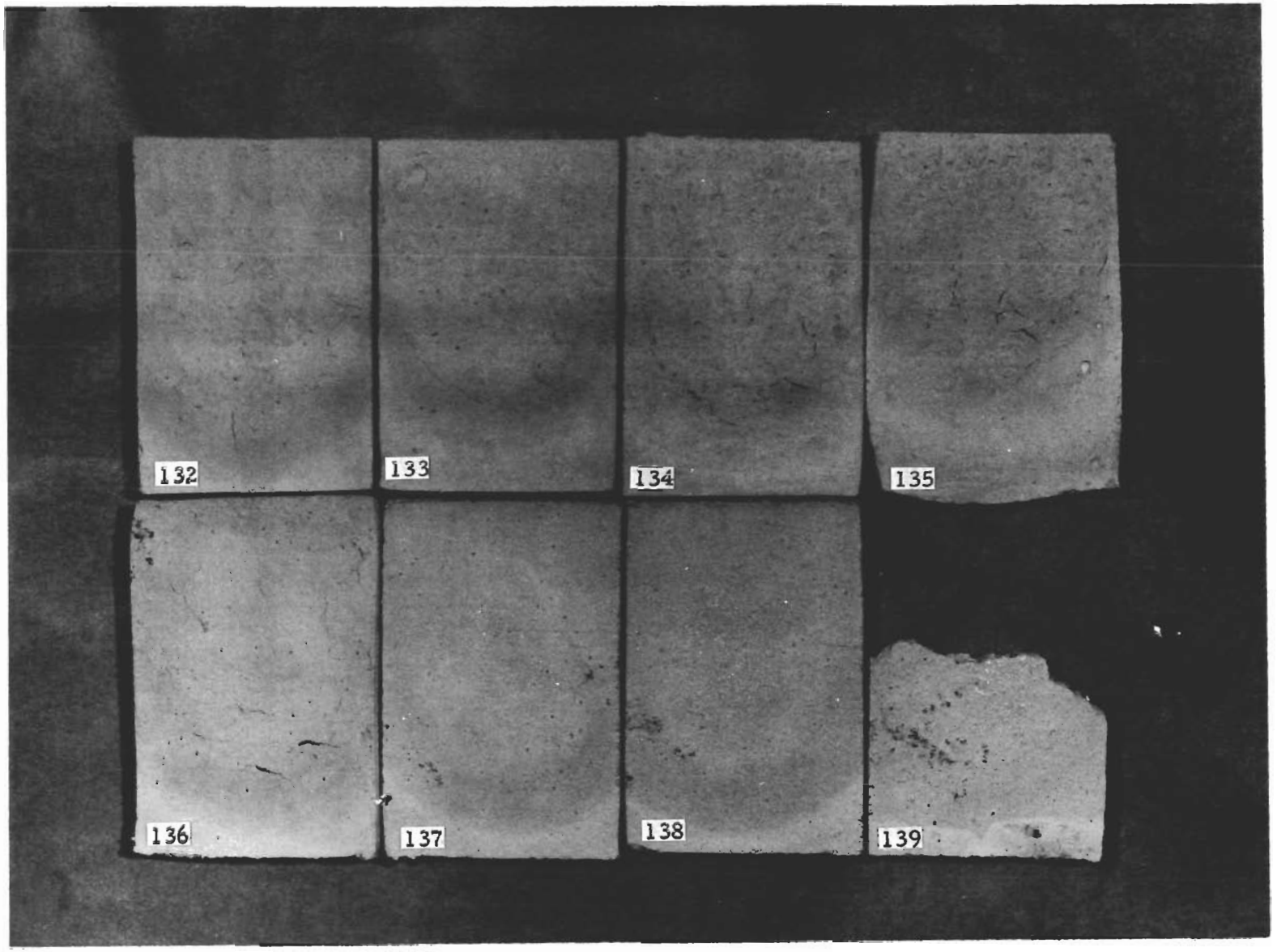

FIGURE 4. TherMarq ZSF-132 through -139 after 4000°F Exposure

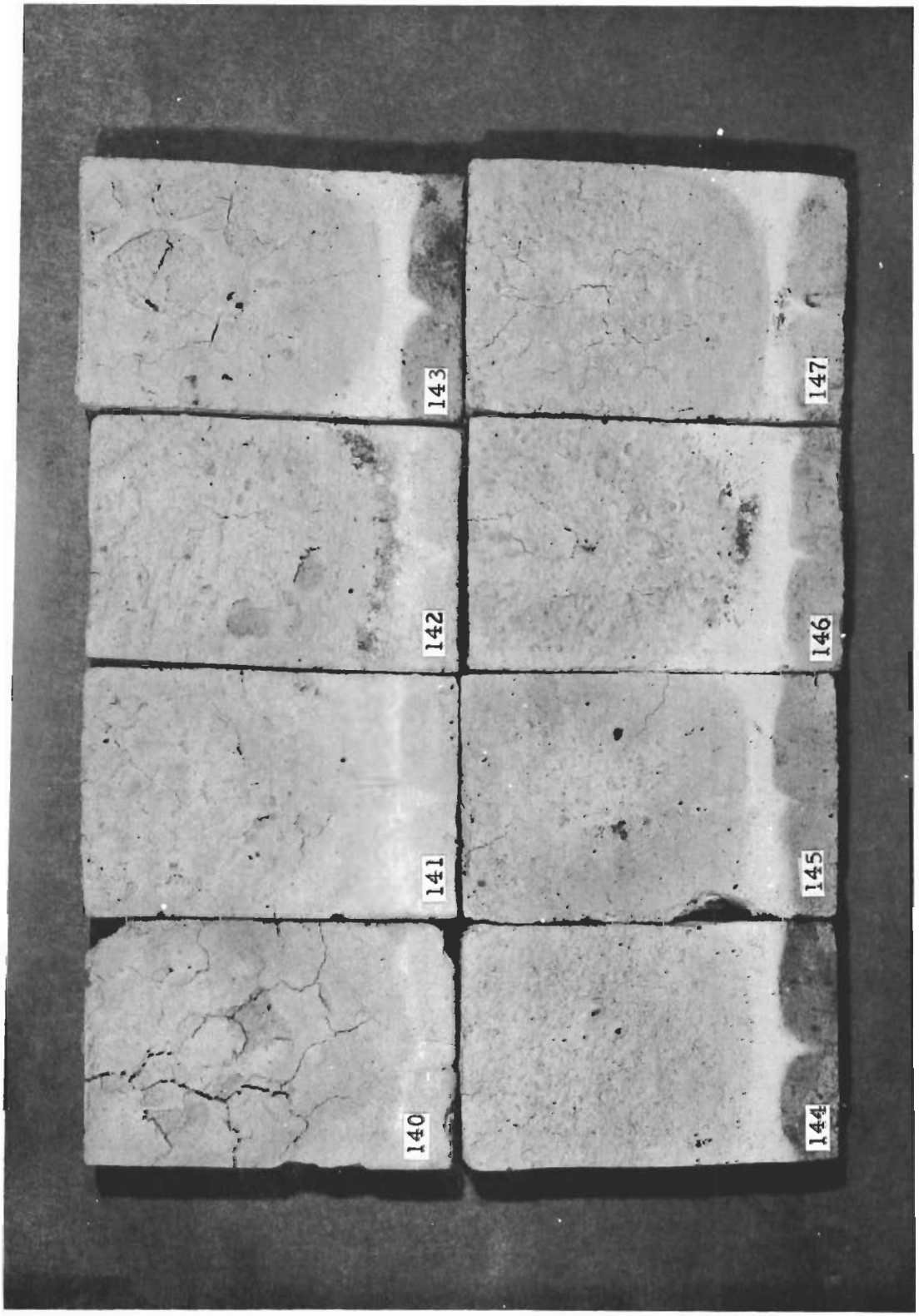

FIGURE 5. TherMarq ZSF-140 through -147 after 4000°F Exposure

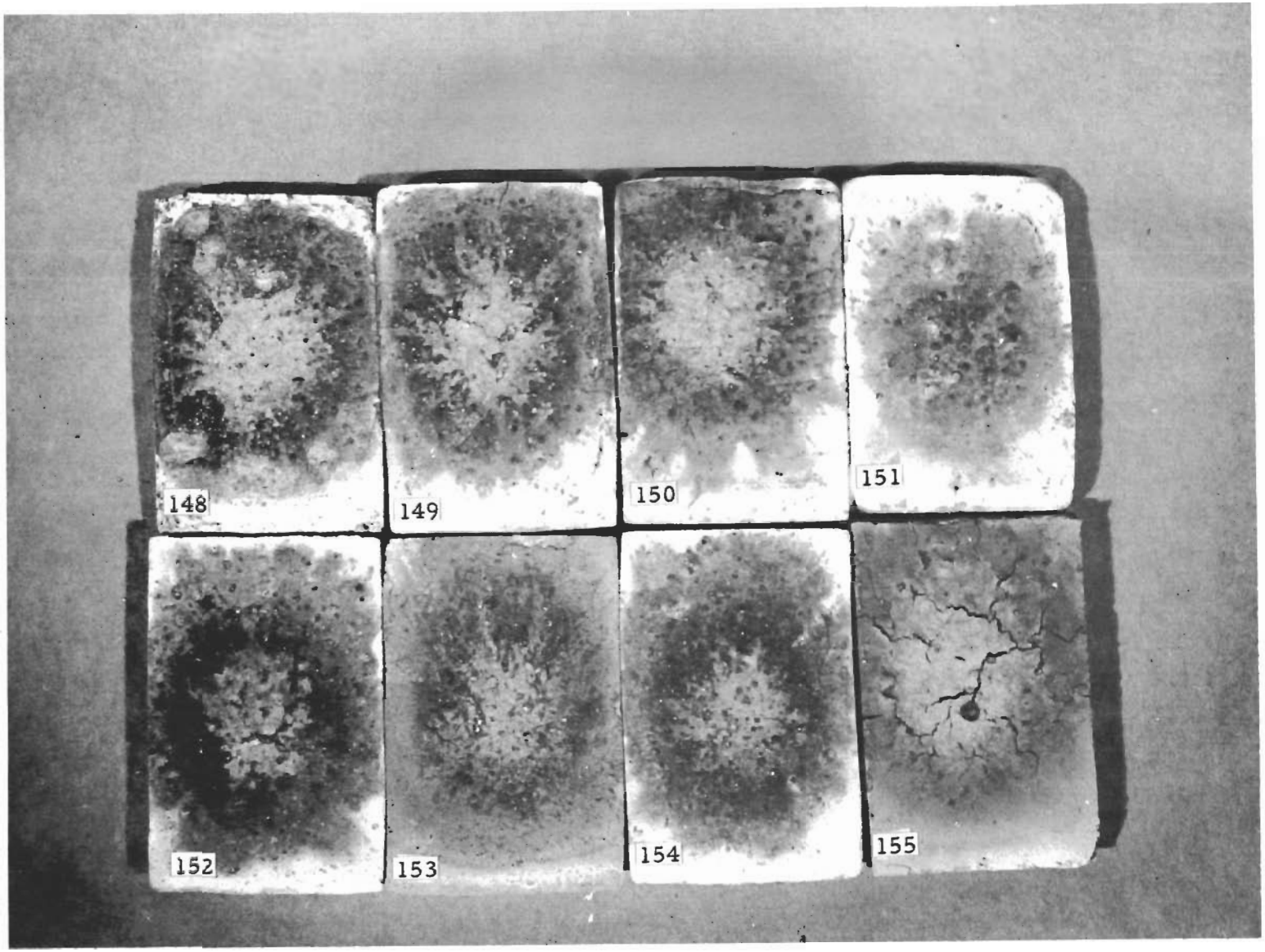

FIGURE 6. TherMarq ZSF-148 through -155 after 4000°F Exposure

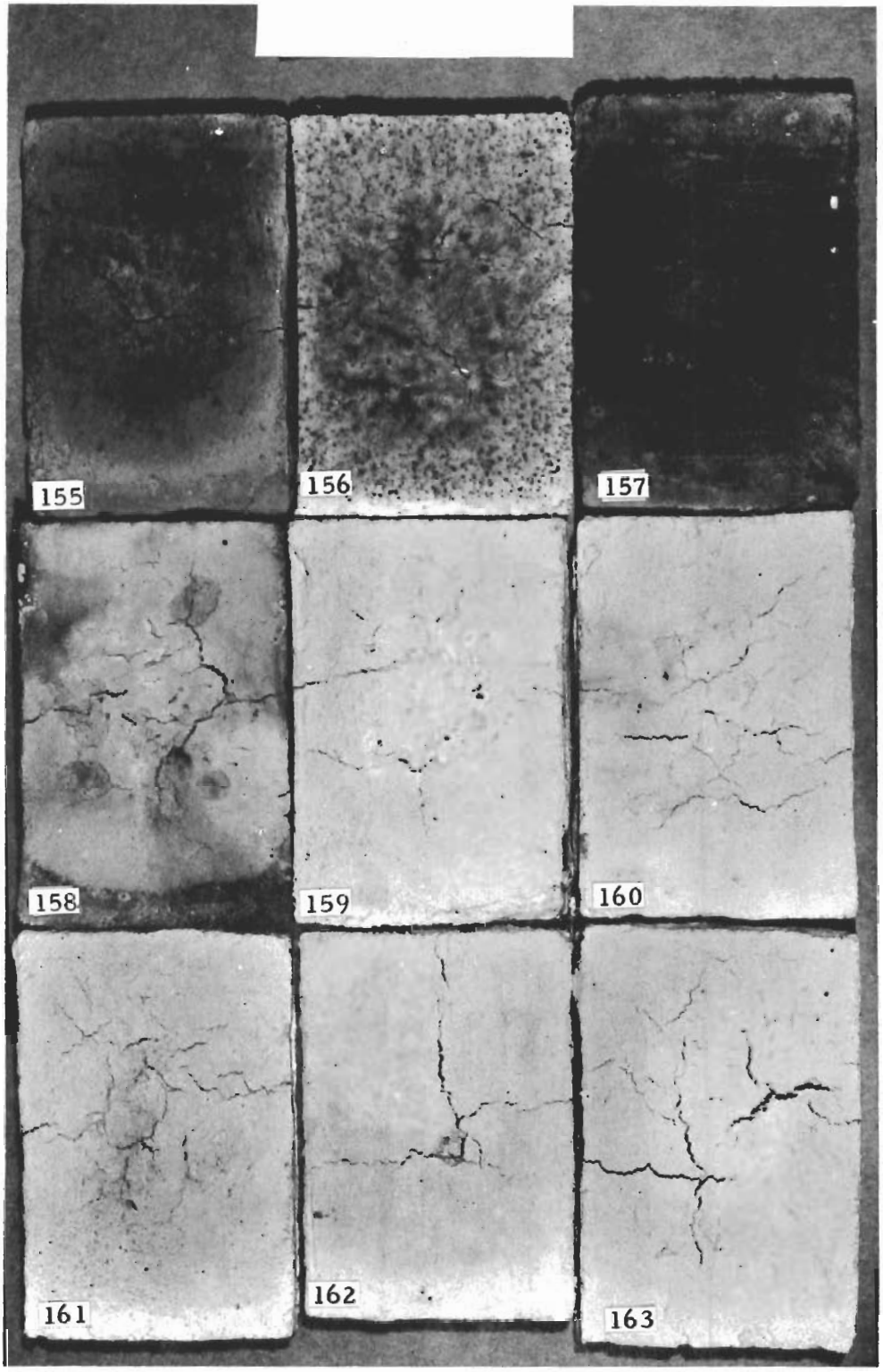

FIGURE 7. TherMarq ZSF-155 through -163 after 4000°F Exposure

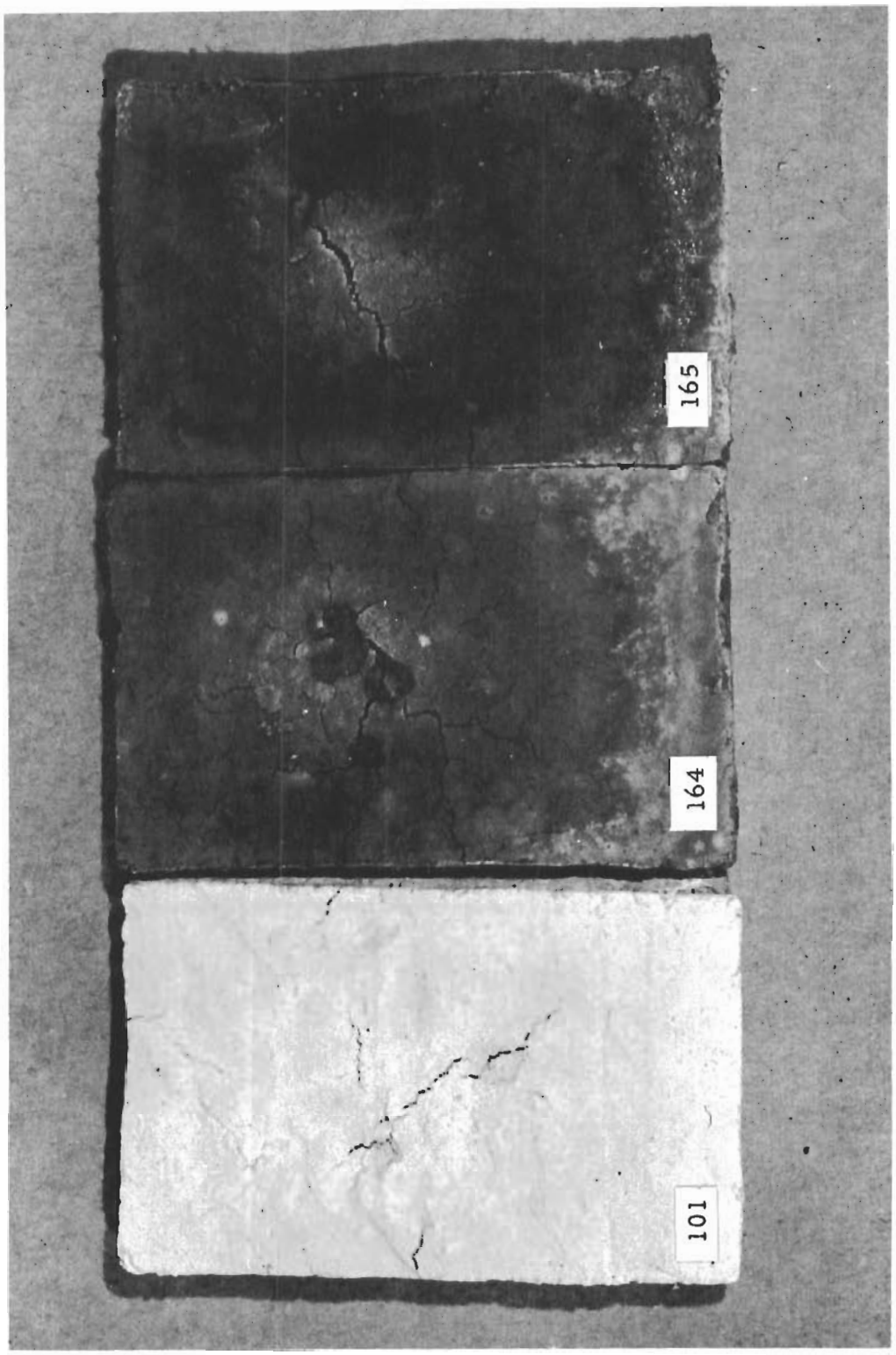

FIGURE 8. ThermarQ ZSF-101, -164, and -165 after 4000°F Exposure

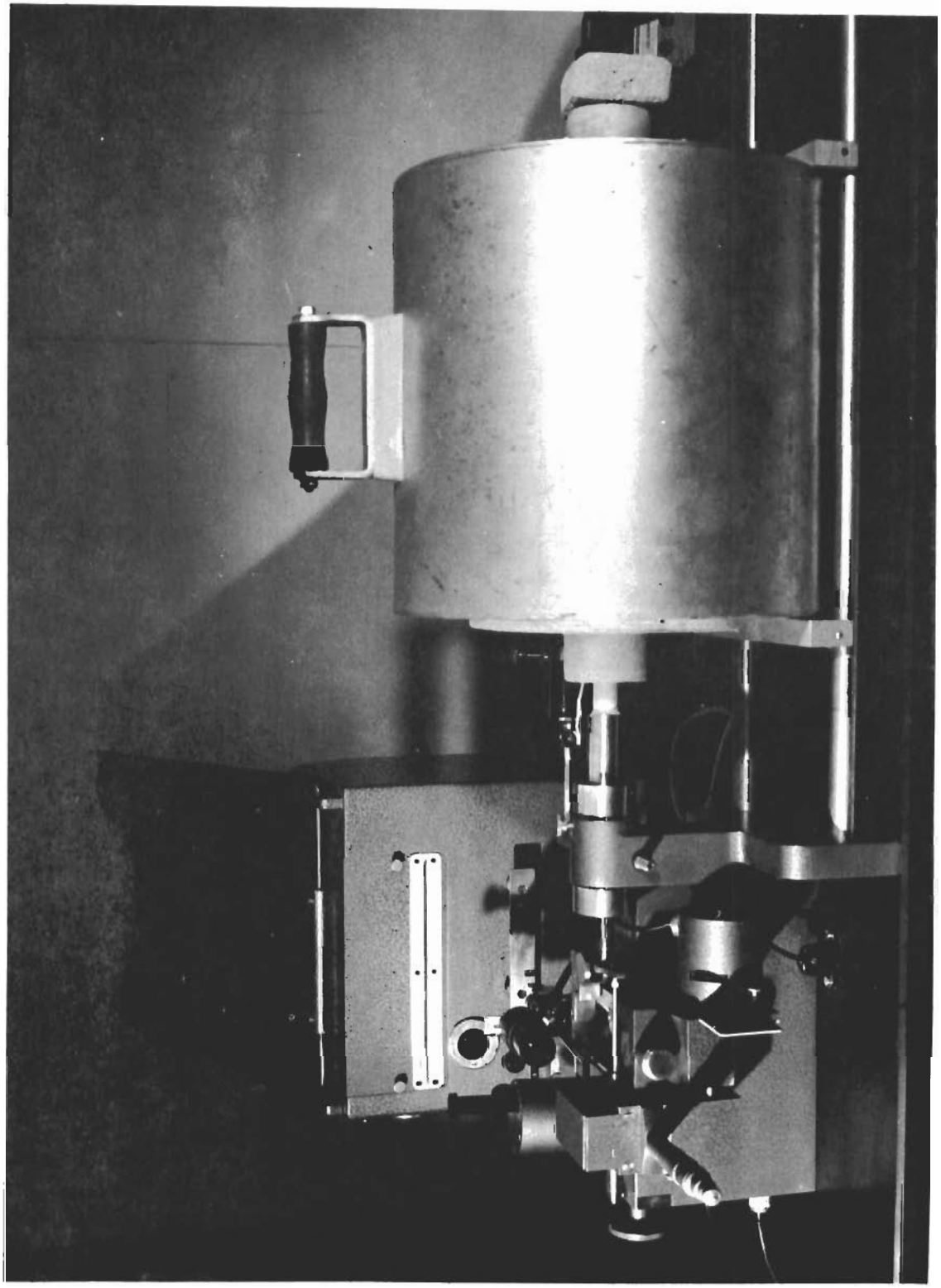

FIGURE 9. Thermal Expansion Apparatus

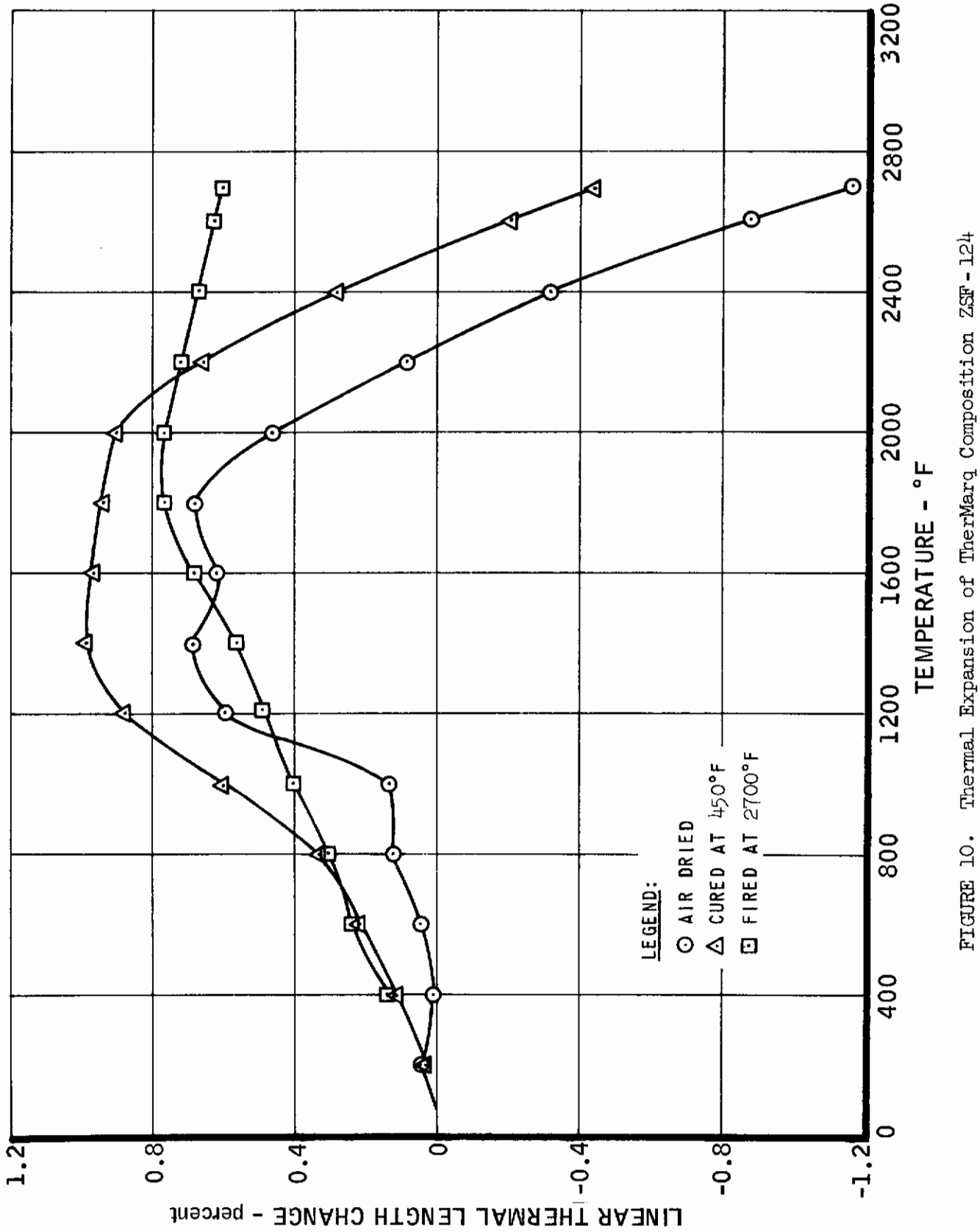

FIGURE 10. Thermal Expansion of TherMarq Composition ZSF-124

FIGURE 11. Differential Thermal Analysis Apparatus

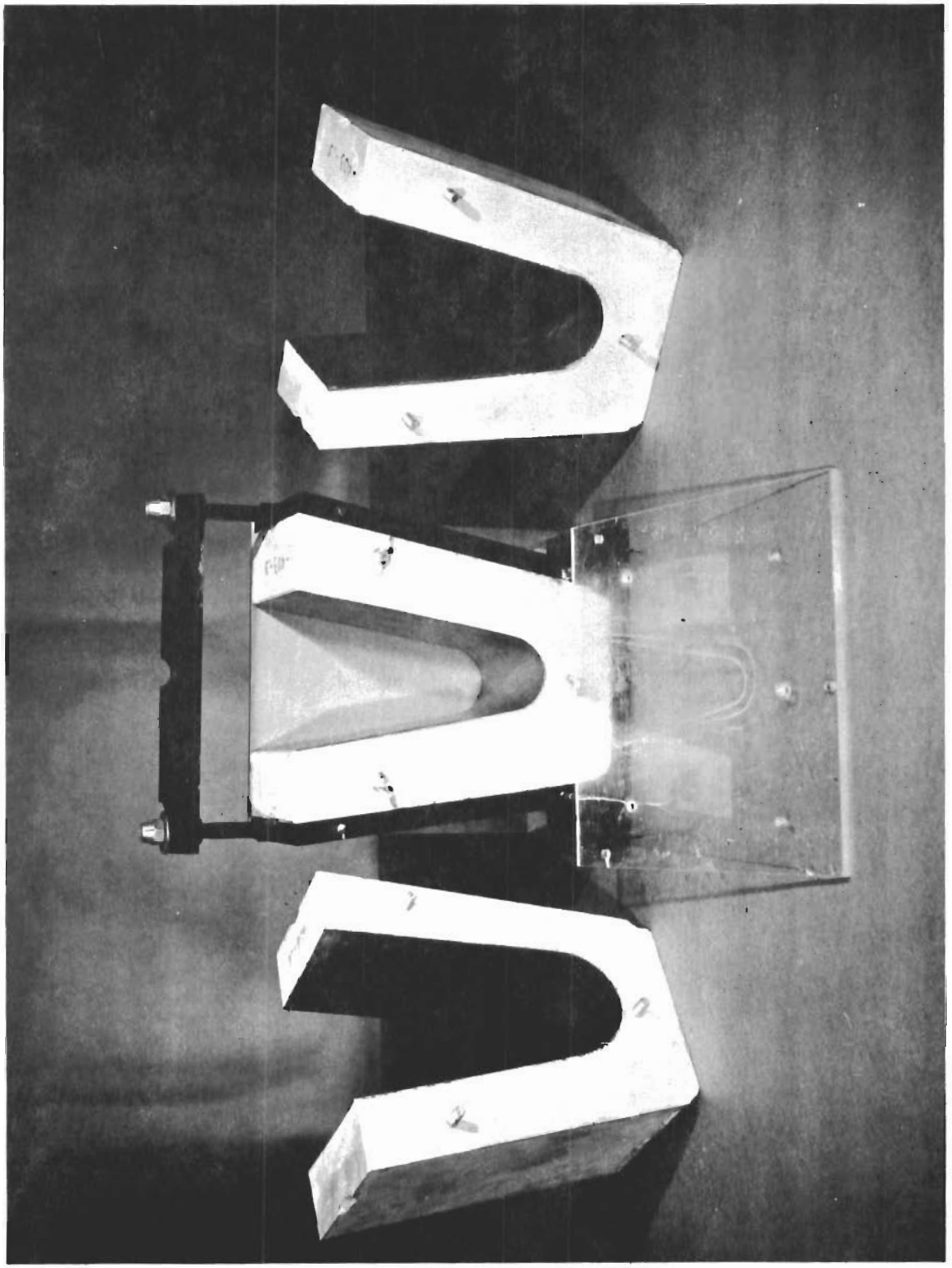

FIGURE 12. Small Scale Leading Edge Mold with Interchangeable Inserts

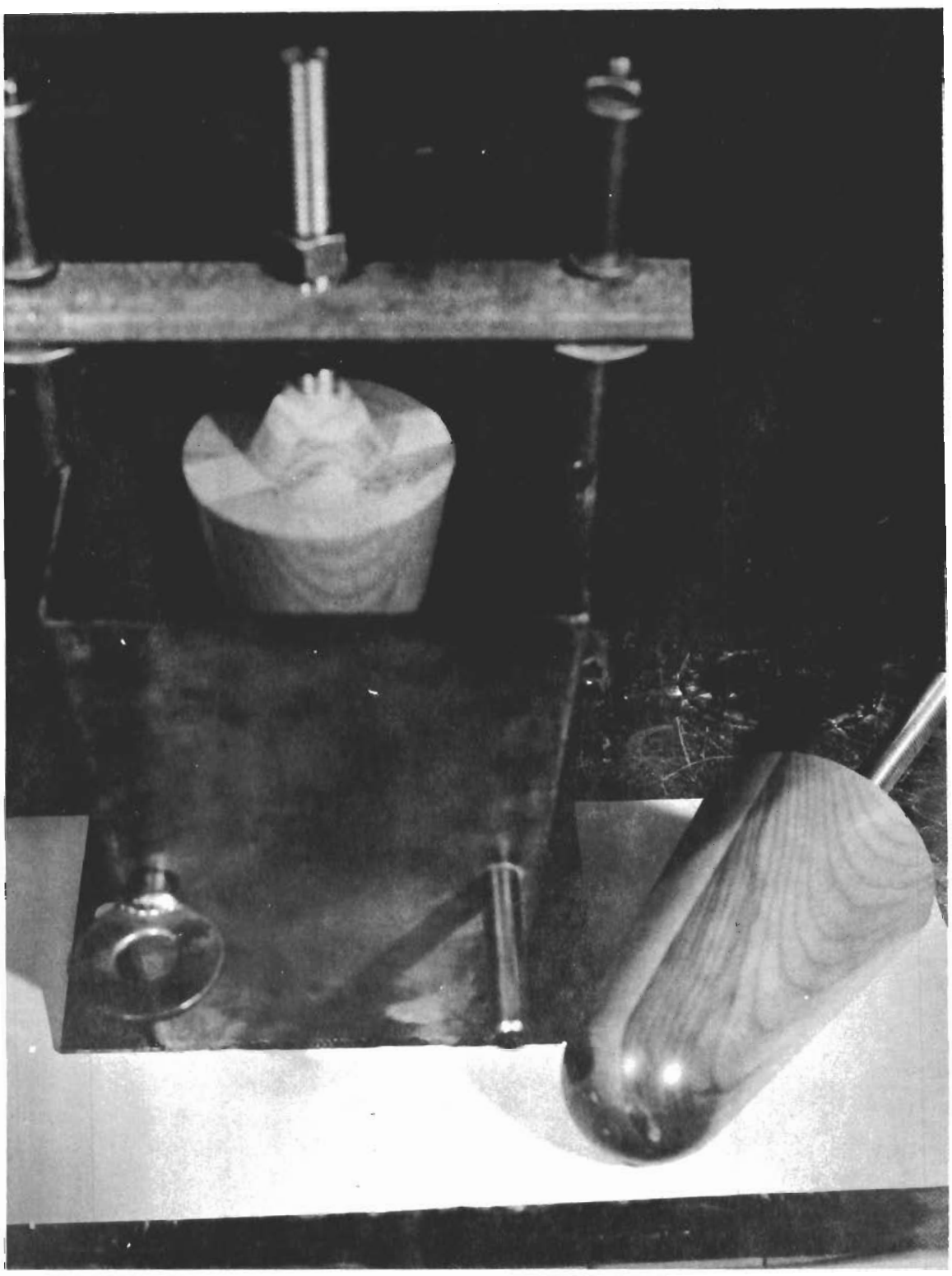

FIGURE 13. Nose Cone Mold before Plaster Casting

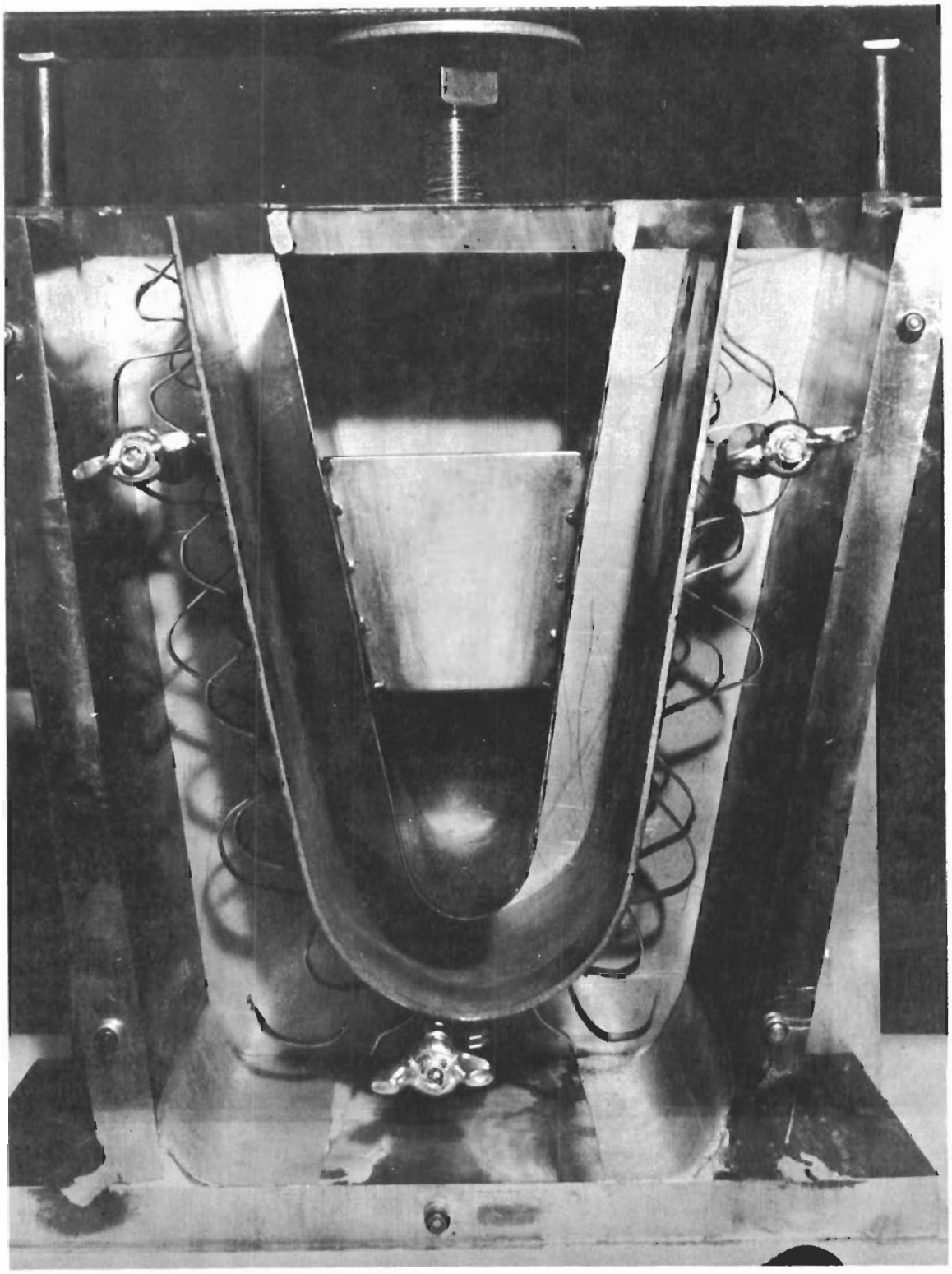

FIGURE 14. Leading Edge Mold before Plaster Support Casting

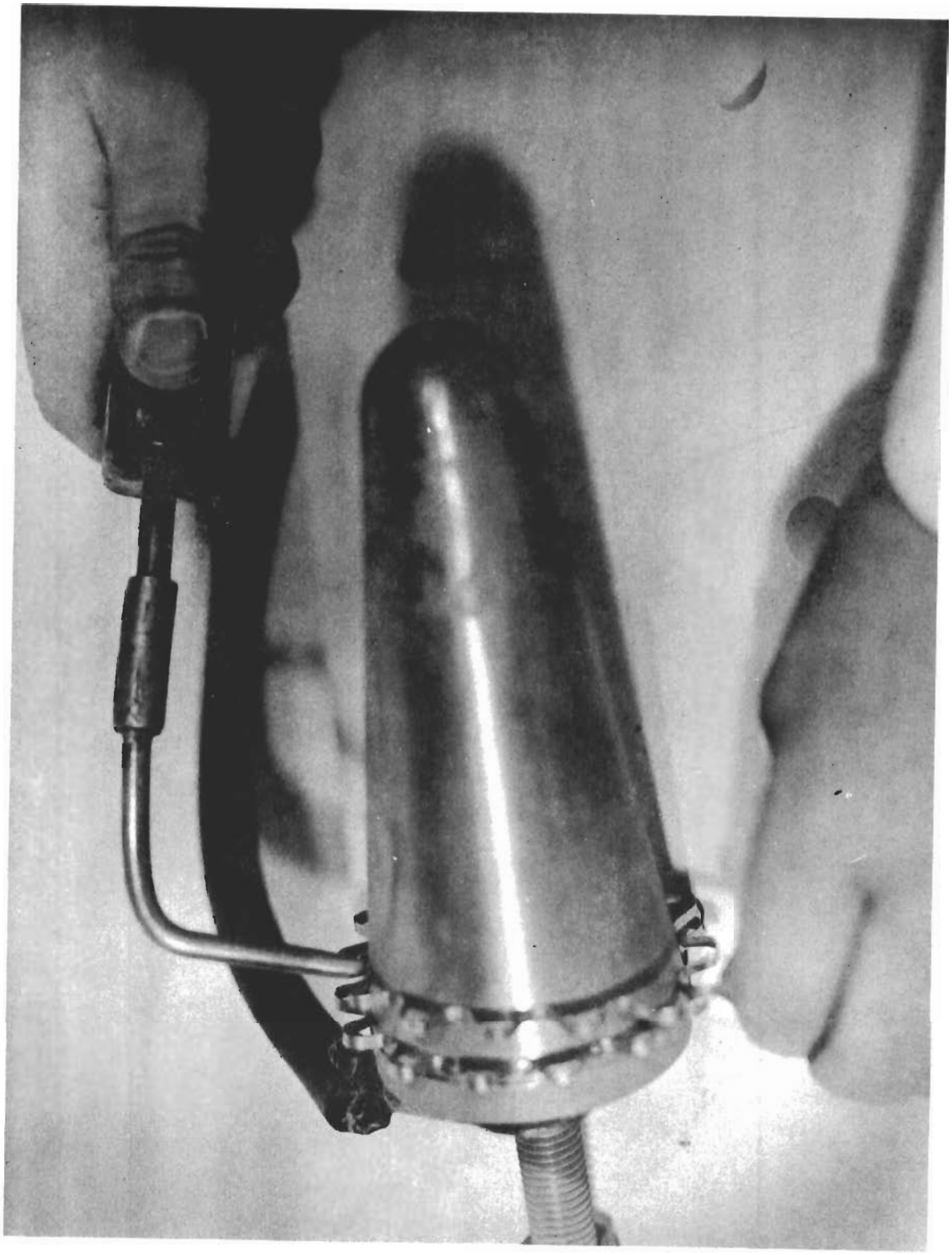

FIGURE 15. Welding Reinforcement Strip on Model Nose Cone

