FABRICATION AND TESTING OF BATTERY SEPARATOR MATERIAL FROM MODIFIED POLYETHYLENE

Final Report

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L. M. Adams
W. W. Harlowe, Jr.
G. C. Lawrason

Project No. 01-1842

Purchase Order No. CA-384805

Prepared for NAS-7-100

Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California 91103

Attn: H. E. Patterson
Senior Contract Negotiator
Mail Station 190-212

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SOUTHWEST RESEARCH INSTITUTE
SAN ANTONIO HOUSTON

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APPROVED:

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ABSTRACT

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Polyethylene film was crosslinked with divinylbenzene and then grafted with acrylic acid using procedures described in the JPL Advanced Development Engineering Note No. 342011. A number of difficulties were encountered. These difficulties are discussed.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Dr. Ralph W. Lutwack and Mr. Werner von Hartmann of JPL for their cooperation and guidance during this program.

The authors also wish to thank Mr. A. M. Nicholls and Mr. W. Nation for their assistance in radiation and experimental aspects of the research.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS AND TABLES

I. INTRODUCTION

The Jet Propulsion Laboratory of the California Institute of Technology (JPL) has developed a sterilizable battery separator material of modified polyethylene film. Basically, the polyethylene film is crosslinked with dinvinylbenzene and then grafted with acrylic acid. The crosslinking and grafting reactions are initiated by irradiation from a Cobalt-60 source.

The objective of the work covered by this report was to prepare 200 linear feet of this battery separator material to meet specifications established by JPL by using the procedure supplied by JPL. Specifications for the material after sterilization in hot potassium hydroxide include a maximum resistance of 60 milliohm-in^2 and a minimum tensile strength of 700 psi.

II. SUMMARY

Approximately 200 feet of polyethylene film, crosslinked and grafted in accordance with JPL Advanced Development Engineering Note No. 342011 and subsequently regrafted, was evaluated and submitted to the Sponsor (Table 1). The regrafting, a deviation from the initially established procedure, was necessary since insufficient grafting took place during the initial operation.

A summary of the films submitted and their respective properties is presented in Table 2. The key to the film nomenclature and test sample procedure used in this and other tables is presented as Appendix A. In general, the films exhibited satisfactory resistance values after sterilization; exceptions appear to be the result of nonuniformity of grafting. The tensile strength values were generally somewhat lower than the specified minimum of 700 psi, possibly because of degradation resulting from the irradiation dosage required for regrafting.

III. EXPERIMENTAL PROGRAM

The preparation of the sterilizable battery separator material was carried out in accordance with JPL Advanced Development Engineering Note No. 342011 (see Appendix B). The composition and purity of the materials used in this investigation were equivalent to those specified in the aforementioned document and are listed in Table 3 along with irradiation dose rates.

Separate discussions of the various preparation and evaluation phases are presented below.

A. Irradiation Technique

Irradiation crosslinking and grafting of polyethylene was carried out at the Southwest Research Institute Radiation Effects Facility. A detailed description of this facility is given in Appendix C.

1. Irradiation Configuration

Analysis of the required dose rates and irradiation parameters indicated that Cobalt-60 source configuration of 3000 curies would be suitable. Since it was desirable to irradiate two glass tubes containing polyethylene at the same time, a small platform was constructed in one of the cells of the facility. On this platform, two 16-rpm turntables were modified to hold the target tubes. The Cobalt-60

configuration was attached to one of the source transfer carts so that it could be remotely withdrawn and stored. The relationship between the glass tube platform and the cart holding the cobalt was fixed by steel plates bolted to the floor so that the center line of the target tubes was 38 centimeters from the center of the cobalt configuration. This distance was calculated to produce 25,000 R/hour and, with the addition of a 3-centimeter shim to the cart stop flange, 20,000 R/hour. Figure 1 is a general view of the cell with target tubes and cobalt holders in place on the cart.

A combination rolling device and washing bath with motorized reels was constructed to process the polyethylene target material as set forth in the request for proposal work statement. This piece of equipment was essential to roll the polyethylene film and paper toweling together with the accuracy required. Figure 2 illustrates the tank and associated equipment. This equipment has worked satisfactorily for both the rolling of the film on an aluminum spindle and for washing the irradiated film with benzene.

2. Dosimetry and Allied Functions

Bausch and Lomb cobalt glass chip dosimetry [1, 2] was used for the bulk of the dose rate determinations. Three separate irradiations were made with the cobalt glass dosimetry spaced near

the center line throughout the 13-inch target roll width and at the outside of the roll within the glass tube. Results were as follows:

First Determination in Water

R/hr, Top to Bottom Inside Surface of Tube	R/hr, Top to Bottom Center of Tube
25,000	23,500
25,000	23,750
24,250	22,000
25,000	22,000
24,750	21,750

The target-Cobalt 60 relationship was adjusted to provide a better dose distribution, and the results were as follows:

Second Determination in Water

R/hr, Top to Bottom Inside Surface of Tube	R/hr, Top to Bottom Center of Tube
23,500	22,000
23,500	23,000
24,200	22,200
23,500	22,200
23,500	21,200

Third Determination in Air

R/hr, Top to Bottom Inside Surface of Tube	R/hr, Top to Bottom Center of Tube
26,400	25,700
27,000	25,700
26,400	25,700

The results of the cobalt glass dosimetry show that, after minor adjustment of the source and targets, dose distribution was very even within the volume of the target. Further, the figures showed excellent repeatability between runs when the medium (air or water) was considered. Since during the actual irradiation of the polyethylene rolls the fluids in which the targets are immersed will have a density slightly less than that of water, the last Cobalt-60 glass chip dosimetry determination should be very close to the target dose. All dosimetry was determined with the target tubes rotating; irradiation times were varied to make certain the response of the dosimeters was linear with time.