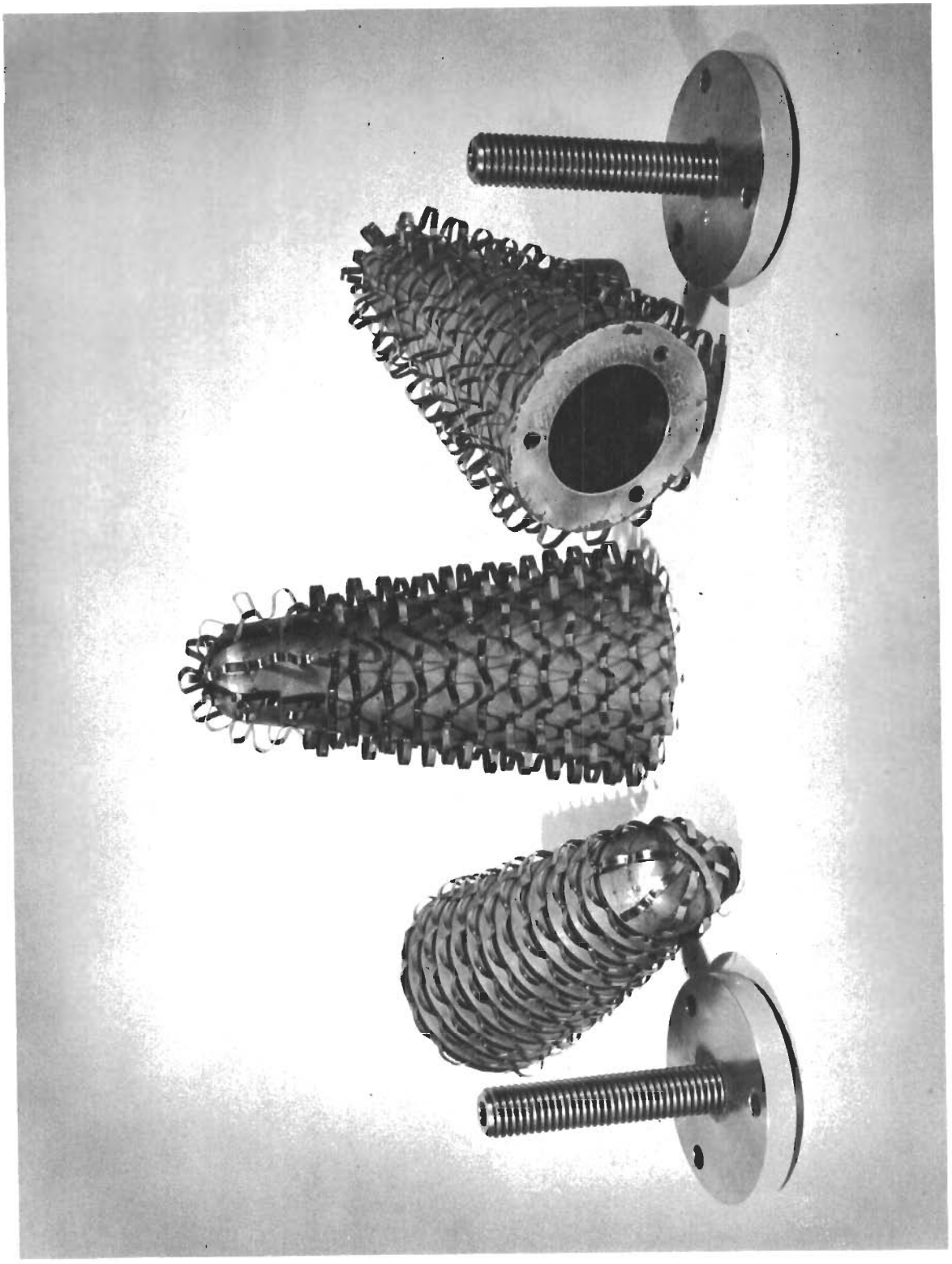

FIGURE 16. Small Scale Model Nose Cones with Reinforcement

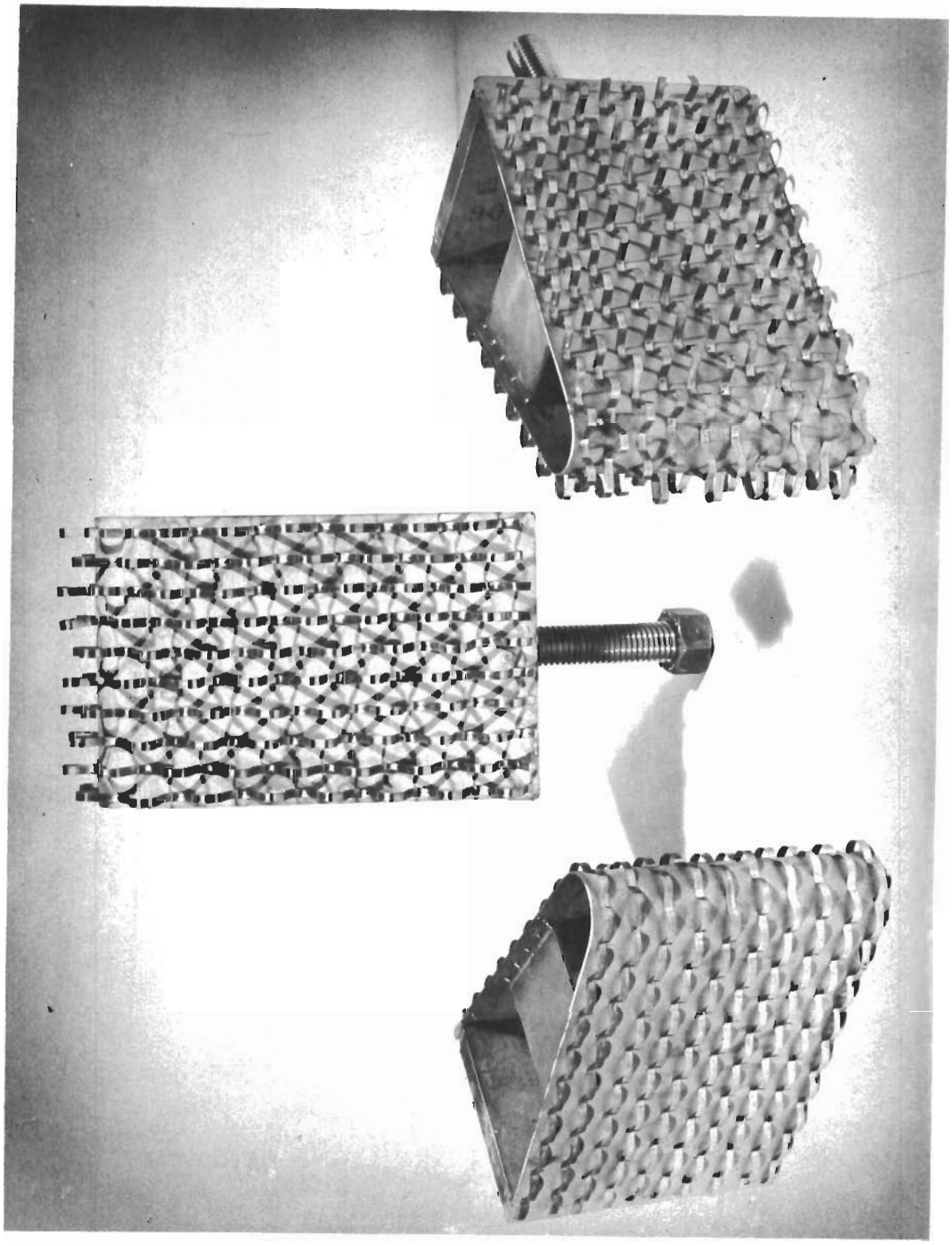

FIGURE 17. Small Scale Model Leading Edges with Reinforcement

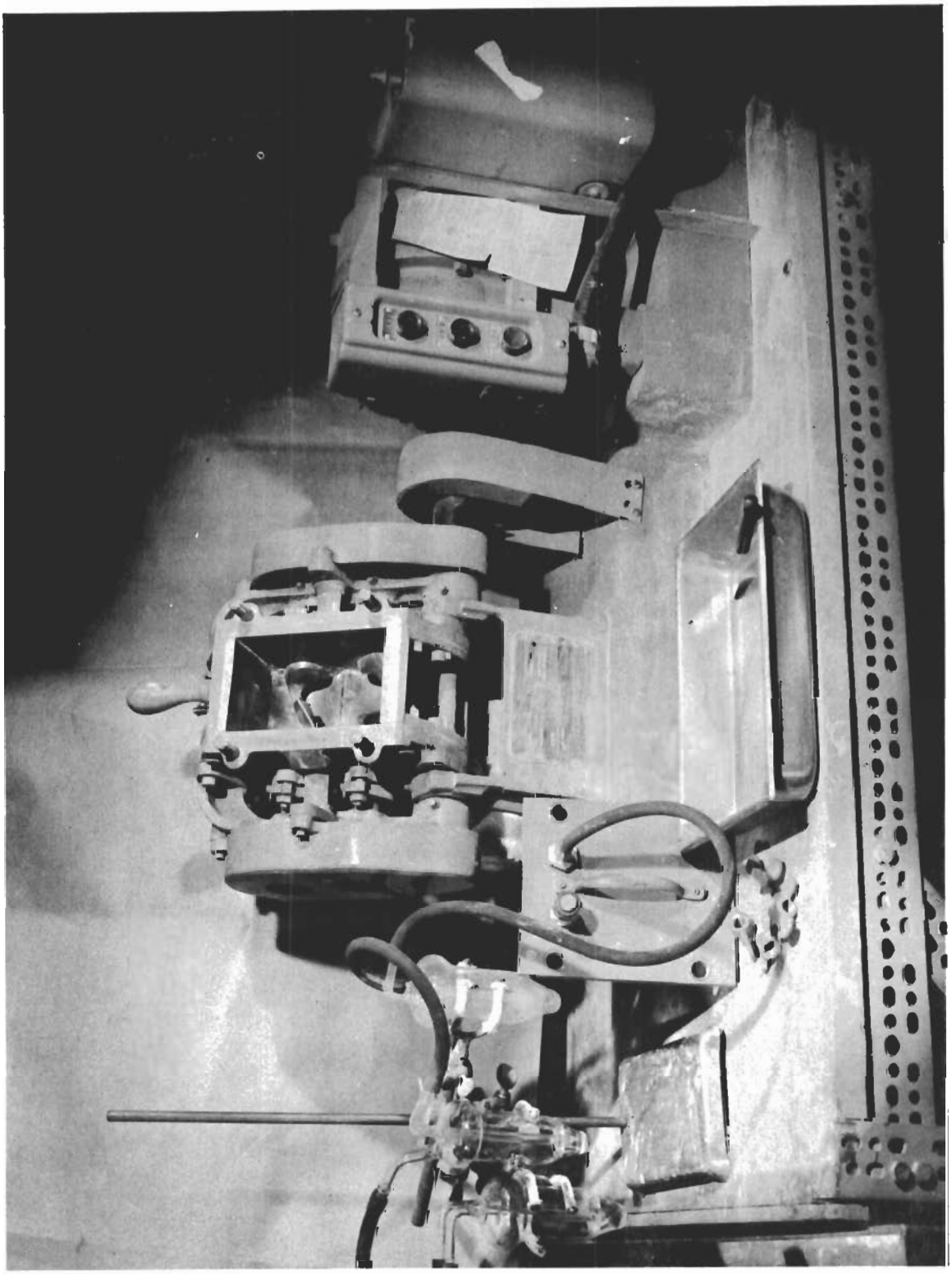

FIGURE 18. Sigma Bladed Vacuum Dough Mixer

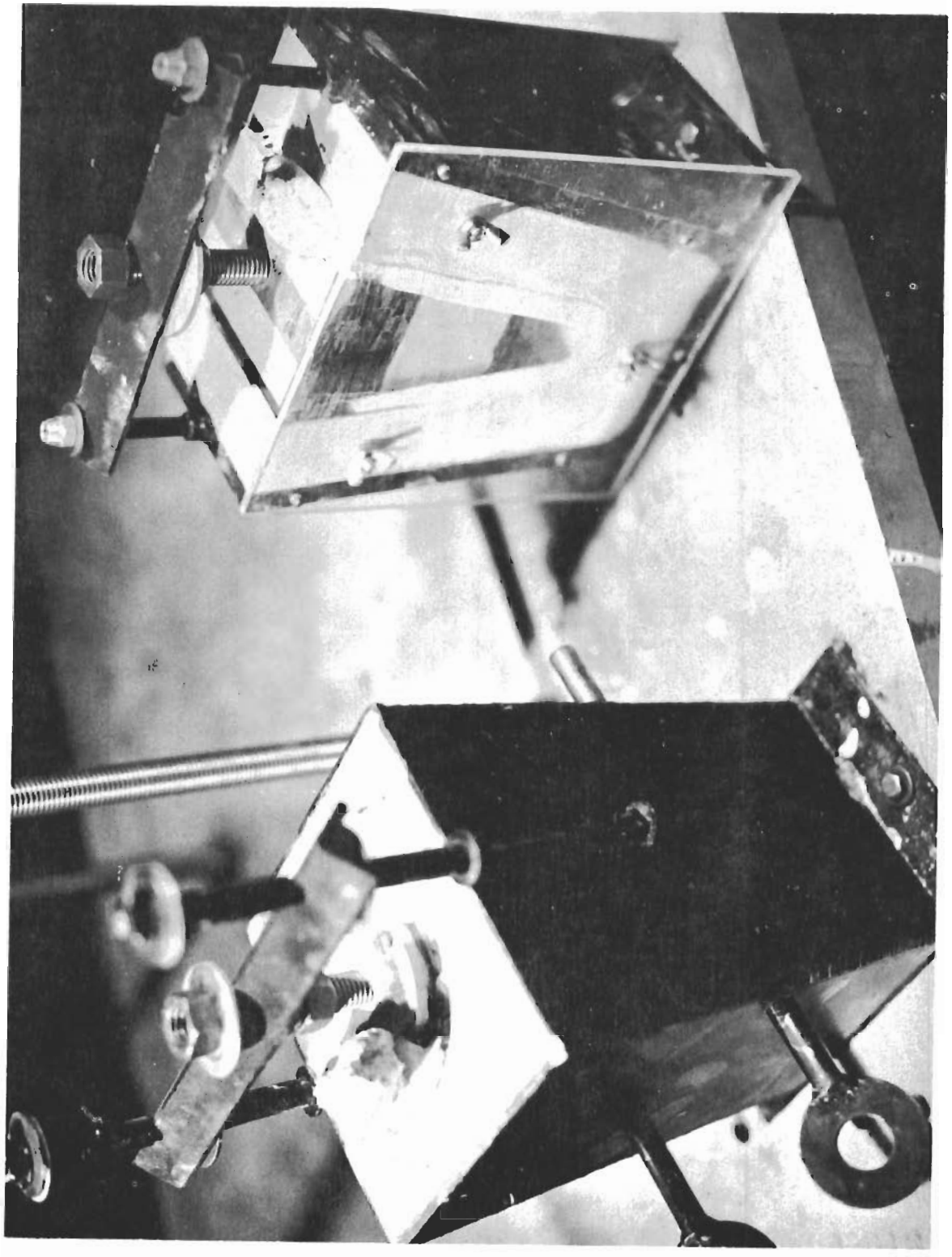

FIGURE 19. Casting ThermarQ ZSF-124 in Model Nose Cone and Leading Edge Molds

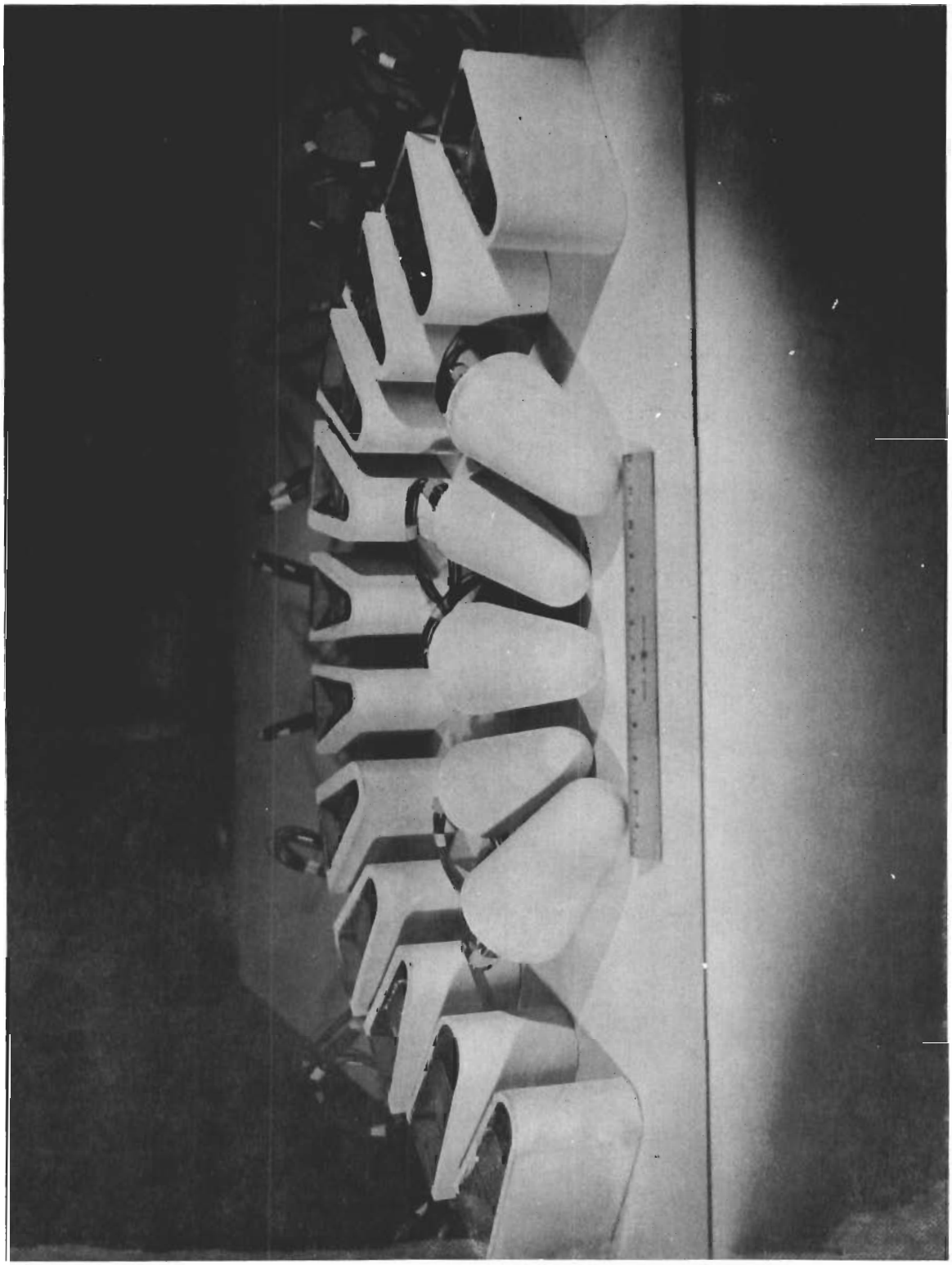

FIGURE 20. Small Scale Model Nose Cones and Leading Edges

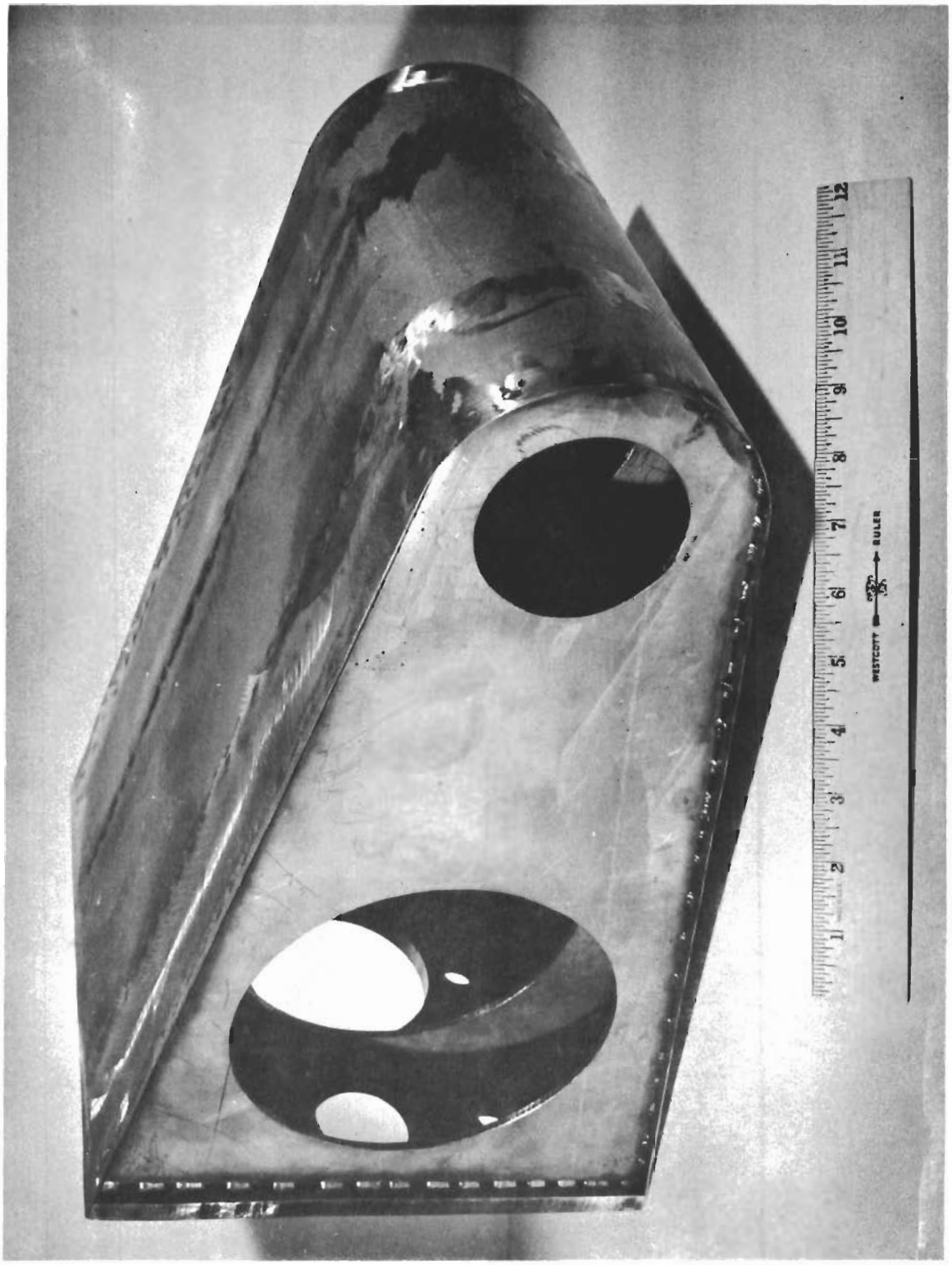

FIGURE 21. 500 square inch Model Leading Edge Substrate

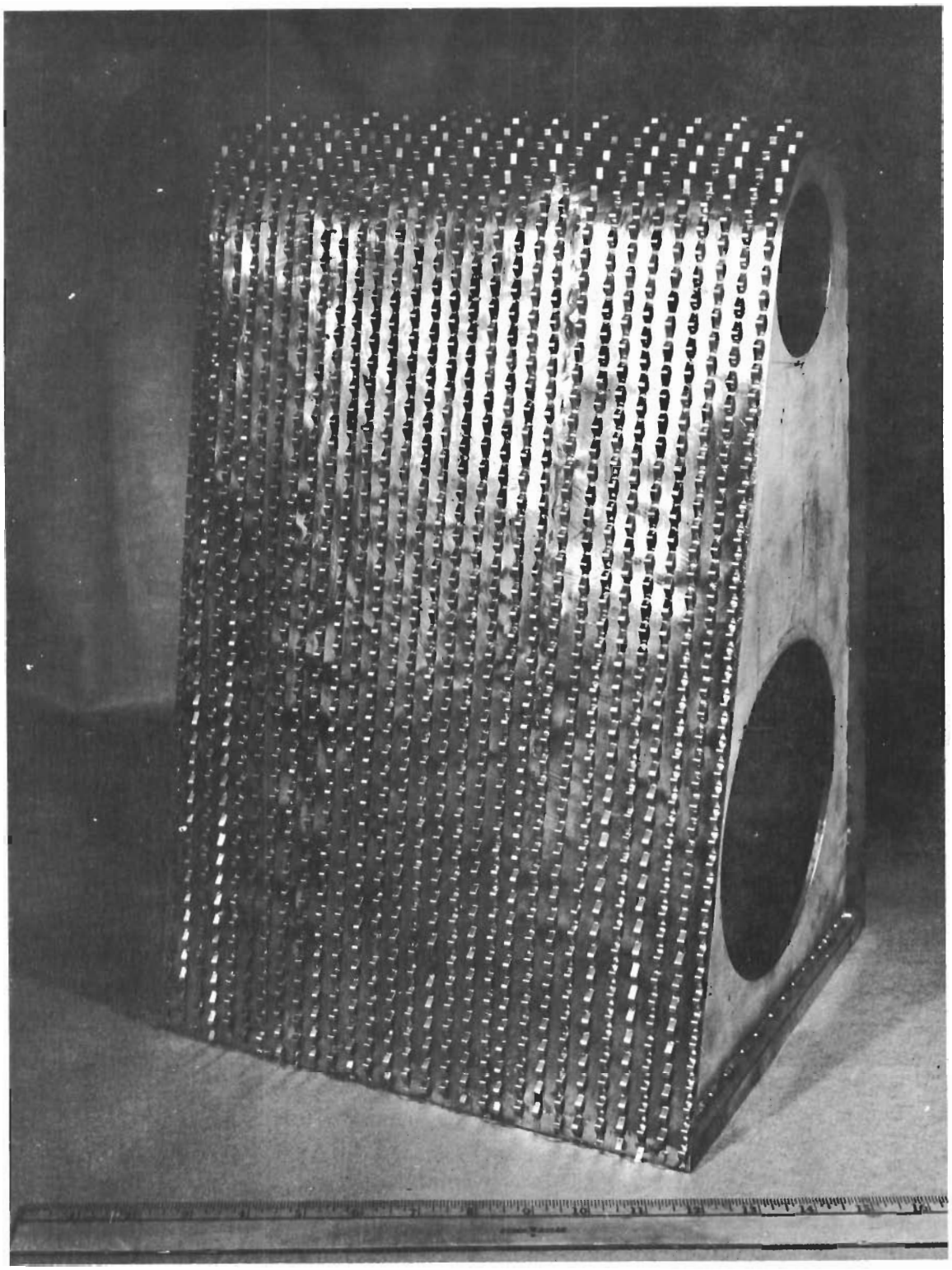

FIGURE 22. 500 square inch Model Leading Edge with Reinforcement

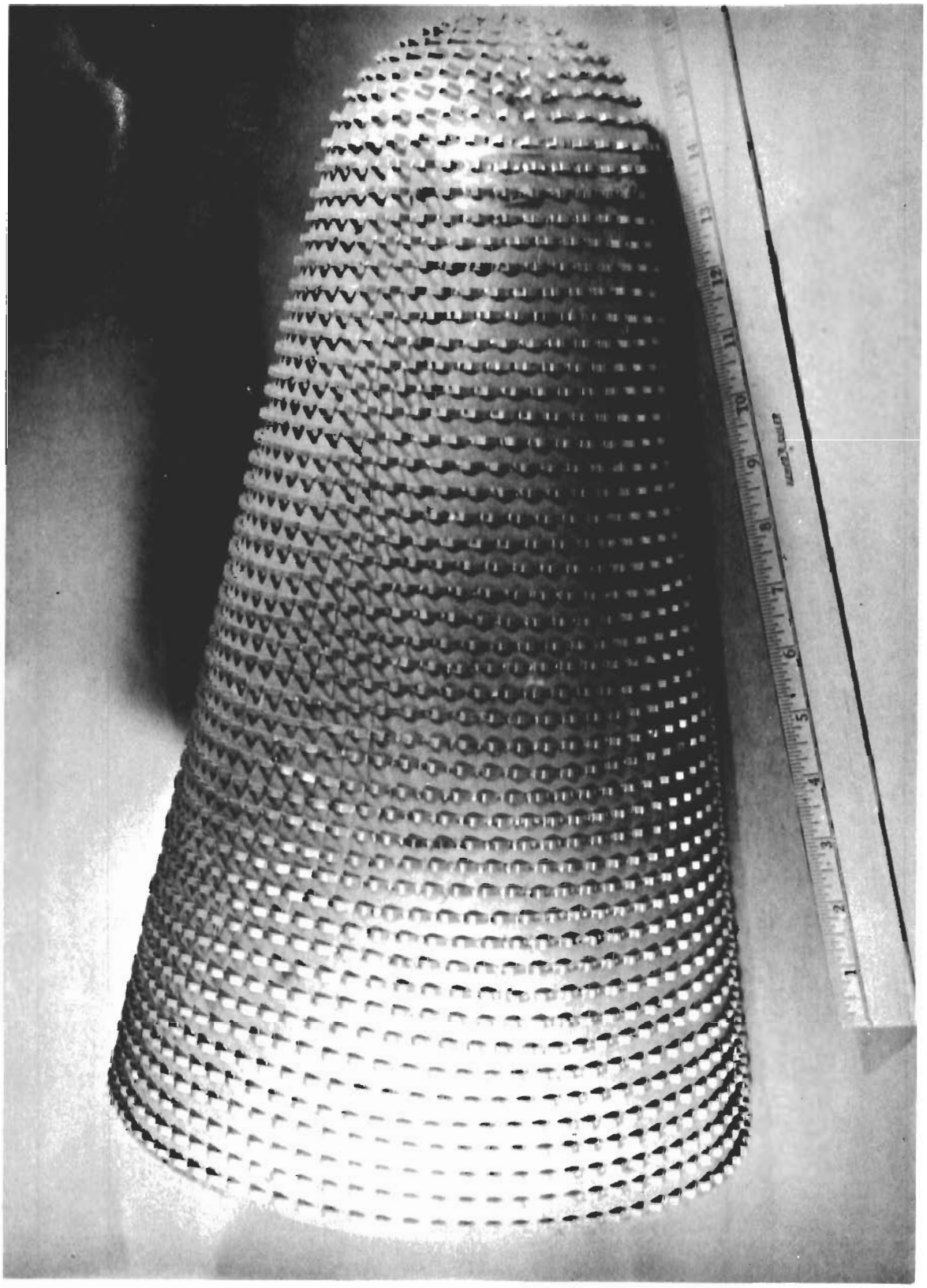

FIGURE 23. 500 square inch Model Nose Cone with Reinforcement

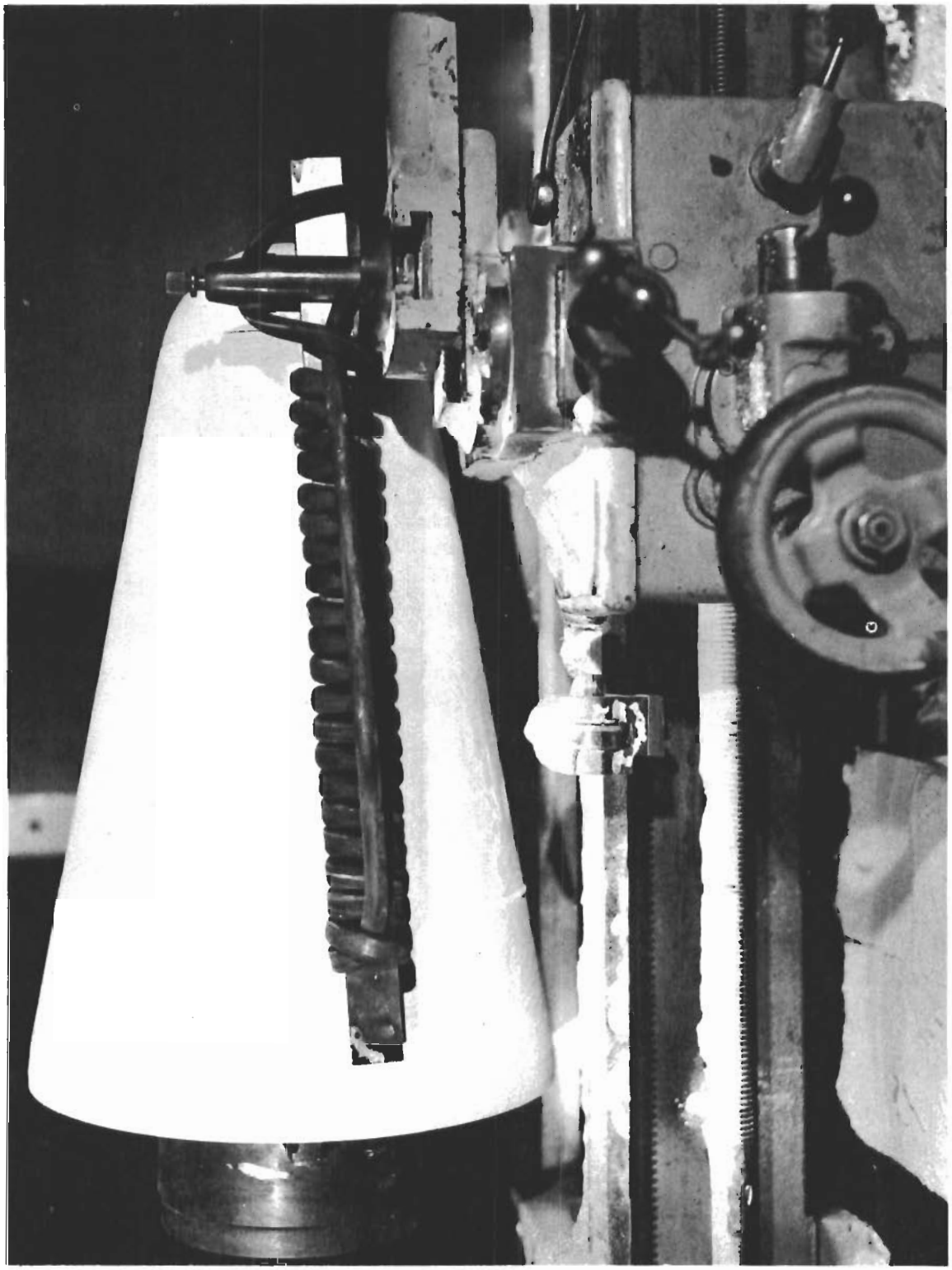

FIGURE 24. Machining 500 square inch Model Nose Cone Mandrel

FIGURE 25. Plaster Mandrel for 500 square inch Nose Cone

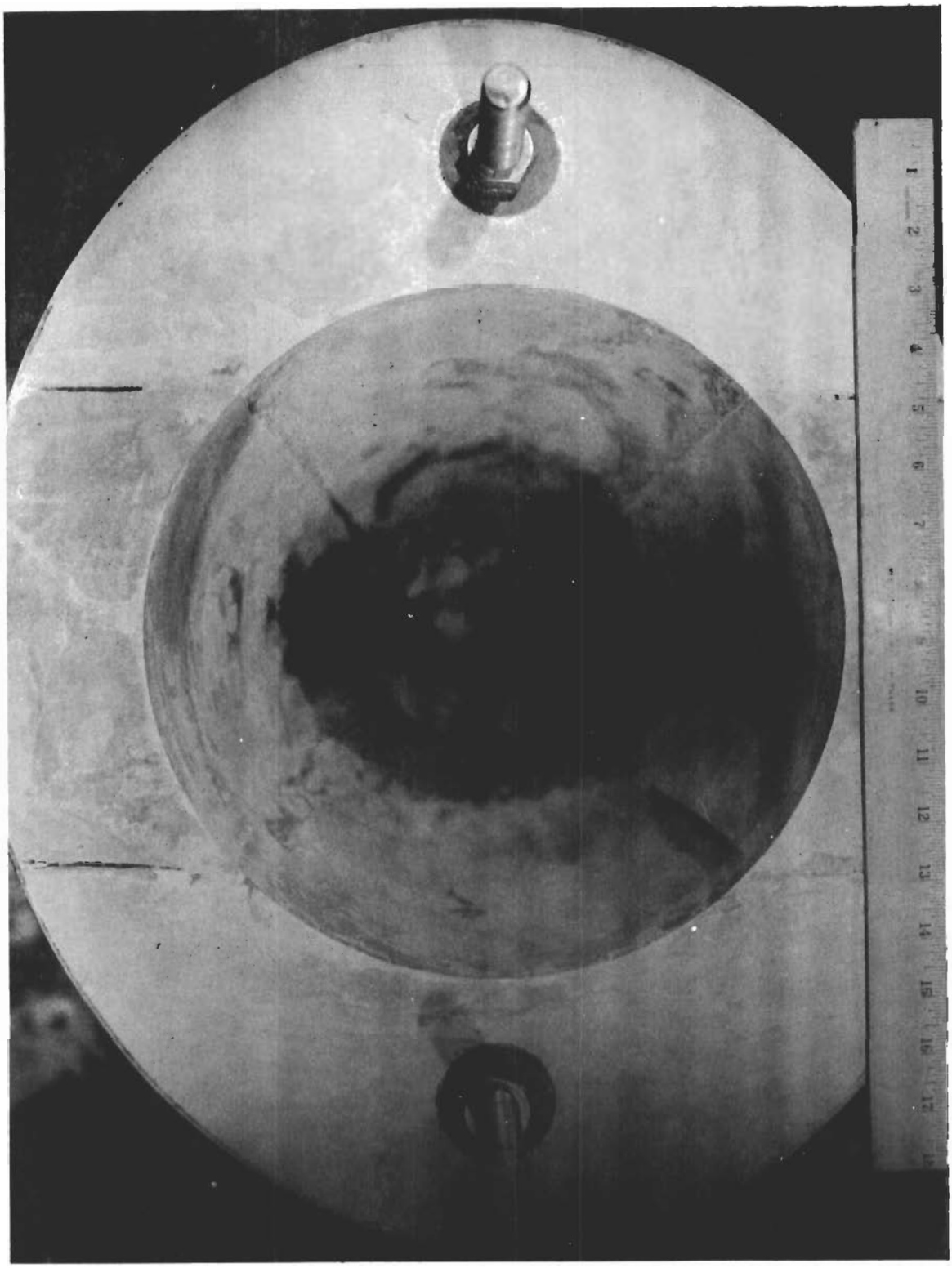

FIGURE 26. 500 square inch Model Nose Cone Mold

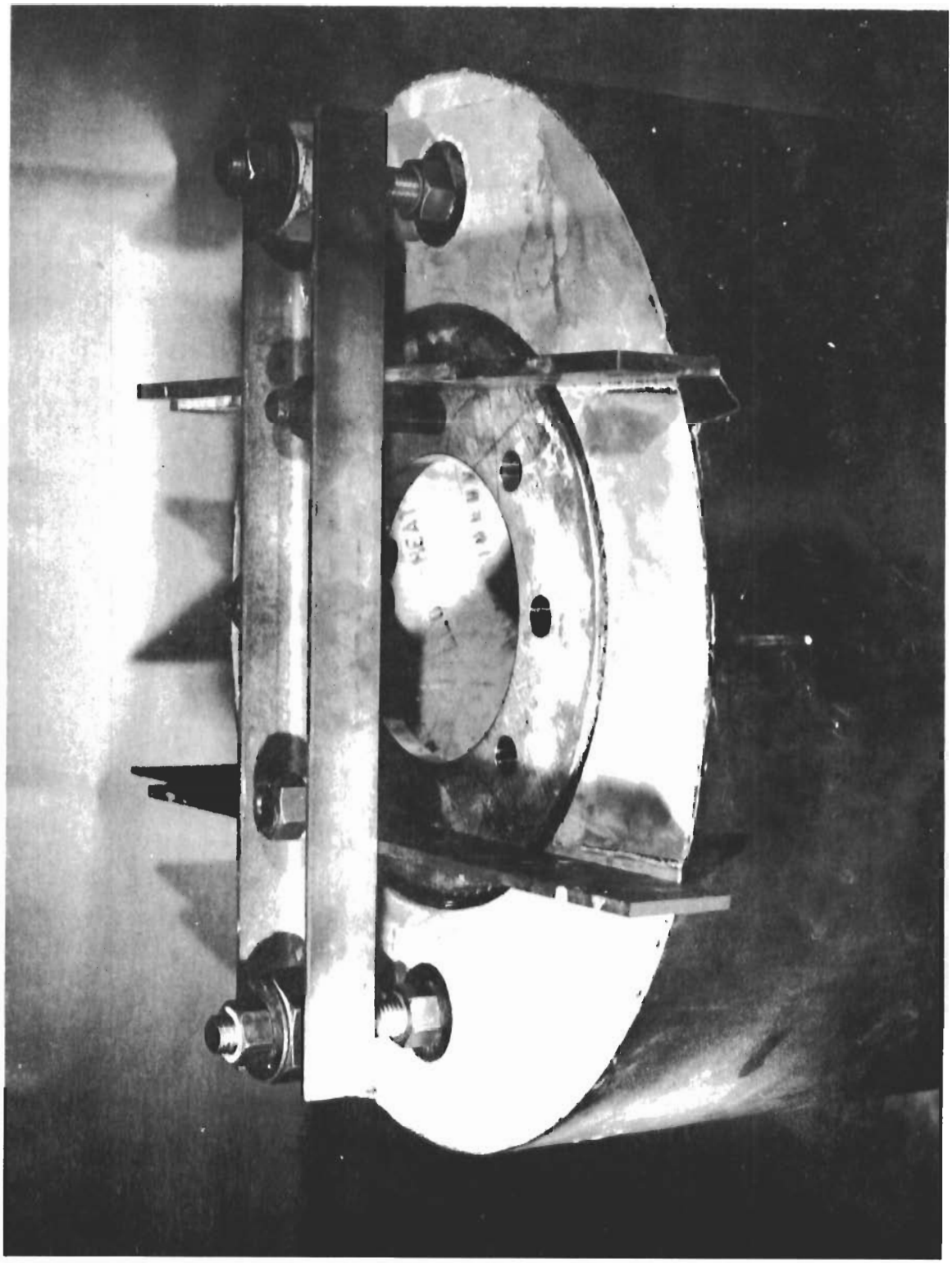

FIGURE 27. 500 square inch Model Nose Cone in Mold--Ready for Refractory Casting