The α-alanine dosimetry[3, 4] technique developed at SwRI was used to check the cobalt glass chip dosimetry. Two separate determinations were made in air. The first determination was unsatisfactory because of a mechanical discrepancy in the rather complex electrical equipment required to read the dosimeters. When the α-alanine dosimetry was rerun, results appeared to be good except that they were about 20% less than the cobalt glass chip readings which were exposed at the same time. Since, at this time, there were many cobalt glass chip determinations, which showed every aspect of accuracy and repeatability, the α-alanine results were discarded. The cobalt glass chip technique has, in the past, proved reliable and repeatable,

and SwRI has more experience with it in the high dose ranges such as those stipulated for this project. Further, the cobalt glass chip dosimetry closely checked the calculated dose.

The required amount of polyethylene was irradiated while utilizing both crosslinking and grafting solutions. The compositions of these solutions are listed in Table 3.

B. Resistance Measurement

A Lucite cell having dimensions specified by JPL, as shown in Figure 3, was fabricated for the resistance measurements. The electrodes were platinized platinum. The resistance values were read to the nearest milliohm on a Leeds and Northrup No. 8067 precision bridge. Alternating current (1000 cycle) was supplied to the system by means of a Hewlett Packard Oscillator No. 200CD. The signal received by the bridge was nulled, and the null was read from a Hewlett Packard AC voltmeter, Model HP403, amplified by means of a Hewlett Packard amplifier No. 466A. A schematic and a photograph of the apparatus are presented in Figures 4 and 5, respectively. The capacitance of the cell was found to be negligible.

The procedure for obtaining the membrane resistance was as follows:

The cell was opened. A washer (0.5-in. ID x 1.0-in. OD) of the separator material was placed into the cell. Care was exercised

to see that the material did not obstruct the hole.

The cell was closed, bolted and filled with 40 wt % KOH. The KOH temperature was recorded to the nearest 0.1 °C, and a cell resistance (Rw) was obtained.

The KOH was drained. The washer was removed and the cell faces wiped with 5% acetic acid and dried.

A disc (0.5-in. diameter) of the separator material to be tested was inserted in the cell so that the material covered the passage (0.25-in. ID) completely.

The cell was again closed, bolted and filled with 40 wt % KOH.

The total resistance (R_T) due to the insertion of the separator membrane was read on the bridge.

The membrane resistance in milliohms-in^2 was obtained from the expression

$$\text{Membrane Resistance} = (R_T - R_w) \times A$$

where:
- R_T = total resistance, milliohms
- R_w = cell resistance, milliohms
- A = film area, square inches

C. Infrared Absorbance

Infrared scans of the final product were made in an attempt to determine the degree of grafting. However, it was not possible to

determine ratios of the ionized carboxyl to methylene groups because infinite absorbance was obtained.

The Model 21 Perkin-Elmer used did not have a reflectance attachment whereby one could measure the reflected infrared.

Several attempts were made to decrease the sample thickness. A piece of the separator material was stretched as thin as possible and rescanned; however, infinite absorbance was again obtained in the two regions of interest.

D. Dimensional Analysis

For design purposes the physical dimensions and weight of each sample were determined dry, wet before sterilization, and wet after sterilization in 40 wt % KOH. Wet dimensional measurements before sterilization were made after the samples had been soaked in 40 wt % KOH for nineteen (19) hours.

A rectangular section of separator material approximately 0.38 inch wide by 6.0 inches long was removed for dimensional analysis. Each strip was blotted with separator paper, weighed on a balance and the weight recorded to the nearest 0.1 milligram. This constitutes a wet measurement.

To obtain the length and width measurements, a strip was placed between two plates of glass and its dimensions read to the nearest fiftieth (1/50) of an inch with a twelve-inch stainless steel ruler.

Film thickness was measured with a Starrett thickness gauge which could be read to the 0.0001 of an inch. The thickness of the strip was measured at three different positions and an average taken.

E. Tensile Strength

The tensile strength of each sample was measured wet with 40 wt % KOH after sterilization by means of a Gardner Tensile Apparatus. Duplicate determinations were made using the rectangular strips described above.

F. Sterilization

Sterilization chambers were fabricated from 12-inch lengths of 1-inch 316 stainless steel pipe and pipe caps. Each chamber contained a film holder consisting of a 316 stainless steel rod which had two pieces of 316 stainless steel screen attached to it. One piece of screen was fastened to the bottom of the rod and the other about 4-inches above the bottom. A photograph of a sterilization chamber is shown in Figure 6.

Sterilization was conducted on samples for subsequent resistance measurement, dimensional analysis, and tensile strength determination. The samples to be sterilized were placed on the film holder between the two screens and immersed in approximately 90 ml of 40 wt % KOH. The containers were sealed and placed in a forced draft oven.

One chamber containing 40 wt % KOH was equipped with a thermocouple well and thermocouple which was connected to a recording potentiometer. This was used to determine the temperature within the sterilization chambers. After one hour, the test samples had reached 145°C. The samples were held for 36 hours at 145°C $\pm$ 2°C, cooled to room temperature, and transferred to plastic vials which contained fresh 40 wt % KOH.

G. Additional Experiments

In addition to the prescribed experimental effort, several additional experiments were conducted in an effort to provide a better understanding of the grafting operation.

In order to establish how much irradiation exposure is required to achieve the desired degree of grafting, a 6-foot portion of film (removed from 2 North, Table 1) was exposed to repeated irradiation in approximately twenty-four hour increments at the prescribed dose rate. After each period of exposure, the film was washed with potassium hydroxide solution, and a 1-foot sample was removed for resistance measurements. Fresh acrylic acid grafting solution was used each time. The data are shown below.

Total Time of Irradiation	Resistance, milliohm-in^2
68 hrs 5 min	266 (initial attempt to graft)
92 hrs 5 min	3000
116 hrs 5 min	3000
136 hrs 10 min	62

Several additional experiments were conducted during the regrafting period. Two samples were placed on a small wooden platform attached behind the target specimen turntables. One sample vial contained uncrosslinked polyethylene in air. This sample was exposed for 68 hours 5 minutes, removed, and then the acrylic acid grafting solution added. It was allowed to stand 72 hours, washed with 5% KOH and dried. An infrared scan showed no grafting had occurred. Resistance was also very high. The other sample contained uncrosslinked polyethylene in a nitrogen atmosphere. After the above procedure was followed, an infrared scan showed no grafting took place.