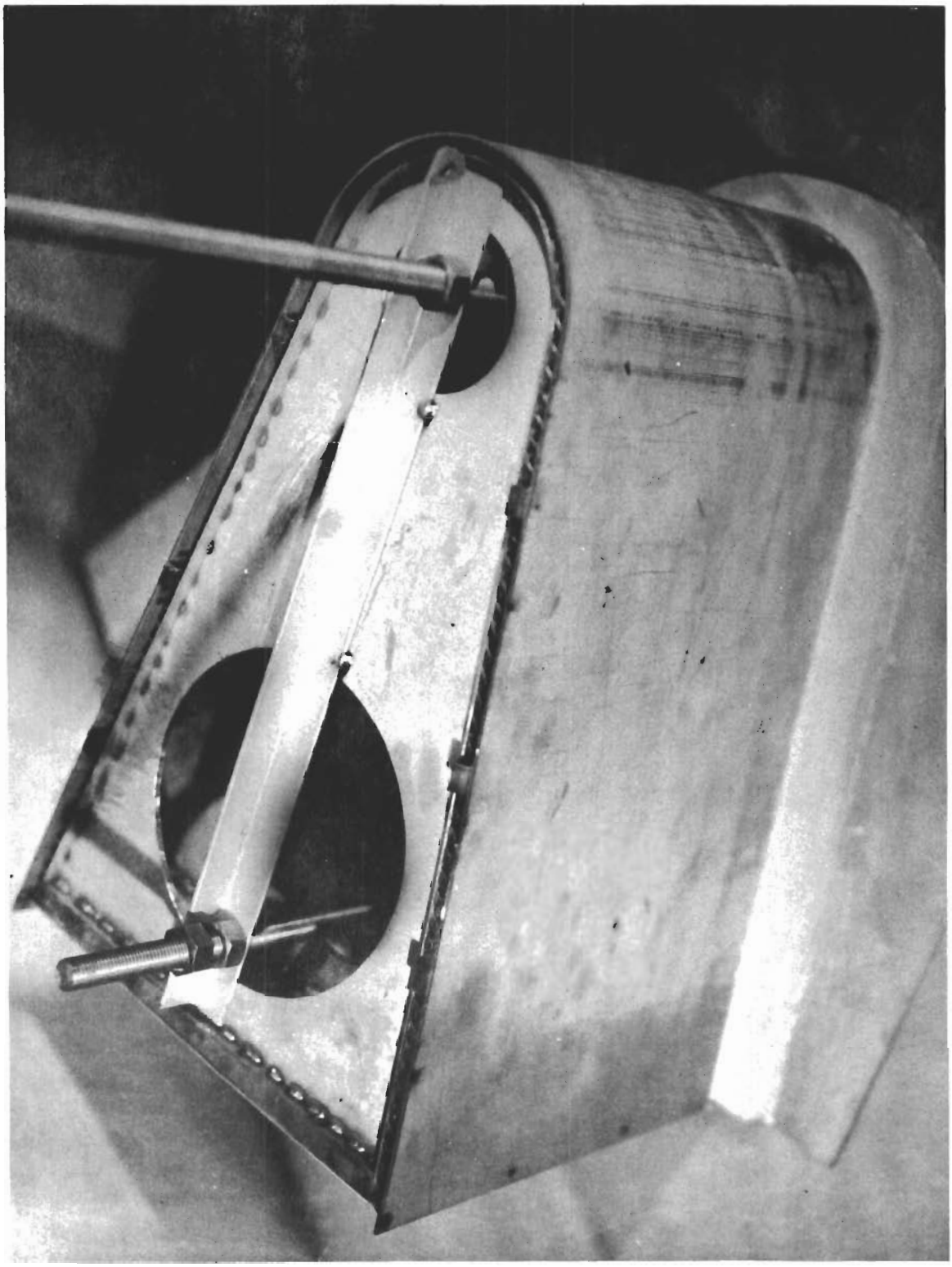

FIGURE 28. 500 square inch Leading Edge Ready for Refractory Casting

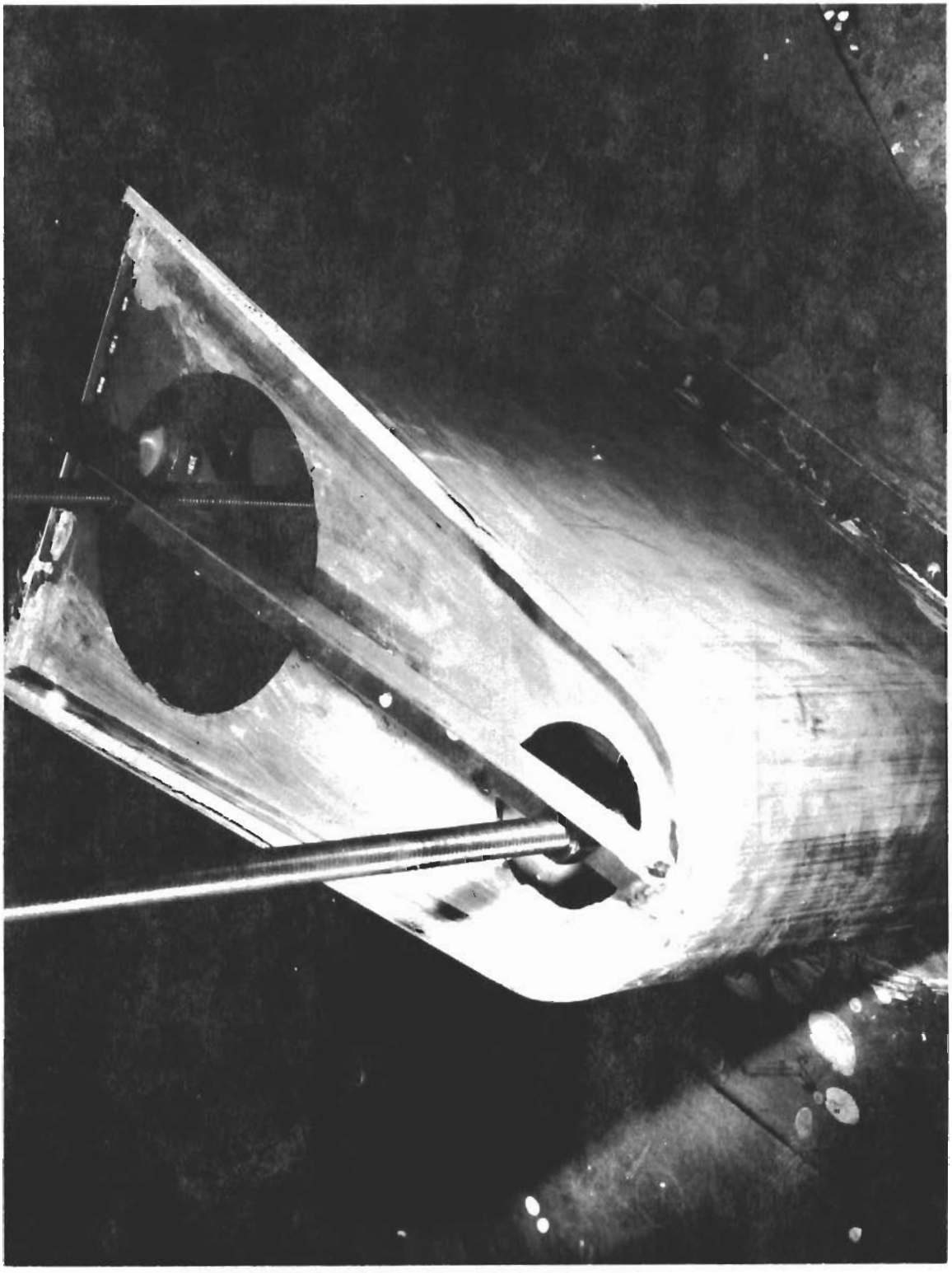

FIGURE 29. 500 square inch Model Leading Edge in Mold after Casting

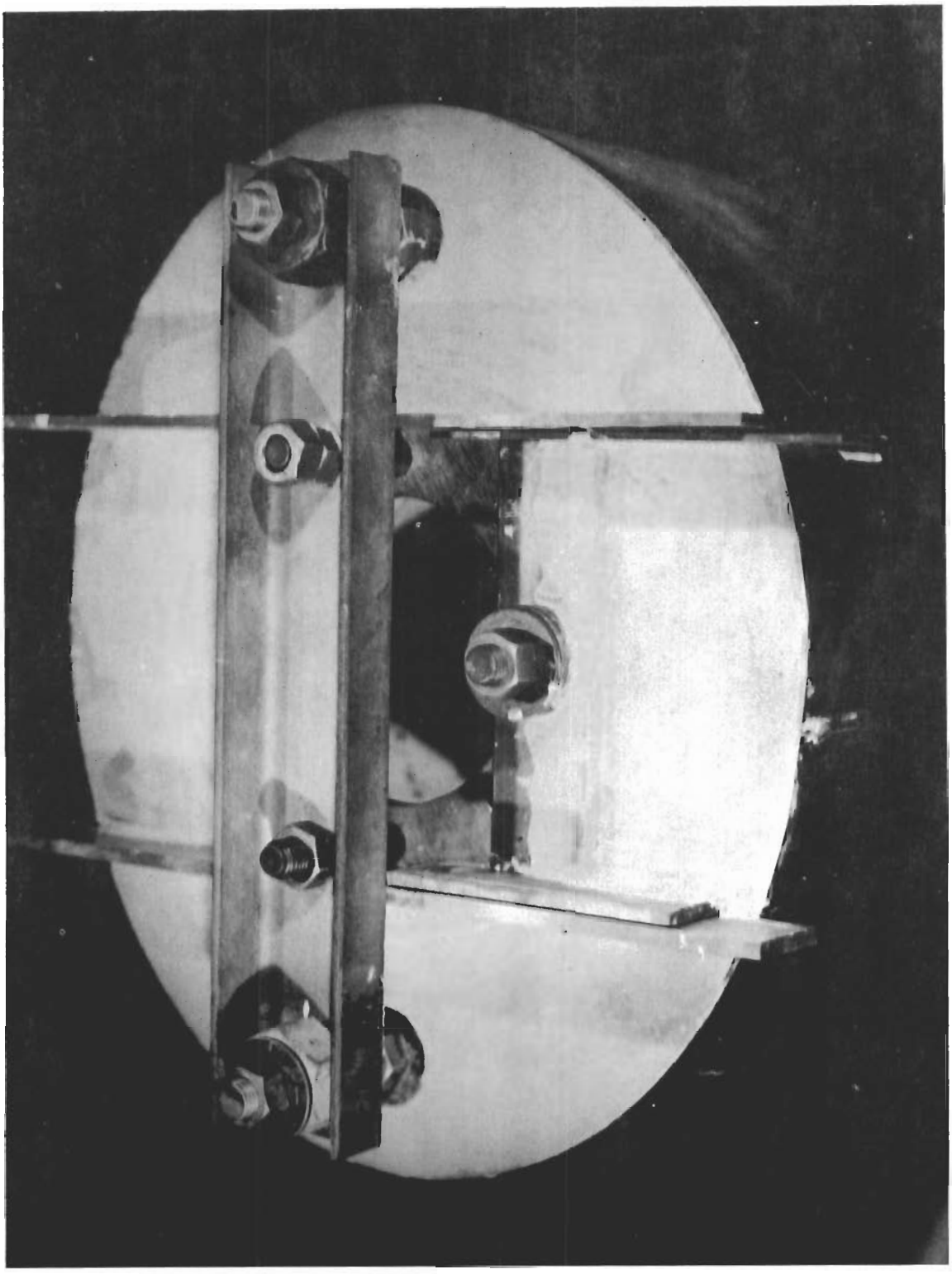

FIGURE 30. 500 square inch Model Nose Cone After Casting

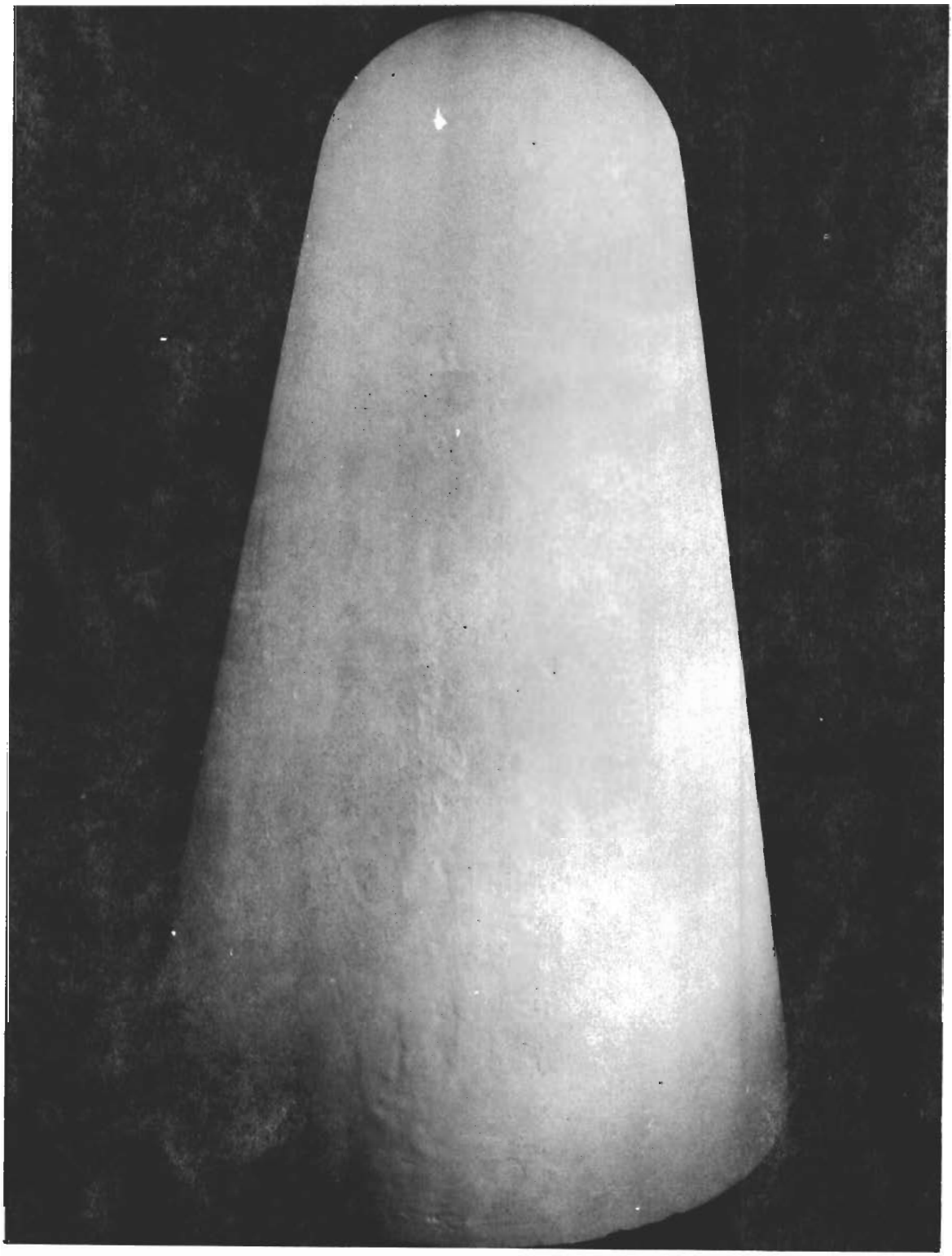

FIGURE 31. 500 square inch Model Nose Cone

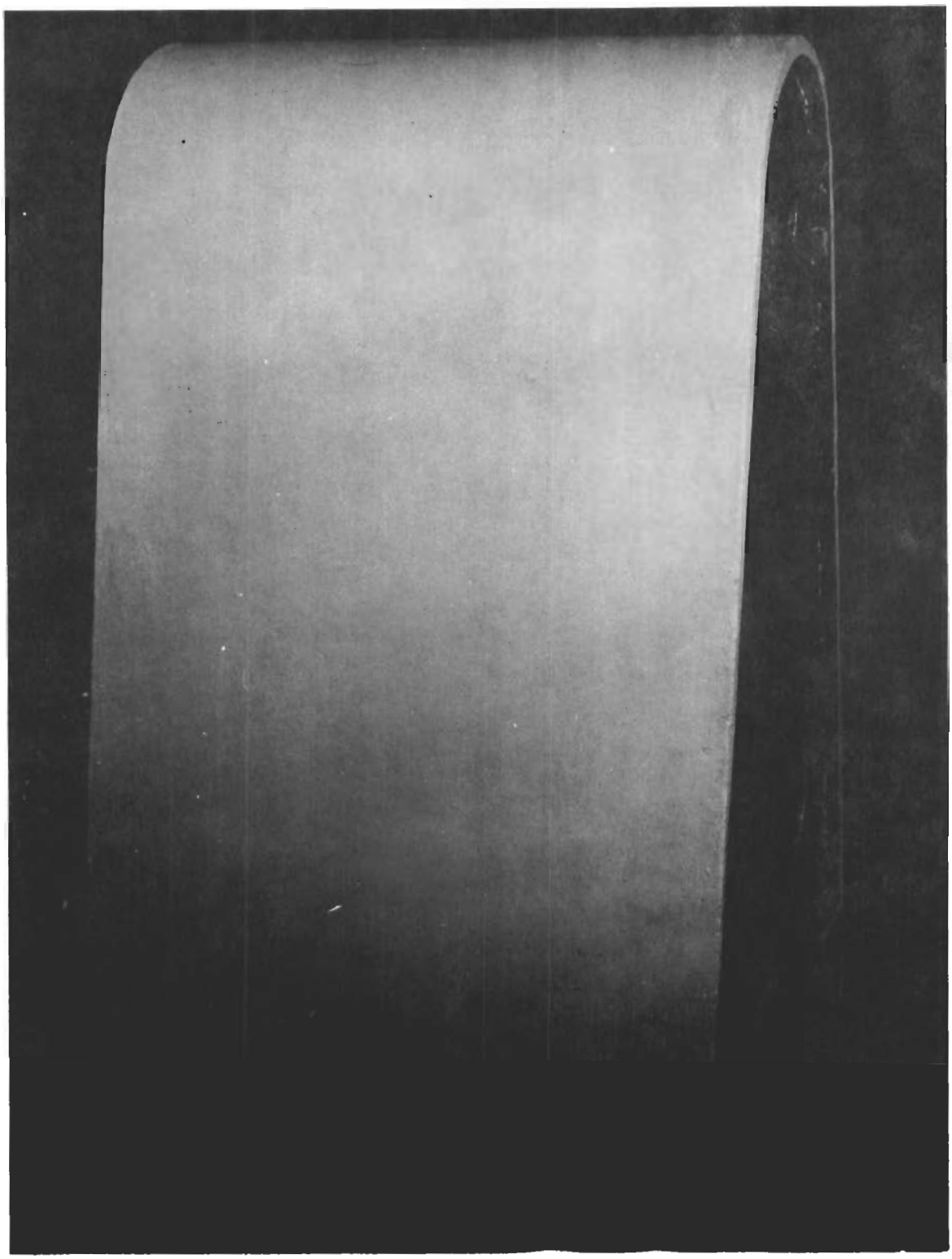

FIGURE 32. 500 square inch Model Leading Edge

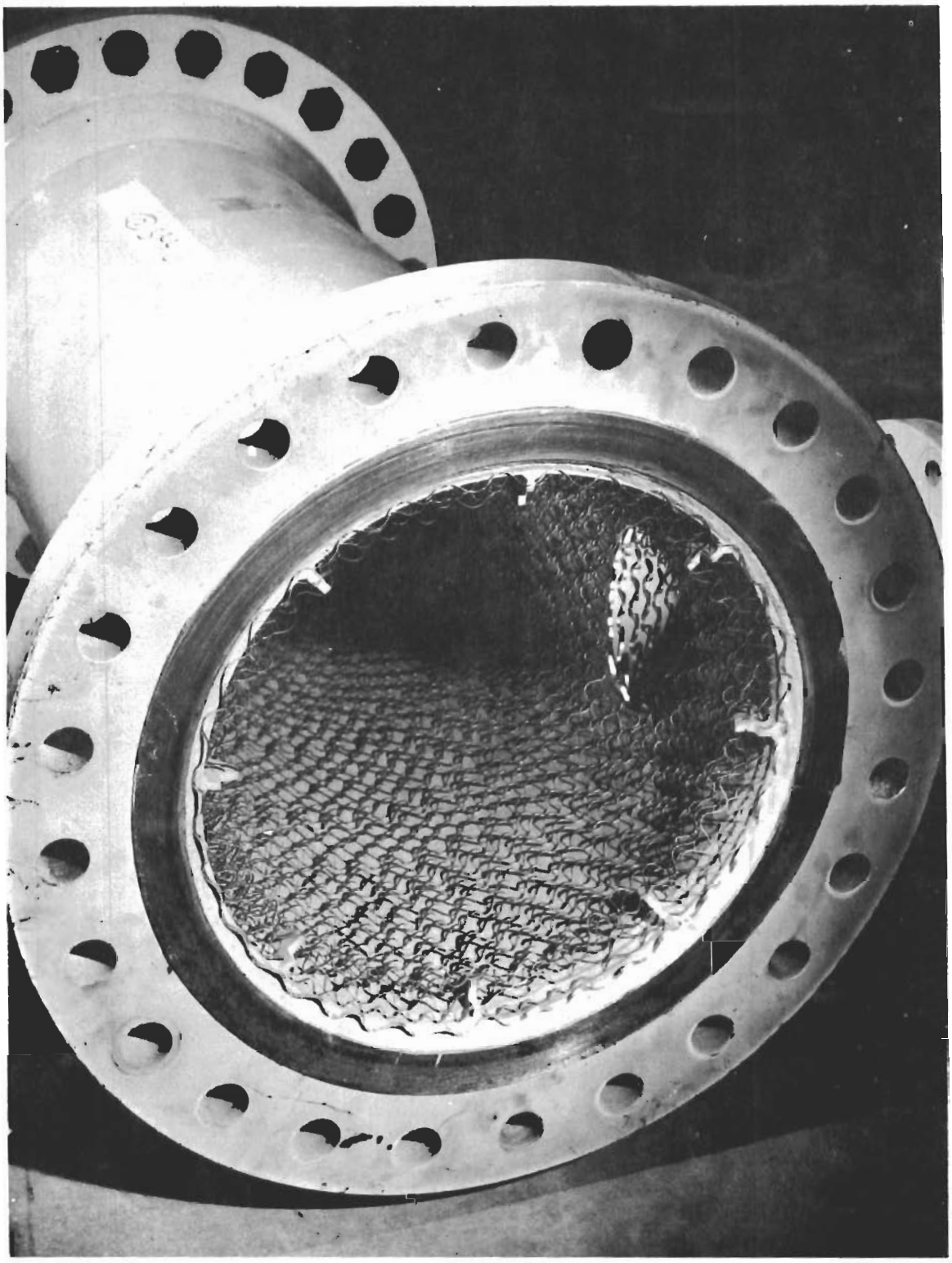

FIGURE 33. Bottom Center Section Showing Reinforcement before Coating

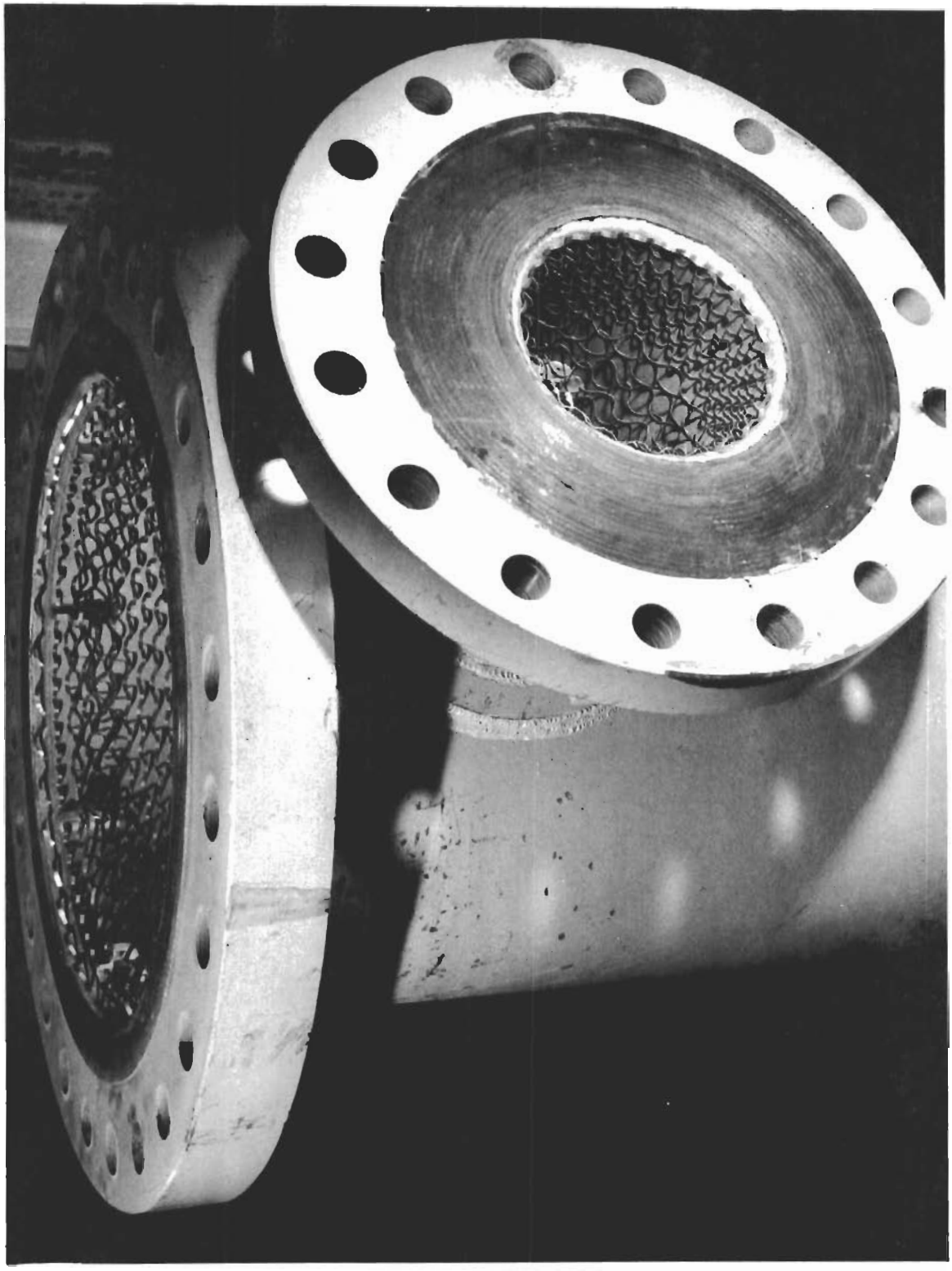

FIGURE 34. Upper Center Section Showing Reinforcement before Coating

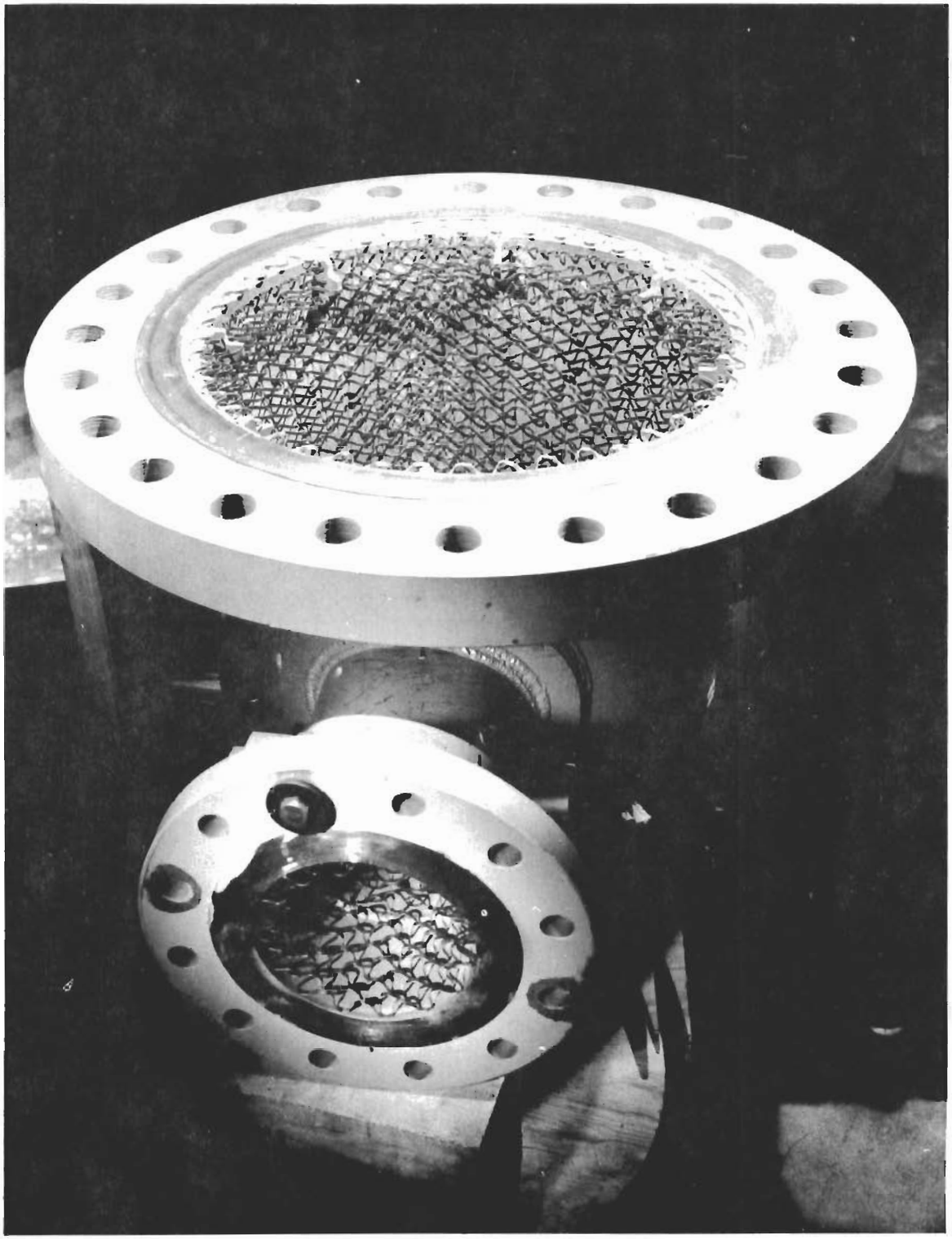

FIGURE 35. Bottom Section with Reinforcement before Coating

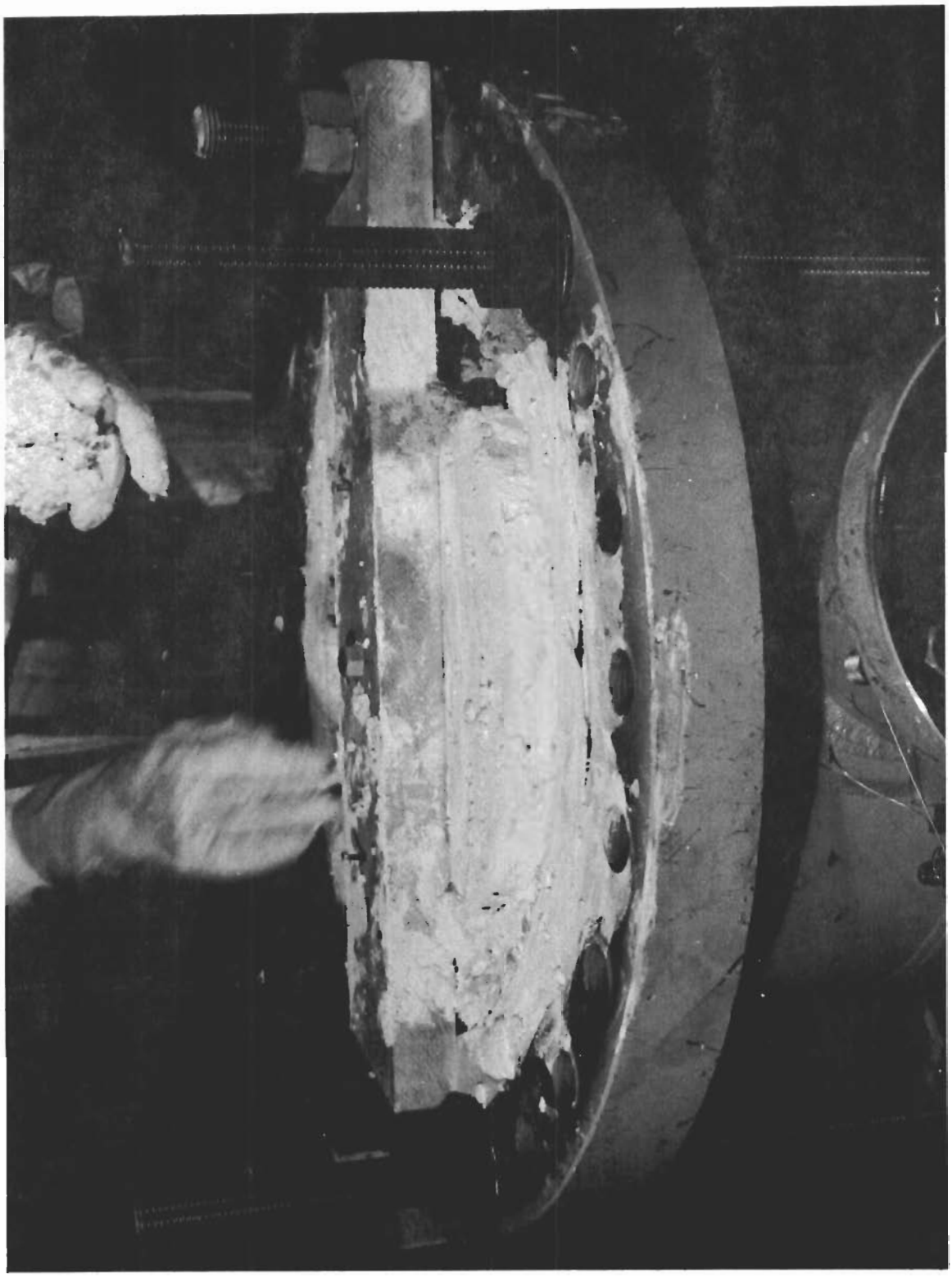

FIGURE 36. Top Dome During Coating Operation

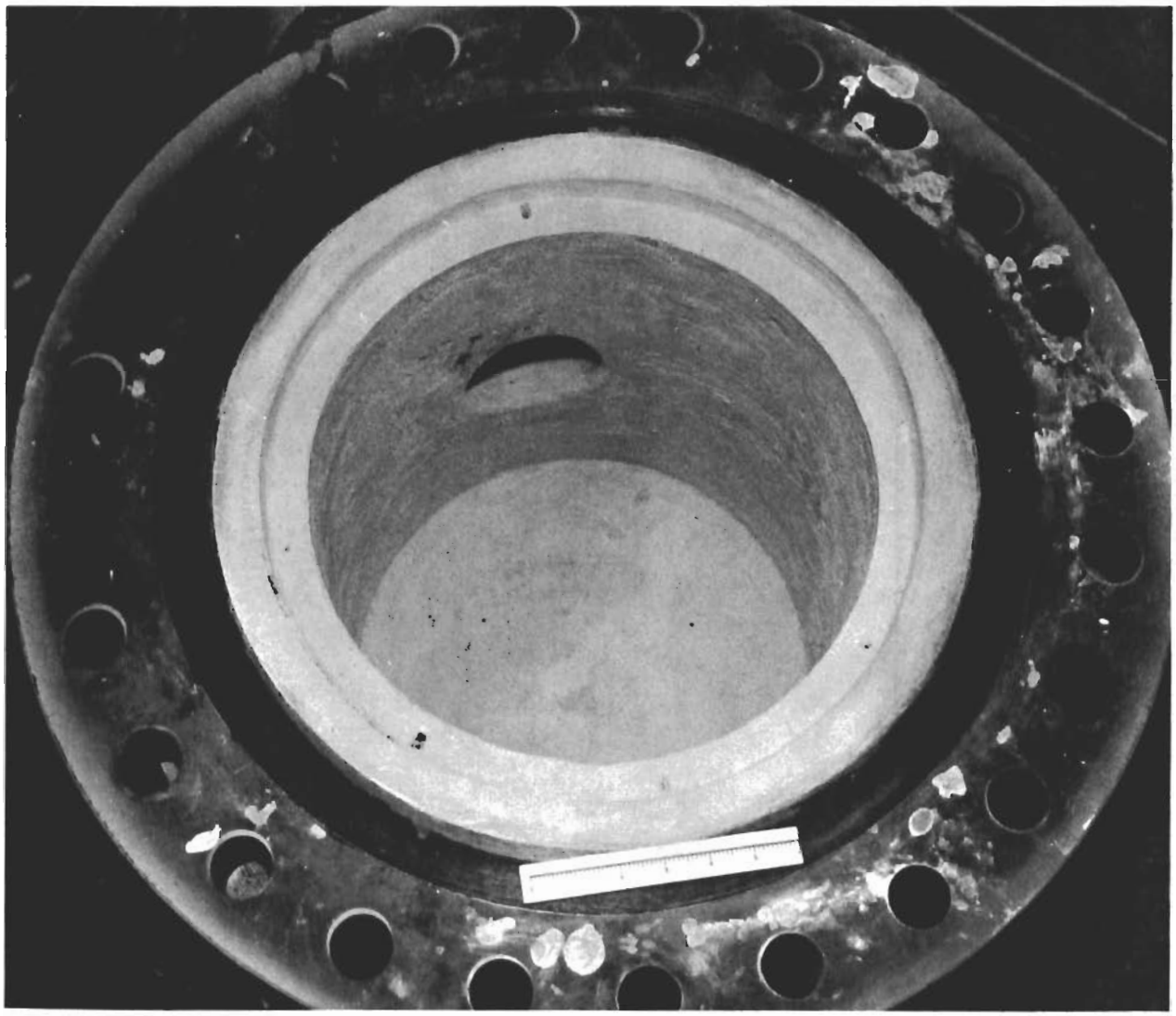

FIGURE 37. Top Dome after Coating

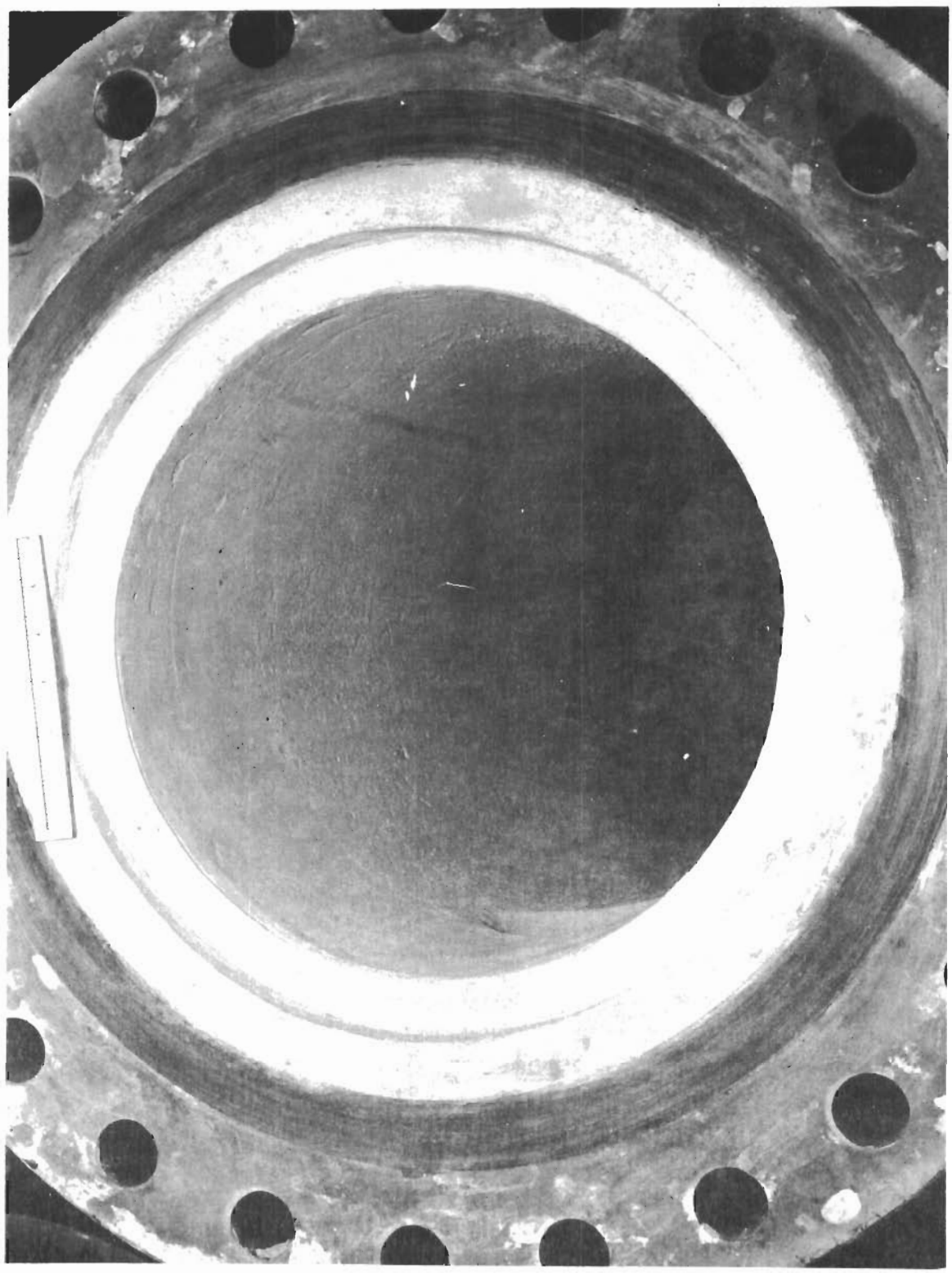

FIGURE 38. Upper Center Section after Coating

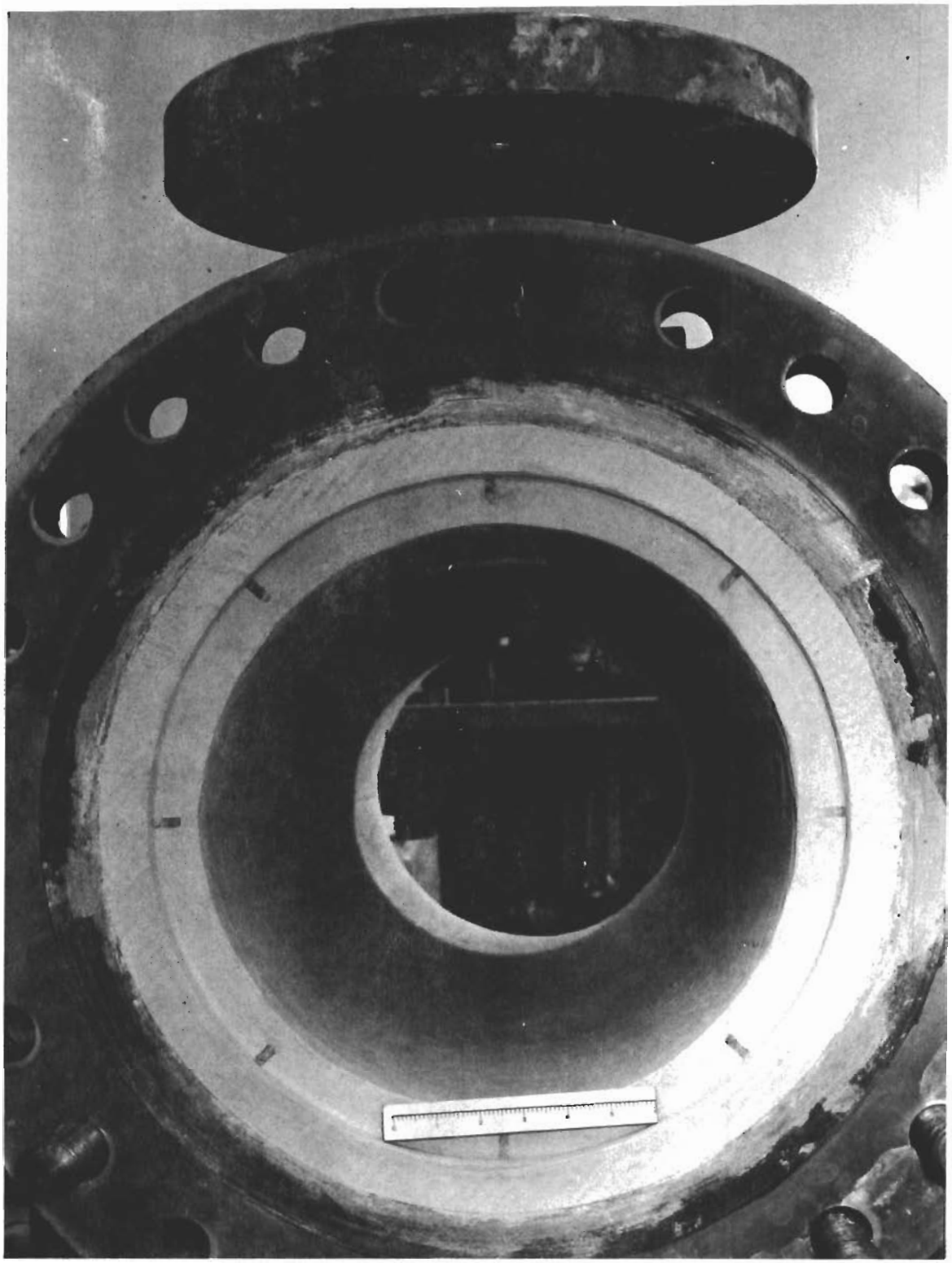

FIGURE 39. Bottom Center Section after Coating

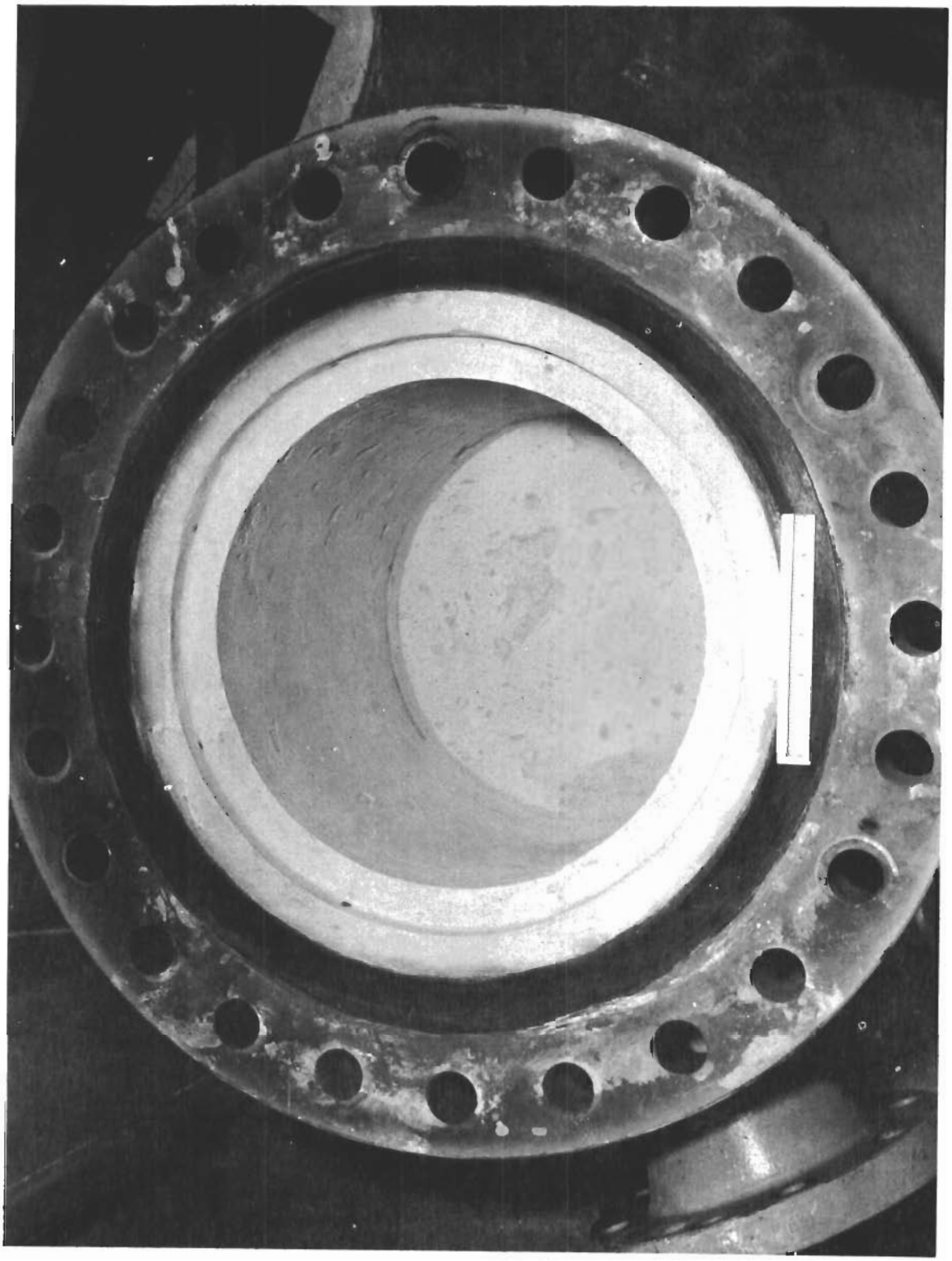