IV. DISCUSSION OF RESULTS

A. Crosslinking with Divinylbenzene

In the preparation of sterilizable battery separator material utilizing the procedure specified by JPL (Appendix B), the crosslinking of polyethylene film appeared to take place smoothly, and no difficulties were noted.

B. Grafting with Acrylic Acid

After crosslinking with divinylbenzene, the polyethylene film supplied by JPL was subjected to grafting with acrylic acid. The sample designations appearing in the various tables follow the nomenclature key presented in Appendix A. After following the prescribed grafting procedure, samples of the polyethylene were removed for analysis before sterilization, and the data are presented as irradiation run Nos. 1 through 4 in Table 4. The resistance values were found to be very high; infrared scans showed some grafting had taken place in all samples with the exceptions of the first irradiation (1 N and 1 S).

During the grafting, precipitation of a white substance in the grafting solution was noted. Presumably, this was poly(acrylic acid). Examination of samples 1 N and 1 S indicated little or no grafting occurred. Although grafted polyethylenes were produced in the next three irradiations, the excessively high resistance values rendered

them unacceptable. Because of these difficulties, a change order was issued by the Sponsor to provide for regrafting of the films in an attempt to produce an acceptable product. This change order also reduced the number of evaluations required to meet the terms of the contract.

Regrafting was conducted on the initial irradiation sample Nos. 2 through 4, North and South, as shown in Table 1. After regrafting, infrared scans before sterilization showed infinite absorbance of methylene and carboxyl groups, indicating grafting had occurred. In general, resistance values obtained before sterilization were in the desired range. These values are shown in Table 4 along with the values of the films grafted only once. Sterilization and subsequent evaluations were conducted with the regrafted materials. These evaluation data are presented in Tables 2 and 5.

In one case (2 SI), the electrical resistance of the regrafted film increased to a very high value after sterilization, while the remainder retained low resistance after sterilization. The only known difference in treatment of this sample is the time lapse between irradiation and washing with the 5% potassium hydroxide. The sample which increased in resistance after sterilization was processed within 2 hours after irradiation. The other samples remained in the grafting solution for 24 to 72 hours before processing. It appears that the

grafting is diffusion limited and that much of the grafting of the internal portion of the film occurs after the irradiation exposure is terminated. Irregularities in the grafting could well cause the observed variation in resistance values.

Considerable acrylic acid homopolymer is formed during the grafting step. This produced a solid mass in the reaction tubes, and in nearly every case, regardless of the amount of film used, it was necessary to break the glass reaction tube to remove the film. The presence of the large quantity of hompolymer caused excessive pressure on the polyethylene film. It is thought that the pressure was exerted in a nonuniform manner and contributed to the nonuniformity in grafting and thus to the variation in properties.

A satisfactory explanation for the absence of acrylic acid grafting on the first attempt is not available at this time. It has been suggested that an inhibitor is present in the starting polyethylene film and that this inhibitor was destroyed during the first grafting attempt, thereby permitting the grafting to take place during the second treatment. If this is true, it is not completely understood why the crosslinking with divinylbenzene appeared to take place. Further discussion of the grafting is given in the following section.

It was necessary to unroll the film on the rolling and rinsing device and pass it through hot 5% potassium hydroxide solution before

placing it in the hot 5% potassium hydroxide bath. If this pre-wetting was not done, excessive cohesion of the film occurred in the bath.

The temperature was monitored during one of the regrafting runs by means of a thermocouple and recorder. There was a 2°C rise which occurred after 38 hours of irradiation. This temperature increase lasted for 10 hours, after which the temperature returned to ambient.

The tensile strengths of the regrafted films were lower than the specified minimum of 700 psi. The additional exposure to high energy irradiation required for regrafting may have caused some degradation with a resultant reduction in tensile strength.

Infrared absorbance was determined by transmission through the film. In all cases where grafting occurred, infinite absorbance was exhibited in both the 1540 cm^{-1} (carboxyl group) and the 2920 cm^{-1} (methylene group) regions. As a consequence, the ratio of the absorption for these two groups could not be determined.

V. RECOMMENDATIONS

It is recommended that the preparation of a sterilizable battery separator from polyethylene be studied to determine an optimum procedure for its production. The following is a discussion of some of the approaches which should be investigated in this study.

The grafting of divinylbenzene crosslinked polyethylene film which occurs when the film is immersed in an acrylic acid solution and irradiated at normal ambient temperature is obviously diffusion limited. This causes grafting to proceed more rapidly on the surface of the film than in the interior portion. This produces a nonhomogeneous graft.

Increasing the temperature of the grafting solution should increase the swelling of the film and thereby increase the rate of diffusion of the acrylic acid into the film. Also, as the crystalline areas of the film do not graft at room temperature, it will be necessary to raise the temperature to a point where the crystallites disappear if a completely homogeneous graft is to be obtained. A completely homogeneous graft should offer the lowest resistance when immersed in a potassium hydroxide solution.

The use of lower dose rates may also favor grafting over homopolymer formation. If necessary, the total dose can be kept the same

as presently used. Lower dose rates and/or intermittent irradiation should permit the reaction to be less diffusion controlled. These approaches, combined with increased temperature, may produce a superior battery separator material.

It has been reported that irradiation of polyethylene in air to form peroxides and subsequent immersion in grafting solutions can produce homogeneous grafts even in crystalline polyethylene. This approach should also be considered.

Although preliminary experiments using irradiation of the dry film followed by immersion in the grafting solution were unsuccessful, this failure may have been due to the inhibitor present in the acrylic acid or to the fact that the grafting solution was not degassed. Inhibitor removal may be of value with this technique.

The presence of inhibitor in the acrylic acid may be the cause of failure in the first grafting attempt. After the film is washed in potassium hydroxide and given only one rinse in hot water, some potassium hydroxide probably remains on the film. During the re-grafting, this residual alkali may be sufficient to inactivate the small amount of inhibitor present in the acrylic acid. Because of this, either removal of the inhibitor or presoaking of the film in potassium hydroxide before grafting should be investigated. The addition of potassium acrylate or potassium hydroxide to the acrylic acid may accomplish the same result.

The effect of water in the grafting solution and film should also be investigated, as it is known that water will accelerate polymerizations produced by irradiation. This acceleration is due to the ease of free radical formation from water.

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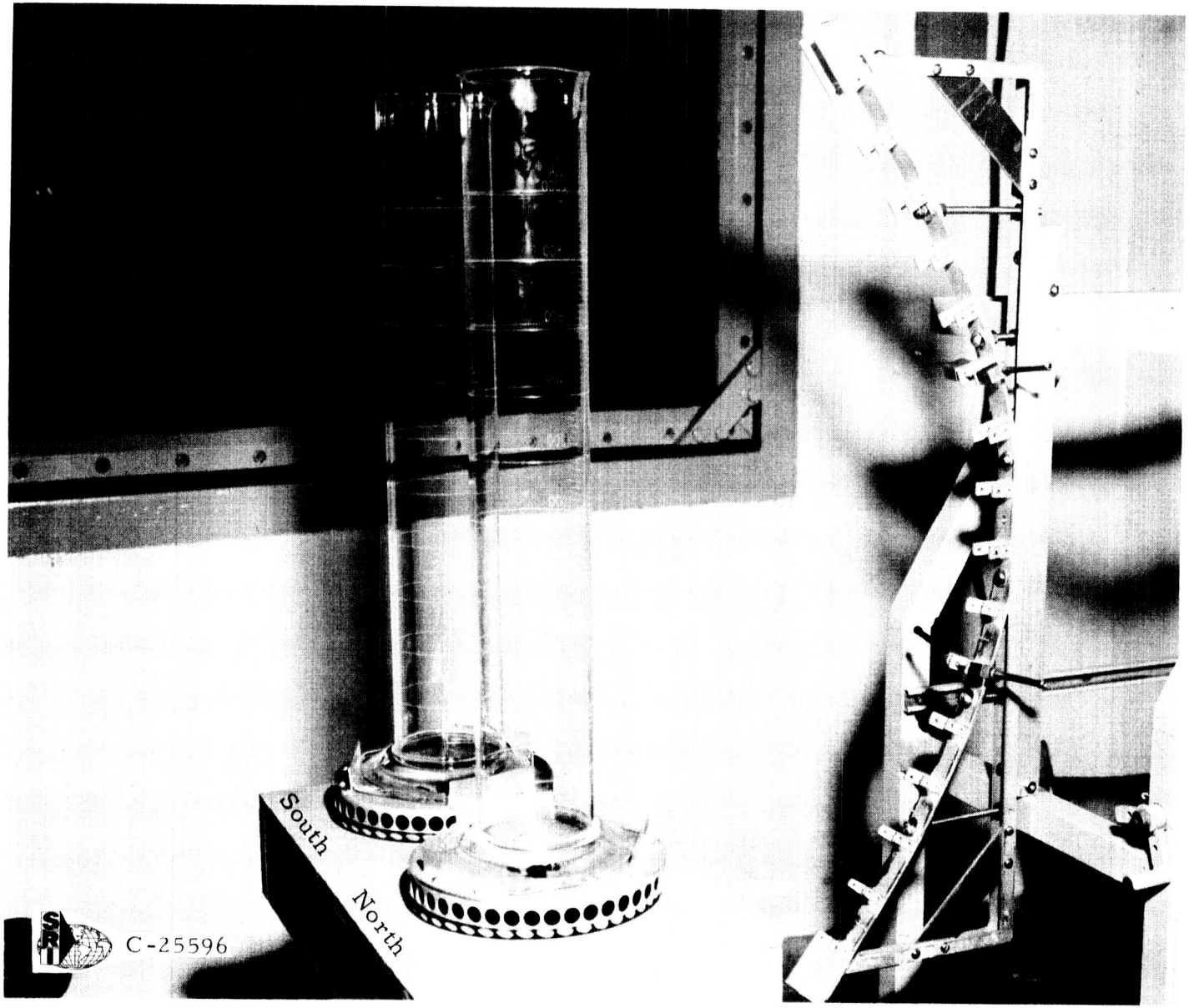