FIGURE 40. Coating in Bottom Section

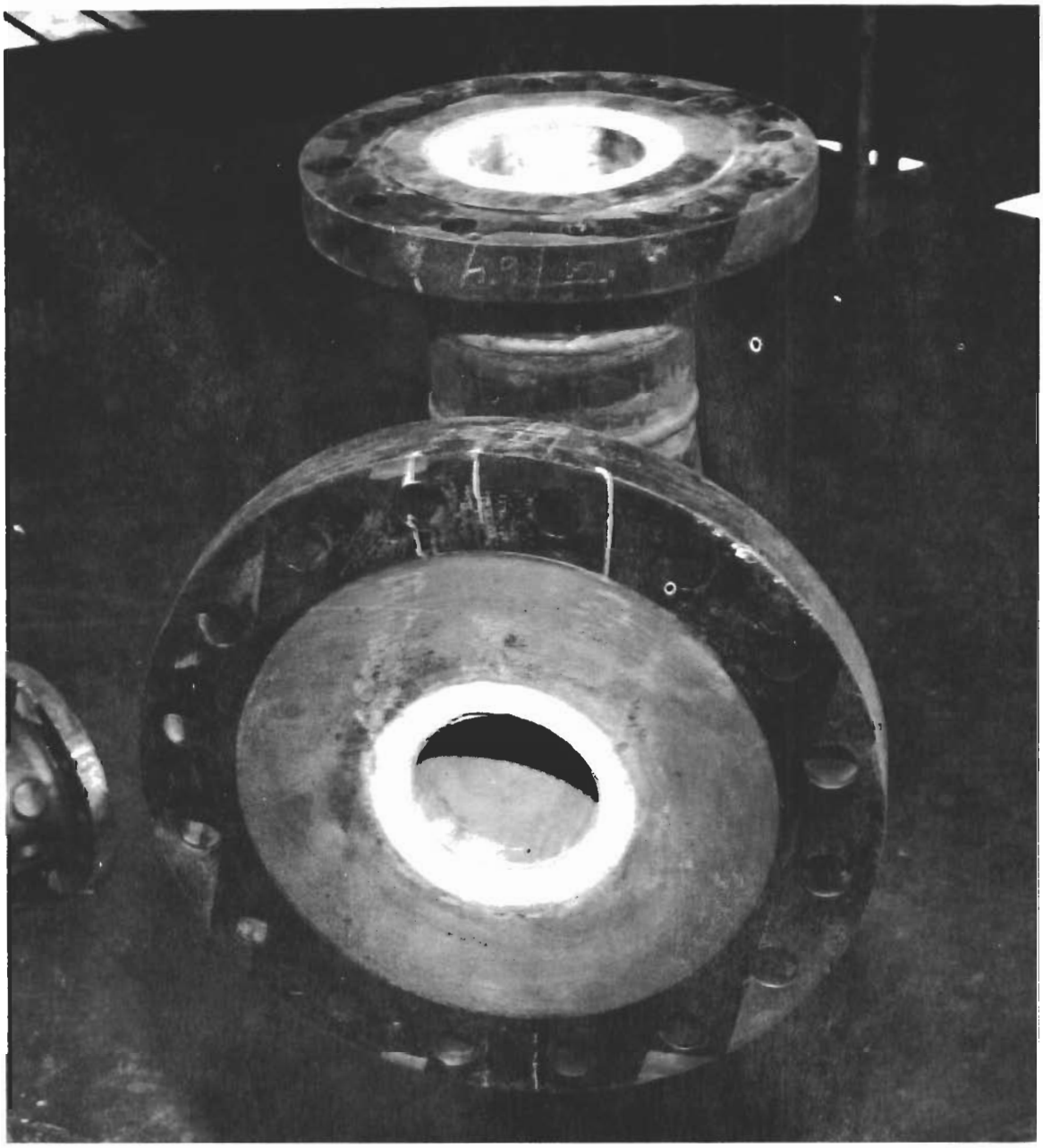

FIGURE 41. Accessory Pipe Ready for Service

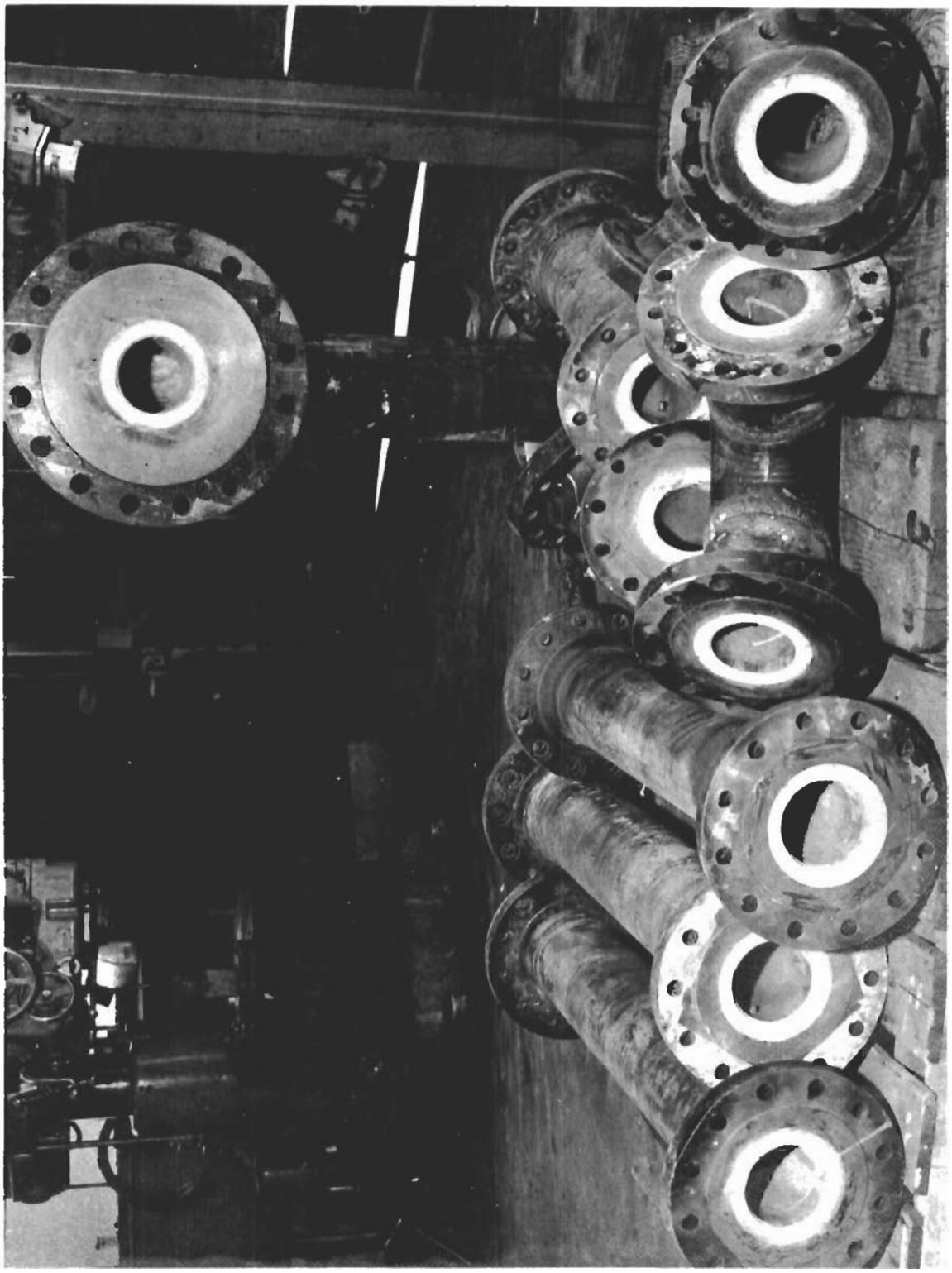

FIGURE 42. Accessory Pipes after Coating

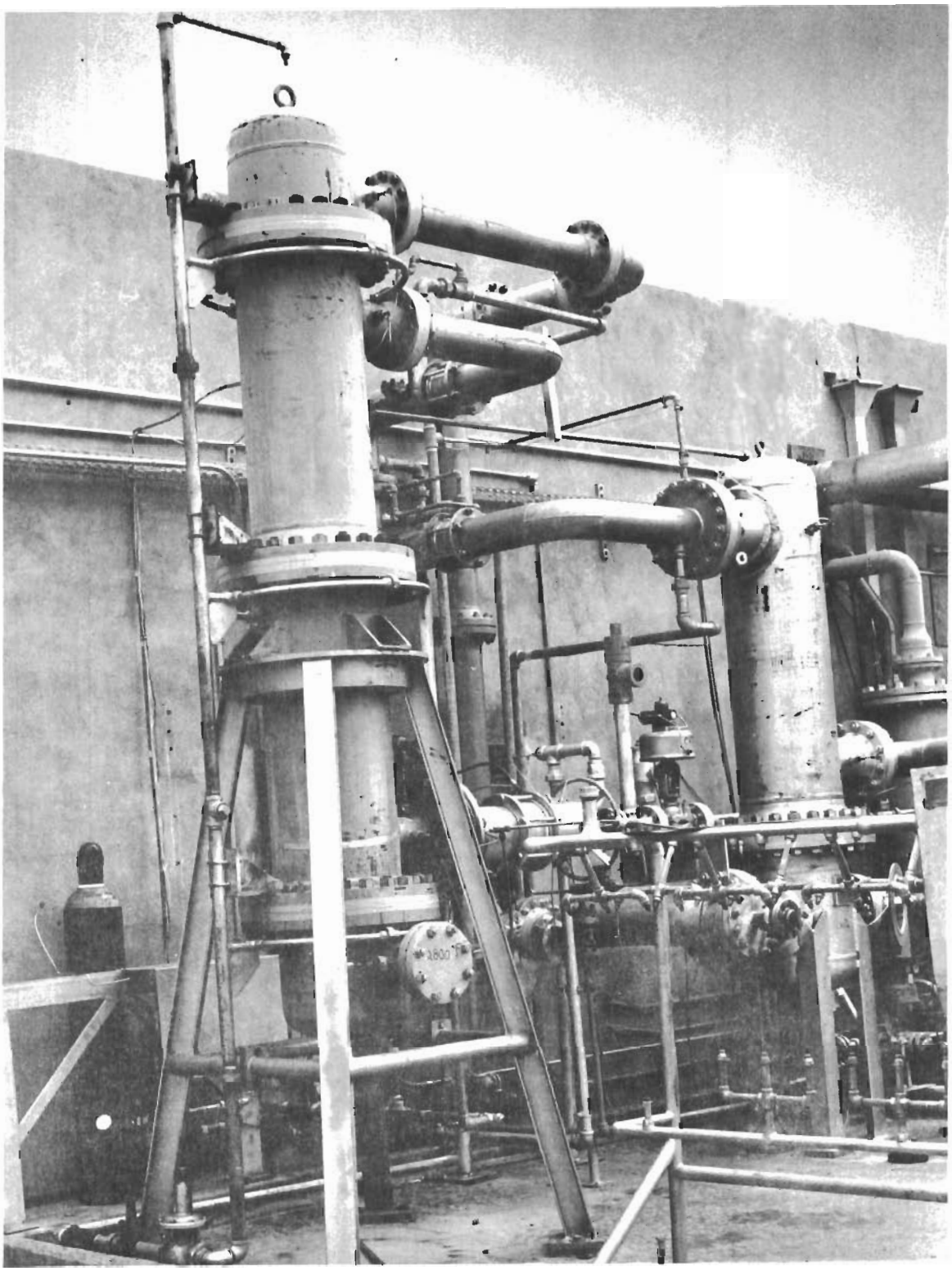

FIGURE 43. Heat Exchanger Assembly

APPENDIX I

SOURCE DATA FOR MATERIALS
DISCUSSED IN THIS REPORT

APPENDIX I

SOURCE DATA FOR MATERIALS DISCUSSED IN THIS REPORT

No.	Material	Vendor
1.	Tantalum ribbon (0.010 inch thick by 0.125 inch wide)	Kawecki Chemical Co.
2.	0.5% Ti-Mo ribbon (0.010 inch thick by 0.125 inch wide)	Fansteel Metallurgical Corporation
3.	321 stainless steel ribbon (0.010 inch thick by 0.125 inch wide)	H. K. Porter Co., Inc.
4.	N-155 alloy sheet	Haynes Stellite (Div. of Union Carbide Corp.)
5.	Hydrofluosilicic Acid (H_2SiF_6)(Baker & Adamson)	Allied Chemical & Dye Corp.
6.	Hydrofluosilicic Acid (H_2SiF_6)	J.T. Baker Chemical Co.
7.	Hydrofluosilicic Acid (H_2SiF_6)	Davison Chemical Co.
8.	Hydrofluosilicic Acid (H_2SiF_6)	The Harshaw Chemical Co.
9.	Fluosulfonic Acid (HSO_3F)	Allied Chemical & Dye Corp.
10.	Monofluorophosphoric Acid (H_2PO_3F)	Ozark-Mahoning Co.
11.	Fused zirconia - Norton H, 30F	Norton Company
12.	Fused zirconia - Norton H, 36F	Norton Company
13.	Fused zirconia - Norton I, 325F	Norton Company
14.	Fused zirconia - Zircoa B, 325 mesh	Zirconium Corporation of America
15.	Ammonium dihydrogen phosphate ($NH_4H_2PO_4$)	(J.T. Baker Chemical Co. (Braun Chemical Co.
16.	Fiberfrax bulk fiber	The Carborundum Co.
17.	Chrome oxide (Cr_2O_3)	Varlacoid Chemical Co.
18.	Cerium zirconate ($CeZrO_4$)	B.F. Wagner & Co.

APPENDIX I (Continued)

No.	Material	Vendor
19.	Strontium zirconate ($SrZrO_3$)	B.F. Wagner & Co.
20.	Sodium silicate, "S-35" Brand	Philadelphia Quartz
21.	Potassium silicate-"Kasil"	Philadelphia Quartz
22.	Pyro-Chrome	Preferred Utilities Corp.
23.	CP-44 (Ceramic paint developed by the University of Illinois)	The Marquardt Corporation
24.	Alkaphos C	Monsanto Chemical Co.
25.	Aluminum powder -325 mesh	Kaiser Aluminum Co.
26.	Brolite	Andrew Brown Co.
27.	Chromium powder -325 mesh	Kawecki Chemical Corp.
28.	Nicrobraz cement	Wall Colmonoy Corp.
29.	Columbium powder -325 mesh	Wah Chang Co.
30.	Vanadium powder -325 mesh	Vanadium Corporation of America
31.	Nickel powder -325 mesh	Metals Disintegrating Co.
32.	Nichrome powder -325 mesh	Metallizing Engineering Co., Inc.