FIGURE 1. RADIATION ASSEMBLY

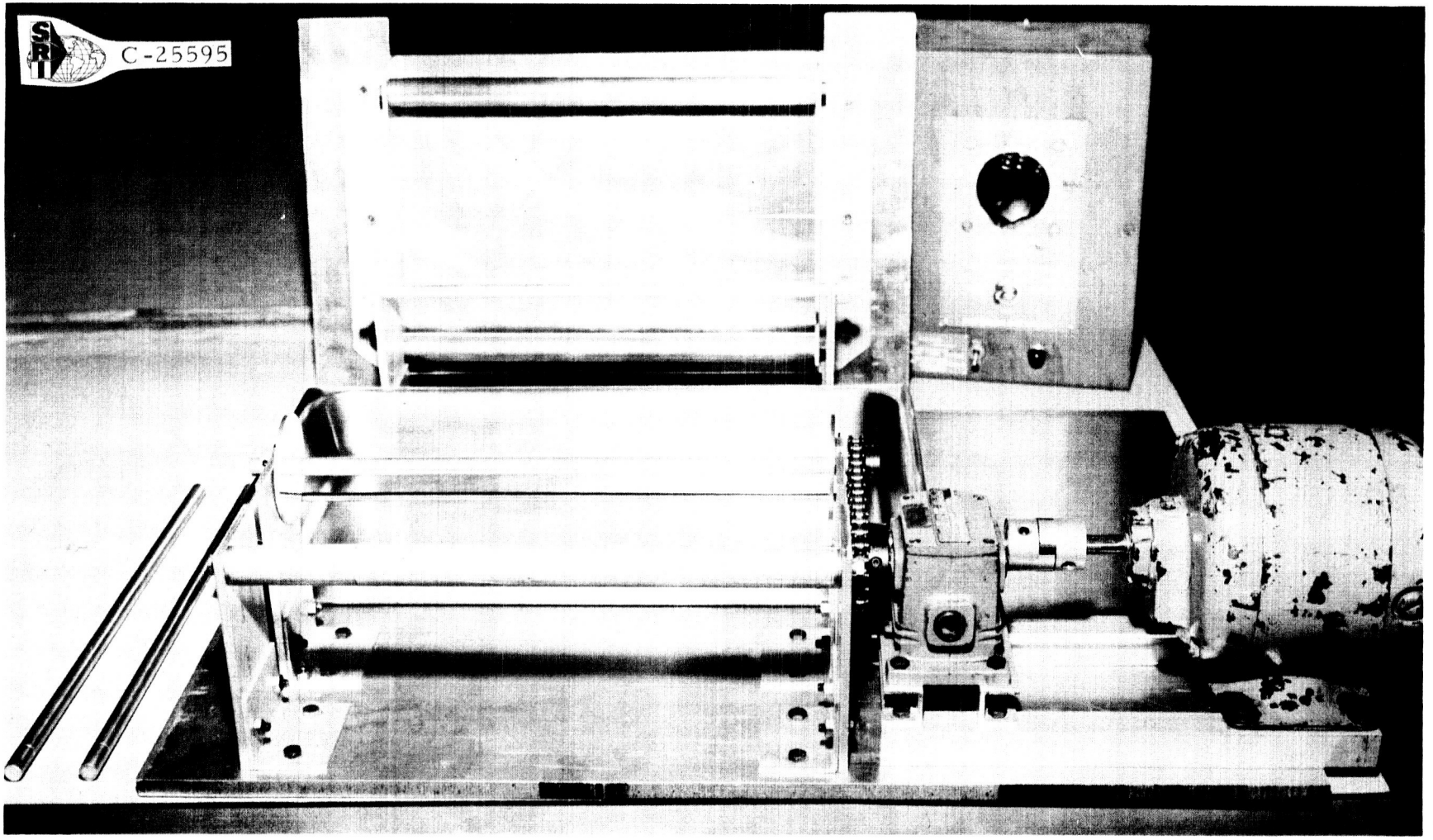

FIGURE 2. FILM ROLLING AND WASHING DEVICE

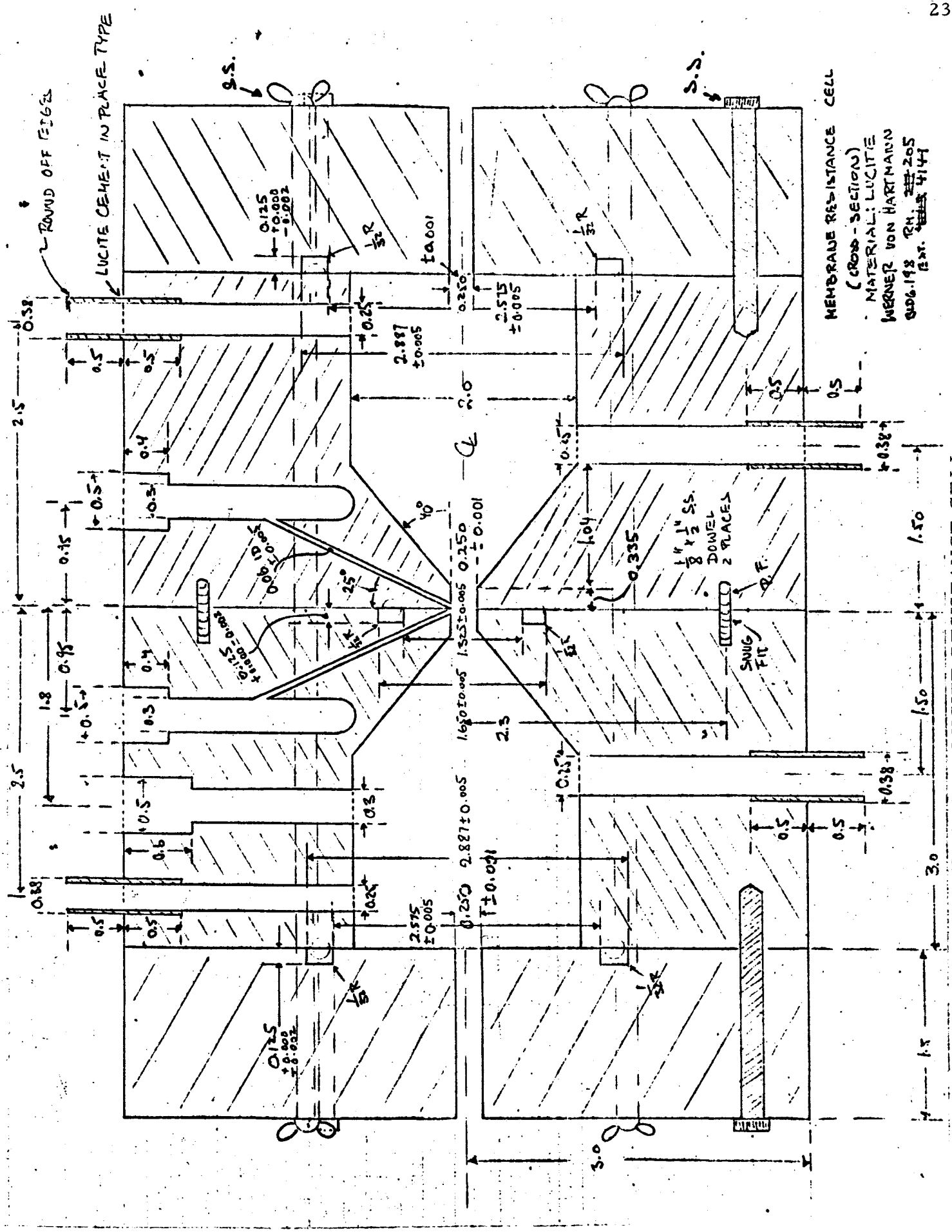

FIGURE 3. LUCITE RESISTANCE CELL

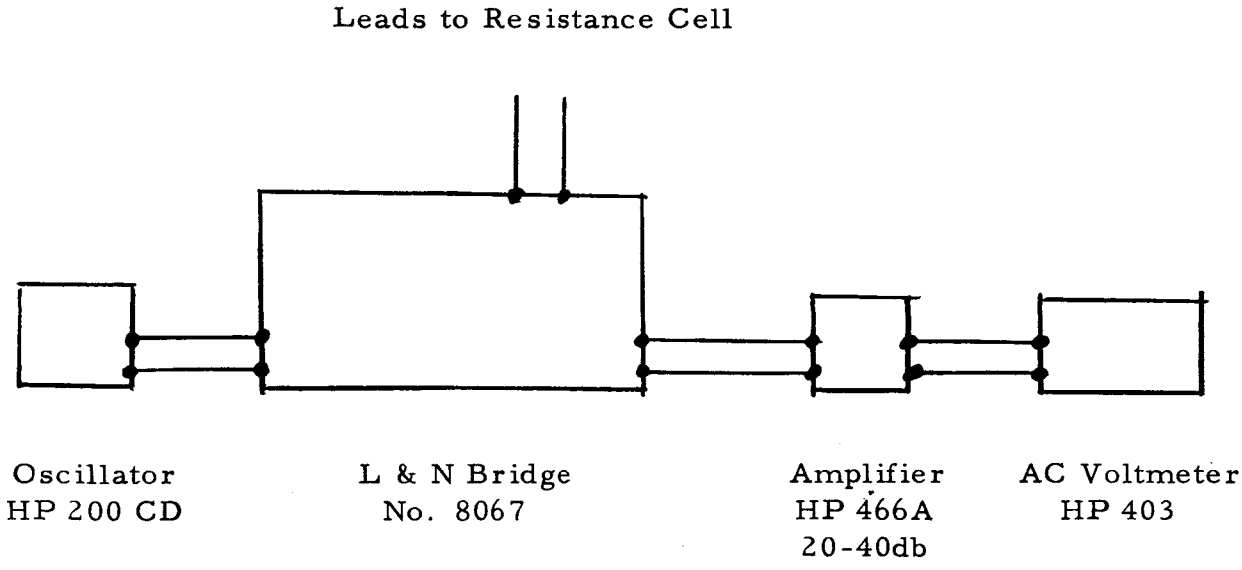

FIGURE 4. RESISTANCE APPARATUS SCHEMATIC

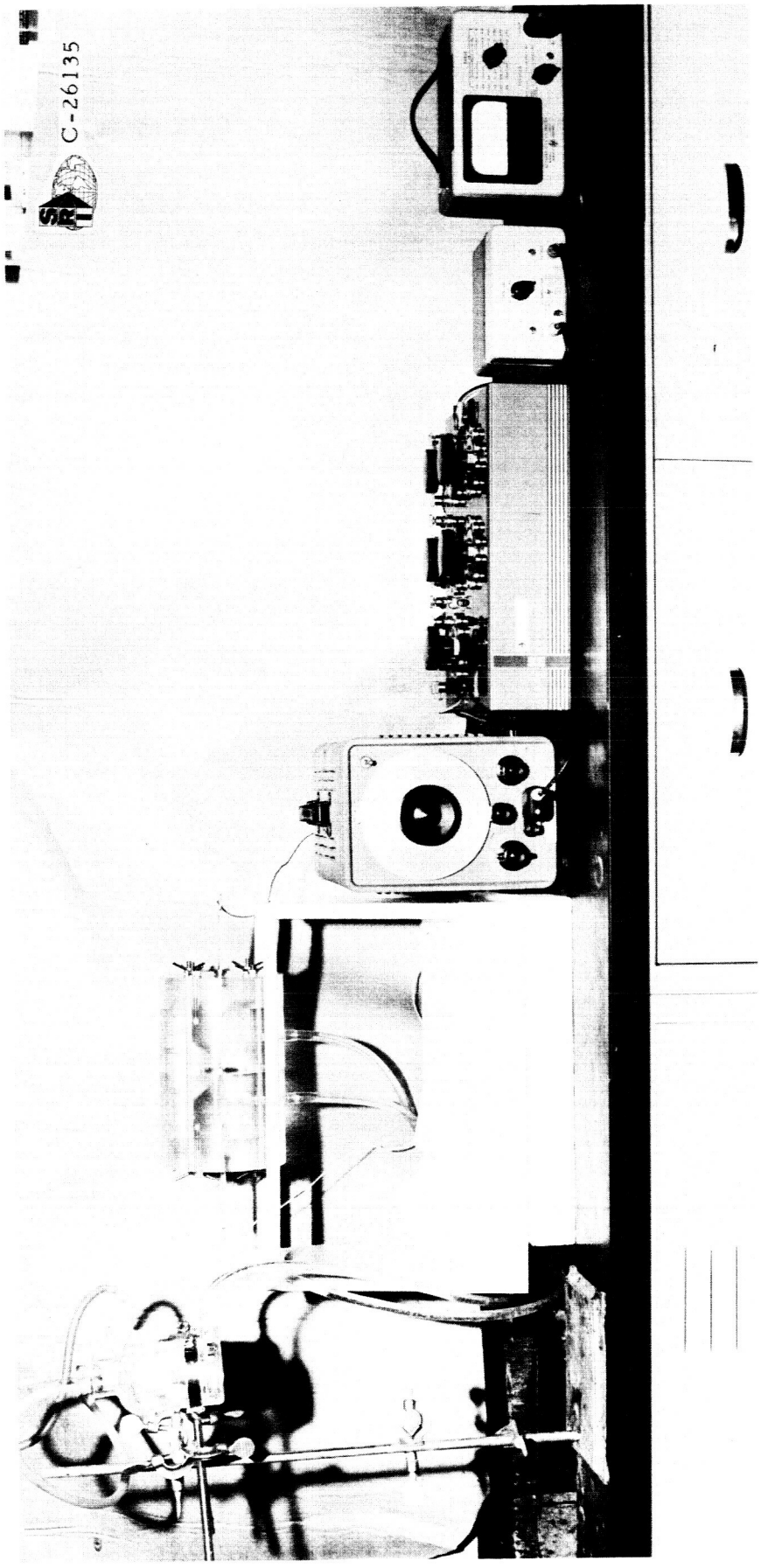

FIGURE 5. RESISTANCE APPARATUS

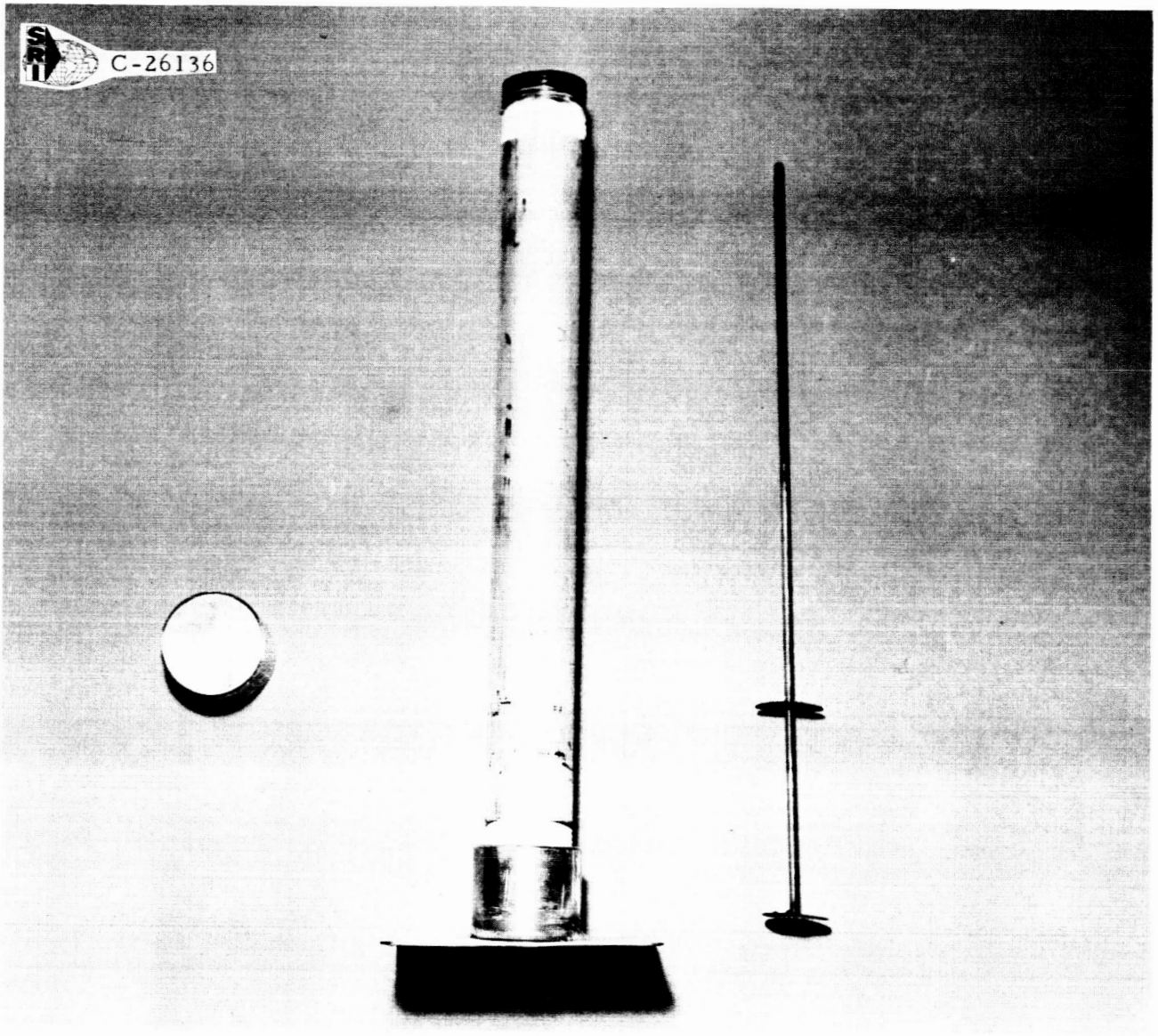

FIGURE 6. STERILIZATION CHAMBER

TABLE 1

QUANTITY OF POLYETHYLENE CROSSLINKED AND GRAFTED