33.	Silver paint	Sherwin-Williams
34.	Aluminum paint	Westinghouse Electric
35.	Alumina paint (Al_2O_3 + H_2PO_3F)	The Marquardt Corporation
36.	Phosphatherm	Alpha Molykote Corp.
37.	Zirconia paint (ZrO_2 + H_2PO_3F)	The Marquardt Corporation
38.	Zirconium sulfate ($Zr(SO_4)_2 \cdot 2\ H_2O$)	The Carborundum Co.
39.	Zirconium tetrafluoride (ZrF_4)	Allied Chemical, Baton Rouge Dev. Lab.

APPENDIX I (Continued)

No.	Material	Vendor
40.	Hydrofluoric acid (HF)	Mallinckrodt Chemical Works
41.	Ammonium fluoride (NH_4F)	Allied Chemical & Dye Corp.
42.	Ammonium chloride (NH_4Cl)	J.T. Baker Chemical Co.
43.	Ammonium vanadate (NH_4VO_3)	J.T. Baker Chemical Co. and Fisher Scientific Co.
44.	Chromium fluoride ($CrF_3 \cdot 3\ 1/2\ H_2O$	Allied Chemical & Dye Corp.
45.	Zirconium powder - 200 mesh	Zirconium Corporation of America
46.	Lithium zirconate ($LiZrO_3$)	Lithium Corporation of America, Inc.
47.	Ammonium silicofluoride $(NH_4)_2\ SiF_6$	American Agricultural Chemical Company
48.	L-1155 wetting agent	Minnesota Mining & Manufacturing Co.
49.	L-1159 wetting agent	Minnesota Mining & Manufacturing Co.
50.	Manganese dioxide (MnO_2)	Mallinckrodt Chemical Works & Allied Chemical and Dye Corp.