Sample	Quantity Crosslinked, feet	Quantity Grafted, feet	Feet Recovered	Quantity Regrafted, feet	Feet Recovered	Feet Removed for Analysis	Final Product, feet	Time Lapse before 5% KOH wash, hrs
1 North (1 N)	54	46	38	-	-	-	-	72
1 South (1 S)	58	46	38	-	-	-	-	72
2 North (2 N)	51	40	43	-	-	-	-	2
2 South (2 S)	51	40	43	-	-	-	-	2
3 North (3 N)	50	40	43	-	-	-	-	2
3 South (3 S)	50	40	43	-	-	-	-	2
4 North (4 N)	15	15	16	-	-	-	-	2
4 South (4 S)	15	15	16	-	-	-	-	2
2 North Inner (2 NI)	-	-	-	16	17	-	17	2
2 South Inner (2 SI)*	-	-	-	23	18	3	15	2
2 North Outer (2 NO)*	-	-	-	23	25.5	2	23.5	72
2 South Outer (2 SO)	-	-	-	15.5	16.5	-	16.5	72
3 North Inner (3 NI)*	-	-	-	21	25	2	23	24
3 South Inner (3 SI)	-	-	-	20	25	-	25	24
3 North Outer (3 NO)	-	-	-	20	11	-	11	72
3 South Outer (3 SO)*	-	-	-	20	12	2	11	72
3 North Outer/ 3 South Outer (3 NO/3 SO)	-	-	-	-	17	-	17	72
4 North (4 N)*	-	-	-	16	19	2	17	48
4 South (4 S)	-	-	-	16	19	-	19	48