51.	Cobaltic oxide (Co_2O_3)	Harshaw Chemical Co. and L.H. Butcher Co.
52.	Iron (Ferric) oxide (Fe_2O_3)	Harshaw Chemical Co.
53.	Holmium oxide (Ho_2O_3)	Michigan Chemical Corp.
54.	Gadolinium oxide (Gd_2O_3)	Michigan Chemical Corp.
55.	Erbium oxide (Er_2O_3)	Michigan Chemical Corp.
56.	Polyvinyl chloride resin	Escambia Chemical Corp.
57.	Lanthanum oxide (La_2O_3)	Vitro Chemical Co.
58.	Tungstic anhydride (WO_3)	Fisher Scientific Co.

APPENDIX I (Continued)

No.	Material	Vendor
59.	Zirconium oxide - E-220 (ZrO_2)	Harshaw Chemical Co.
60.	Colloidal zirconia - #180	E.I. DuPont de Nemours
61.	Tin flake	Metals Disintegrating Co., Inc.
62.	Aluminum flake	Metals Disintegrating Co., Inc.
63.	KEL-F soft wax, Grade 40	E.I. DuPont de Nemours

APPENDIX II

BIBLIOGRAPHY OF REINFORCED REFRACTORY CERAMIC COATINGS AND RELATED ART

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BIBLIOGRAPHY OF REINFORCED REFRACTORY CERAMIC COATINGS AND RELATED ART

B-I. REINFORCED REFRACTORY CERAMIC COATINGS

1. WADC TR 57-577, Part I, ASTIA No. AD 150957, "Development and Evaluation of Insulating Type Refractory Coatings", The Marquardt Corporation, S. Sklarew, et al, February 1958.

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APPENDIX III

TABULATION OF COMPOSITIONS

FORMULATION OF TherMarq ZFS- COMPOSITIONS

Constituent	Parts by Weight									
	101	102	103	104	105	106				
ZrO_2 (30m) Norton H	40	40	40	40	40	40				
ZrO_2 (325m) Norton I	30	30	30	30	30	25.9				
$NH_4H_2PO_4$	1	1	--	1	1	--				
$(NH_4)_2SiF6$	--	--	--	--	--	--				
H_2PO_3F	--	--	--	--	2.5	--				
H_2SiF6	--	--	--	--	--	--				
H_2O	5	5	2.5	4	6	5.1				
HSO_3F	5	6	--	5	2.5	--				
HF	--	--	2.5	--	--	--				
H_2SO_4	--	--	6.1	--	--	--				
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	11.4				
ZrF_4	--	--	--	--	--	2.1				
Zr (200m)	--	--	--	--	--	--				
$(NH_4)_2 CO_3$	--	--	--	--	--	--				
NH_4F	--	--	--	--	--	--				
NH_4Cl	--	--	--	--	--	--				
Cr_2O_3	--	--	--	--	--	--				
NH_4VO_3	--	--	--	--	--	--				
$CrF_3 \cdot 3.5 H_2O$	--	--	--	--	--	--				
$SrZrO_3$	--	--	--	--	--	--				
Cr (325m)	--	--	--	--	--	--				
ZrO_2 (60 x 150)	--	--	--	--	--	--				
Lithium Zirconate	--	--	--	--	--	--				
Fiberfrax	--	--	--	--	--	--				
$CeZrO_4$	--	--	--	--	--	--				
Co_2O_3	--	--	--	--	--	--				
La_2O_3	--	--	--	--	--	--				
MnO_2	--	--	--	--	--	--				
WO_3	--	--	--	--	--	--				
ZrO_2 (36m)	--	--	--	--	--	--				
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--				
L 1155	--	--	--	--	--	--				
L 1159	--	--	--	--	--	--				
Fe_2O_3	--	--	--	--	--	--				
Ho_2O_3	--	--	--	--	--	--				
Gd_2O_3	--	--	--	--	--	--				
Er_2O_3	--	--	--	--	--	--				

FORMULATION OF TherMarq ZPF- COMPOSITIONS

Constituent	Parts by Weight									
	100	101	102	103	104	105	106	107	108	
ZrO_2 (30m) Norton H	40	--	--	--	40	40	40	50	50	
ZrO_2 (325m) Norton I	30	20	17.5	17.5	27.5	25	20	17.5	20	
$NH_4H_2PO_4$	1	9	9	9	1	1	1	1	1	
$(NH_4)_2SiF6$	--	--	--	--	--	--	--	--	--	
H_2PO_3F	5	5	5	5	5	5	5	5	5	
H_2SiF6	--	--	--	--	--	--	--	--	--	
H_2O	2	3	3	3	2	2	2	2	2	
HSO_3F	--	--	--	--	--	--	--	--	--	
HF	--	--	--	--	--	--	--	--	--	
H_2SO_4	--	--	--	--	--	--	--	--	--	
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--	--	
ZrF_4	--	--	--	--	--	--	--	--	--	
Zr (200m)	--	--	--	--	--	--	--	--	--	
$(NH_4)_2 CO_3$	--	--	--	--	--	--	--	--	--	
NH_4F	--	--	--	--	--	--	--	--	--	
NH_4Cl	--	--	--	--	--	--	--	--	--	
Cr_2O_3	--	--	--	--	--	--	--	--	--	
NH_4VO_3	--	--	--	--	--	--	--	--	--	
$CrF_3 \cdot 3.5 H_2O$	--	--	--	--	--	--	--	--	--	
$SrZrO_3$	--	--	--	--	--	--	--	--	--	
Cr (325m)	--	--	2.5	--	2.5	5	10	2.5	--	
ZrO_2 (60 x 150)	--	80	80	80	--	--	--	--	--	
Lithium Zirconate	--	--	--	2.5	--	--	--	--	--	
Fiberfrax	--	--	--	--	--	--	--	--	--	
$CeZrO_4$	--	--	--	--	--	--	--	--	--	
Co_2O_3	--	--	--	--	--	--	--	--	--	
La_2O_3	--	--	--	--	--	--	--	--	--	
MnO_2	--	--	--	--	--	--	--	--	--	
WO_3	--	--	--	--	--	--	--	--	--	
ZrO_2 (36m)	--	--	--	--	--	--	--	--	--	
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--	--	--	--	
L 1155	--	--	--	--	--	--	--	--	--	
L 1159	--	--	--	--	--	--	--	--	--	
Fe_2O_3	--	--	--	--	--	--	--	--	--	
Ho_2O_3	--	--	--	--	--	--	--	--	--	
Gd_2O_3	--	--	--	--	--	--	--	--	--	
Er_2O_3	--	--	--	--	--	--	--	--	--	

FORMULATION OF TherMarq ZSF- COMPOSITIONS

Constituent	Parts by Weight									
	101	102	103	104	105	106	107	108	109	110
ZrO_2 (30m) Norton H	40	40	40	48	40	40	40	40	40	40
ZrO_2 (325m) Norton I	30	30	30	33	30	30	30	30	30	30
$NH_4H_2PO_4$	1	--	--	--	--	--	--	--	--	--
$(NH_4)_2SiF6$	--	--	--	--	--	--	--	--	--	--
H_2PO_3F	--	--	--	--	--	--	--	--	--	--
H_2SiF6	7	7	8	9	7	7	7	7	7	7
H_2O	--	--	--	--	--	--	--	--	--	--
HSO_3F	--	--	--	--	--	--	--	--	--	--
HF	--	--	--	--	--	--	--	--	--	--
H_2SO_4	--	--	--	--	--	--	--	--	--	--
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--	--	--
ZrF_4	--	--	--	--	--	--	--	--	--	--
Zr (200m)	--	--	--	10	--	--	--	--	--	--
$(NH_4)_2 CO_3$	--	--	--	--	1.4	--	--	--	--	--
NH_4F	--	--	--	--	--	1	--	2	--	--
NH_4Cl	--	--	--	--	--	--	1	--	2	--
Cr_2O_3	--	--	--	--	--	--	--	--	--	1
NH_4VO_3	--	--	--	--	--	--	--	--	--	--
$CrF_3 \cdot 3.5\ H_2O$	--	--	--	--	--	--	--	--	--	--
$SrZrO_3$	--	--	--	--	--	--	--	--	--	--
Cr (325m)	--	--	--	--	--	--	--	--	--	--
ZrO_2 (60 x 150)	--	--	--	--	--	--	--	--	--	--
Lithium Zirconate	--	--	--	--	--	--	--	--	--	--
Fiberfrax	--	--	--	--	--	--	--	--	--	--
$CeZrO_4$	--	--	--	--	--	--	--	--	--	--
Co_2O_3	--	--	--	--	--	--	--	--	--	--
La_2O_3	--	--	--	--	--	--	--	--	--	--
MnO_2	--	--	--	--	--	--	--	--	--	--
WO_3	--	--	--	--	--	--	--	--	--	--
ZrO_2 (36m)	--	--	--	--	--	--	--	--	--	--
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--	--	--	--	--
L 1155	--	--	--	--	--	--	--	--	--	--
L 1159	--	--	--	--	--	--	--	--	--	--
Fe_2O_3	--	--	--	--	--	--	--	--	--	--
Ho_2O_3	--	--	--	--	--	--	--	--	--	--
Gd_2O_3	--	--	--	--	--	--	--	--	--	--
Er_2O_3	--	--	--	--	--	--	--	--	--	--

FORMULATION OF TherMarq ZSF- COMPOSITIONS

Constituent	Parts by Weight									
	111	112	113	114	115	116	117	118	119	120
ZrO_2 (30m) Norton H	40	40	40	40	40	80	40	40	40	40
ZrO_2 (325m) Norton I	30	30	30	30	22	5	26.5	26.5	26.5	26.5
$NH_4H_2PO_4$	--	--	--	1	1	9	--	--	--	--
$(NH_4)_2SiF_6$	--	--	--	--	--	--	--	--	--	--
H_2PO_3F	--	--	--	7	--	--	--	--	--	--
H_2SiF_6	7	7	7	--	6.2	6.2	6.2	6.2	6.2	6.2
H_2O	--	--	3	--	--	--	--	--	--	--
HSO_3F	--	--	--	--	--	--	--	--	--	--
HF	--	--	--	--	--	--	--	--	--	--
H_2SO_4	--	--	--	--	--	--	--	--	--	--
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--	--	--
ZrF_4	--	--	--	--	--	--	--	--	--	--
Zr (200m)	--	--	--	--	--	--	--	--	--	--
$(NH_4)_2 CO_3$	--	--	--	--	--	--	--	--	--	--
NH_4F	--	--	--	--	--	--	--	--	--	--
NH_4Cl	--	--	--	--	--	--	--	--	--	--
Cr_2O_3	--	--	--	--	8	15	--	--	--	--
NH_4VO_3	1	--	--	--	--	--	--	--	1.75	--
$CrF_3 \cdot 3.5\ H_2O$	--	1	--	--	--	--	--	--	--	--
$SrZrO_3$	--	--	1	--	--	--	--	1.75	--	--
Cr (325m)	--	--	--	--	--	--	--	--	--	--
ZrO_2 (60 x 150)	--	--	--	--	--	--	--	--	--	--
Lithium Zirconate	--	--	--	--	--	--	--	--	--	--
Fiberfrax	--	--	1/16" layer	--	--	--	--	--	--	--
$CeZrO_4$	--	--	--	--	--	--	1.75	--	--	--
Co_2O_3	--	--	--	--	--	--	--	--	--	3.5
La_2O_3	--	--	--	--	--	--	--	--	--	--
MnO_2	--	--	--	--	--	--	--	--	--	--
WO_3	--	--	--	--	--	--	--	--	--	--
ZrO_2 (36m)	--	--	--	--	--	--	--	--	--	--
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--	--	--	--	--
L 1155	--	--	--	--	--	--	--	--	--	--
L 1159	--	--	--	--	--	--	--	--	--	--
Fe_2O_3	--	--	--	--	--	--	--	--	--	--
Ho_2O_3	--	--	--	--	--	--	--	--	--	--
Gd_2O_3	--	--	--	--	--	--	--	--	--	--
Er_2O_3	--	--	--	--	--	--	--	--	--	--

FORMULATION OF TherMarq ZSF- COMPOSITIONS

Constituent	Parts by Weight									
	121	122	123	124	125	126	127	128	129	
ZrO_2 (30m) Norton H	40	40	40	40	40	40	40	40	40	
ZrO_2 (325m) Norton I	26.5	26.5	26.5	30	30	30	30	30	30	
$NH_4H_2PO_4$	--	--	--	1	1	1	1	1	1	
$(NH_4)_2SiF_6$	--	--	--	--	--	--	--	--	--	
H_2PO_3F	--	--	--	--	--	--	--	--	--	
H_2SiF_6	6.2	6.2	6.2	7	13	5	5	4	3	
H_2O	--	--	--	--	--	--	1.7	2.3	3.3	
HSO_3F	--	--	--	--	--	--	--	--	--	
HF	--	--	--	--	--	--	--	--	--	
H_2SO_4	--	--	--	--	--	--	--	--	--	
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--	--	
ZrF_4	--	--	--	--	--	--	--	--	--	
Zr (200m)	--	--	--	--	--	--	--	--	--	
$(NH_4)_2CO_3$	--	--	--	--	--	--	--	--	--	
NH_4F	--	--	--	--	--	--	--	--	--	
NH_4Cl	--	--	--	--	--	--	--	--	--	
Cr_2O_3	--	--	--	--	--	--	--	--	--	
NH_4VO_3	--	--	--	--	--	--	--	--	--	
$CrF_3 \cdot 3.5\ H_2O$	--	--	--	--	--	--	--	--	--	
$SrZrO_3$	--	--	--	--	--	--	--	--	--	
Cr (325m)	--	--	--	--	--	--	--	--	--	
ZrO_2 (60 x 150)	--	--	--	--	--	--	--	--	--	
Lithium Zirconate	--	--	--	--	--	--	--	--	--	
Fiberfrax	--	--	--	--	--	--	--	--	--	
$CeZrO_4$	--	--	--	--	--	--	--	--	--	
Co_2O_3	--	--	--	--	--	--	--	--	--	
La_2O_3	1.75	--	--	--	--	--	--	--	--	
MnO_2	--	1.75	--	--	--	--	--	--	--	
WO_3	--	--	1.75	--	--	--	--	--	--	
ZrO_2 (36m)	--	--	--	--	--	--	--	--	--	
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--	--	--	--	
L 1155	--	--	--	--	--	--	--	--	--	
L 1159	--	--	--	--	--	--	--	--	--	
Fe_2O_3	--	--	--	--	--	--	--	--	--	
Ho_2O_3	--	--	--	--	--	--	--	--	--	
Gd_2O_3	--	--	--	--	--	--	--	--	--	
Er_2O_3	--	--	--	--	--	--	--	--	--	

FORMULATION OF TherMarq ZFS- COMPOSITIONS

Constituent	Parts by Weight									
	130	131	132	133	134	135	136	137		
ZrO_2 (30m) Norton H	40	--	40	40	40	40	40	40		
ZrO_2 (325m) Norton I	30	--	30	30	30	30	30	30		
$NH_4H_2PO_4$	1	1	1	1	1	1	2	3		
$(NH_4)_2SiF6$	--	--	--	--	--	--	--	--		
H_2PO_3F	--	--	--	--	--	--	--	--		
H_2SiF6	2	7	5	6	7	8	6	6		
H_2O	4	--	1	--	--	--	--	--		
HSO_3F	--	--	--	--	--	--	--	--		
HF	--	--	--	--	--	--	--	--		
H_2SO_4	--	--	--	--	--	--	--	--		
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--		
ZrF_4	--	--	--	--	--	--	--	--		
Zr (200m)	--	--	--	--	--	--	--	--		
$(NH_4)_2 CO_3$	--	--	--	--	--	--	--	--		
NH_4F	--	--	--	--	--	--	--	--		
NH_4Cl	--	--	--	--	--	--	--	--		
Cr_2O_3	--	--	--	--	--	--	--	--		
NH_4VO_3	--	--	--	--	--	--	--	--		
$CrF_3 \cdot 3.5 H_2O$	--	--	--	--	--	--	--	--		
$SrZrO_3$	--	--	--	--	--	--	--	--		
Cr (325m)	--	--	--	--	--	--	--	--		
ZrO_2 (60 x 150)	--	--	--	--	--	--	--	--		
Lithium Zirconate	--	--	--	--	--	--	--	--		
Fiberfrax	--	--	--	--	--	--	--	--		
$CeZrO_4$	--	--	--	--	--	--	--	--		
Co_2O_3	--	--	--	--	--	--	--	--		
La_2O_3	--	--	--	--	--	--	--	--		
MnO_2	--	--	--	--	--	--	--	--		
WO_3	--	--	--	--	--	--	--	--		
ZrO_2 (36m)	--	40	--	--	--	--	--	--		
ZrO_2 (325m, Zircoa)	--	30	--	--	--	--	--	--		
L 1155	--	--	--	--	--	--	--	--		
L 1159	--	--	--	--	--	--	--	--		
Fe_2O_3	--	--	--	--	--	--	--	--		
Ho_2O_3	--	--	--	--	--	--	--	--		
Gd_2O_3	--	--	--	--	--	--	--	--		
Er_2O_3	--	--	--	--	--	--	--	--		

FORMULATION OF TherMarq ZSF- COMPOSITIONS

Constituent	Parts by Weight									
	138	139	140	141	142	143	144	145	146	147
ZrO_2 (30m) Norton H	40	40	40	40	40	40	40	40	40	40
ZrO_2 (325m) Norton I	30	30	30	30	30	30	30	30	30	30
$NH_4H_2PO_4$	4.0	5.0	--	--	--	1.0	1.0	1.0	1.0	1.0
$(NH_4)_2SiF6$	--	--	0.5	1.0	1.0	--	--	1.0	1.0	--
H_2PO_3F	--	--	--	--	3.5	3.5	3.0	3.0	3.0	3.5
H_2SiF6	6.0	6.0	7.0	7.0	3.5	3.5	3.0	3.0	3.5	3.5
H_2O	3.0	3.0	--	--	--	--	--	--	1.4	1.0
HSO_3F	--	--	--	--	--	--	--	--	--	--
HF	--	--	--	--	--	--	--	--	--	--
H_2SO_4	--	--	--	--	--	--	--	--	--	--
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--	--	--
ZrF_4	--	--	--	--	--	--	--	--	--	--
Zr (200m)	--	--	--	--	--	--	--	--	--	--
$(NH_4)_2 CO_3$	--	--	--	--	--	--	--	--	--	--
NH_4F	--	--	--	--	--	--	--	--	--	--
NH_4Cl	--	--	--	--	--	--	--	--	--	--
Cr_2O_3	--	--	--	--	--	--	--	--	--	--
NH_4VO_3	--	--	--	--	--	--	--	--	--	--
$CrF_3 \cdot 3.5\ H_2O$	--	--	--	--	--	--	--	--	--	--
$SrZrO_3$	--	--	--	--	--	--	--	--	--	--
Cr (325m)	--	--	--	--	--	--	--	--	--	--
ZrO_2 (60 x 150)	--	--	--	--	--	--	--	--	--	--
Lithium Zirconate	--	--	--	--	--	--	--	--	--	--
Fiberfrax	--	--	--	--	--	--	--	--	--	--
$CeZrO_4$	--	--	--	--	--	--	--	--	--	--
Co_2O_3	--	--	--	--	--	--	--	--	--	--
La_2O_3	--	--	--	--	--	--	--	--	--	--
MnO_2	--	--	--	--	--	--	--	--	--	--
WO_3	--	--	--	--	--	--	--	--	--	--
ZrO_2 (36m)	--	--	--	--	--	--	--	--	--	--
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--	--	--	--	--
L 1155	--	--	--	--	--	--	--	--	--	--
L 1159	--	--	--	--	--	--	--	--	--	--
Fe_2O_3	--	--	--	--	--	--	--	--	--	--
Ho_2O_3	--	--	--	--	--	--	--	--	--	--
Gd_2O_3	--	--	--	--	--	--	--	--	--	--
Er_2O_3	--	--	--	--	--	--	--	--	--	--

FORMULATION OF TherMarq ZSF- COMPOSITIONS

Constituent	Parts by Weight									
	148	149	150	151	152	153	154	155	156	
ZrO_2 (30m) Norton H	40	40	40	40	40	40	40	40	40	
ZrO_2 (325m) Norton I	30	28	28	28	30	30	30	29.5	29.5	
$NH_4H_2PO_4$	1.0	1.0	1.5	1.0	1.0	1.0	1.0	1.0	1.0	
$(NH_4)_2SiF6$	1.0	1.0	1.0	1.0	1.0	1.0	1	--	--	
H_2PO_3F	3.0	3.0	3.0	3.0	3.0	3.0	3.0	--	--	
H_2SiF6	3.0	3.0	3.0	3.0	3.0	3.0	3.0	7.0	7.0	
H_2O	0.7	1.0	0.5	1.0	3.0	3.0	2.5	--	--	
HSO_3F	--	--	--	--	--	--	--	--	--	
HF	--	--	--	--	--	--	--	--	--	
H_2SO_4	--	--	--	--	--	--	--	--	--	
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--	--	
ZrF_4	--	--	--	--	--	--	--	--	--	
Zr (200m)	--	--	--	--	--	--	--	--	--	
$(NH_4)_2 CO_3$	--	--	--	--	--	--	--	--	--	
NH_4F	--	--	--	--	--	--	--	--	--	
NH_4Cl	--	--	--	--	--	--	--	--	--	
Cr_2O_3	0.5	1.0	1.0	0.5	0.5	0.5	0.5	0.5	--	
NH_4VO_3	--	--	--	--	--	--	--	--	--	
$CrF_3 \cdot 3.5\ H_2O$	--	--	--	--	--	--	--	--	--	
$SrZrO_3$	--	--	--	--	--	--	--	--	--	
Cr (325m)	--	--	--	--	--	--	--	--	--	
ZrO_2 (60 x 150)	--	--	--	--	--	--	--	--	--	
Lithium Zirconate	--	--	--	--	--	--	--	--	--	
Fiberfrax	--	--	--	--	--	--	--	--	--	
$CeZrO_4$	--	--	--	--	--	--	--	--	--	
Co_2O_3	--	--	--	--	--	--	--	--	--	
La_2O_3	--	--	--	--	--	--	--	--	--	
MnO_2	--	--	--	--	--	--	--	--	0.5	
WO_3	--	--	--	--	--	--	--	--	--	
ZrO_2 (36m)	--	--	--	--	--	--	--	--	--	
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--	--	--	--	
L 1155	--	--	--	--	0.03	--	--	--	--	
L 1159	--	--	--	--	--	0.03	--	--	--	
Fe_2O_3	--	--	--	--	--	--	--	--	--	
Ho_2O_3	--	--	--	--	--	--	--	--	--	
Gd_2O_3	--	--	--	--	--	--	--	--	--	
Er_2O_3	--	--	--	--	--	--	--	--	--	

FORMULATION OF TherMarq ZSF- COMPOSITIONS

Constituent	Parts by Weight									
	157	158	159	160	161	162	163	164	165	
ZrO_2 (30m) Norton H	40	40	40	40	40	40	40	40	40	
ZrO_2 (325m) Norton I	28.5	28.5	28.5	28.5	28.5	29	29	29	28	
$NH_4H_2PO_4$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
$(NH_4)_2SiF6$	--	--	--	--	--	--	--	--	--	
H_2PO_3F	--	--	--	--	--	--	--	--	--	
H_2SiF6	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0	
H_2O	--	--	--	--	--	1.0	--	--	--	
HSO_3F	--	--	--	--	--	--	--	--	--	
HF	--	--	--	--	--	--	--	--	--	
H_2SO_4	--	--	--	--	--	--	--	--	--	
$Zr(SO_4)_2 \cdot 4H_2O$	--	--	--	--	--	--	--	--	--	
ZrF_4	--	--	--	--	--	--	--	--	--	
Zr (200m)	--	--	--	--	--	--	--	--	--	
$(NH_4)_2 CO_3$	--	--	--	--	--	--	--	--	--	
NH_4F	--	--	--	--	--	--	--	--	--	
NH_4Cl	--	--	--	--	--	--	--	--	--	
Cr_2O_3	--	--	--	--	--	--	--	--	--	
NH_4VO_3	--	--	--	--	--	--	--	--	--	
$CrF_3 \cdot 3.5\ H_2O$	--	--	--	--	--	--	--	--	--	
$SrZrO_3$	--	--	--	--	--	1.0	--	--	--	
Cr (325m)	--	--	--	--	--	--	--	--	--	
ZrO_2 (60 x 150)	--	--	--	--	--	--	--	--	--	
Lithium Zirconate	--	--	--	--	--	--	--	--	--	
Fiberfrax	--	--	--	--	--	--	--	--	--	
$CeZrO_4$	--	--	--	--	--	--	1.0	--	--	
Co_2O_3	0.5	--	--	--	--	--	--	1.0	2.0	
La_2O_3	--	--	--	--	--	--	--	--	--	
MnO_2	--	--	--	--	--	--	--	--	--	
WO_3	--	--	--	--	--	--	--	--	--	
ZrO_2 (36m)	--	--	--	--	--	--	--	--	--	
ZrO_2 (325m, Zircoa)	--	--	--	--	--	--	--	--	--	
L 1155	--	--	--	--	--	--	--	--	--	
L 1159	--	--	--	--	--	--	--	--	--	
Fe_2O_3	0.5	--	--	--	--	--	--	--	--	
Ho_2O_3	--	0.5	--	--	--	--	--	--	--	
Gd_2O_3	--	--	0.5	--	--	--	--	--	--	
Er_2O_3	--	--	--	0.5	--	--	--	--	--	