* Samples removed for sterilization and analysis

TABLE 2

PROPERTIES OF FILMS SHIPPED TO SPONSOR

Sample	Thickness, mils: Before Sterilization, Dry	Thickness, mils: Before Sterilization, Wet	Thickness, mils: After Sterilization*, Wet	Resistance, milliohm-in^2 at 25.4°C After Sterilization*	Tensile Strength*, psi
2 SI-0, 1	1.0	1.2	1.9	76	520
	1.0	1.1	1.9	194	570
2 SI-0, 2	1.1	1.1	1.9	2960	580
	1.0	1.1	1.9	>3000	710
2 SI-1, 3	1.0	1.0	1.8	>3000	514
	1.0	1.0	1.8	>3000	770
2 SI-1, 4	1.0	1.0	1.9	>3000	426
	1.0	1.1	1.9	821	482
2 SI-2, 5	1.0	1.2	1.9	>3000	578
	1.0	1.2	1.8	-	484
2 SI-2, 6	1.0	1.1	1.9	>3000	610
	1.0	1.2	1.7	>3000	715
2 NO-0, 1	1.4	1.5	1.9	1	610
	1.4	1.5	1.8	-	545
2 NO-0, 2	1.7	1.7	1.9	15	475
	1.4	1.6	2.0	2	303
2 NO-1, 3	1.2	1.5	2.0	24	980
	1.2	1.5	2.2	40	447
2 NO-1, 4	1.2	1.4	2.0	7	413
	1.3	1.5	2.0	14	680
3 NI-0, 5	1.2	1.3	2.1	11	468
	1.3	1.9	2.1	-	413
3 NI-0, 6	1.3	1.4	2.0	12	435
	1.5	1.6	2.0	-	260

TABLE 2

PROPERTIES OF FILMS SHIPPED TO SPONSOR (Cont'd)

Sample	Thickness, mils: Before Sterilization, Dry	Thickness, mils: Before Sterilization, Wet	Thickness, mils: After Sterilization*, Wet	Resistance, milliohm-in^2 at 25.4°C After Sterilization*	Tensile Strength*, psi
3 NI-1, 7	1.3	1.5	2.0	19	868
	1.2	1.5	2.0	22	840
3 NI-1, 8	1.2	1.5	2.1	47	385
	1.3	1.5	2.0	12	385
3 SO-0, 1	1.3	2.0	2.0	6	507
	1.7	1.8	1.9	7	364
3 SO-0, 2	1.4	1.7	1.8	1	520
	1.4	1.6	1.8	2	508
3 SO-1, 3	1.1	1.3	1.4	11	570
	1.1	1.5	1.7	9	389
3 SO-1, 4	1.4	1.8	1.8	7	718
	1.3	1.8	1.8	8	480
3 N-0, 5	1.5	2.1	2.0	5	421
	1.6	2.0	2.0	6	324
4 N-0, 6	1.3	2.0	1.9	8	-
	1.4	2.0	2.0	16	580
4 N-1, 7	1.3	1.5	1.7	18	388
	1.2	1.7	1.4	19	785
4 N-1, 8	1.3	1.5	1.9	14	695
	1.3	1.5	1.7	18	600

* 36 hours at 145°C in 40 wt % KOH.
The last digit in sample number identifies the sterilization chamber.

TABLE 3

SOLUTION COMPOSITIONS AND DOSE RATES

Crosslinking Solution Volume %	Dose Rate, Mrads/hr	Total Dose Rate, Mrads	Grafting Solution Weight %	Dose Rate, Mrads/hr	Total Dose Rate, Mrads
1.0 Divinylbenzene	0.025	0.55	25.0 Glacial Acrylic Acid	0.021	2.860
1.0 Benzene			70.0 Benzene		
98.0 Methanol			5.0 Carbon tetrachloride		

CHEMICAL SUPPLIERS

Chemical	Grade	Supplier
Divinylbenzene	Practical	Matheson Coleman & Bell
Benzene	1 degree nitration	Texas Solvents & Chem. Co.
Methanol	Histological	Fisher Scientific Co.
Glacial acrylic acid	--	Rohm & Haas
Carbon tetrachloride	Reagent	J. T. Baker Chem. Co.
Potassium hydroxide	Reagent	J. T. Baker Chem. Co.
Polyethylene film	---	Supplied by JPL
Separator paper	---	Supplied by JPL

TABLE 4

RESISTANCE MEASUREMENTS BEFORE STERILIZATION

Sample	Thickness, mils	Resistance milliohms-in^2 at 25.4°C
JPL**	1.4	12
JPL**	1.2	20
1 N	1.0	>3000
1 S	1.0	>3000
2 N	1.1	900
2 S	1.1	2200
3 N	1.0	600
3 S	1.0	601
4 N	1.0	>3000
4 S	0.9	>3000
2 N*	1.2	359
	1.1	1240
	1.1	2750
	1.3	1180
	1.2	>3000
2 SI*	-	7
	-	41
2 NI*	-	36
	-	17
2 SI*	-	47
	-	210
	-	2650
	-	>3000
2 NI*	-	165
	-	404
	-	54
	-	86
	-	34

TABLE 4 (Continued)

RESISTANCE MEASUREMENTS BEFORE STERILIZATION

Sample	Thickness, mils	Resistance milliohms-in^2 at 25.4°C
2 NO*	-	9
	-	57
	-	58
2 SO*	1.1	77
	1.2	9
	1.1	9
3 NI*	-	11
	-	12
	-	10
3 SI*	1.1	>3000
	1.1	11
	1.1	17
3 NO*	1.2	7
	1.3	11
	1.5	52
3 SO	-	1
4 N (regrafted)	-	16
4 S (regrafted)	-	3

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* Samples taken from top to bottom of film

** Sample supplied by Sponsor

TABLE 5

DIMENSIONAL ANALYSIS OF SAMPLES BEFORE AND AFTER STERILIZATION

	Weight, mg			Width, inches			Length, inches		
	Before Sterilization		After Sterilization	Before Sterilization		After Sterilization	Before Sterilization		After Sterilization
Sample	Dry	Wet**	Wet*	Dry	Wet**	Wet*	Dry	Wet**	Wet*
2 SI-0,1	42.0	58.7	55.9	0.38	0.40	0.38	6.00	6.28	5.96
	39.0	55.0	51.2	0.38	0.38	0.36	6.00	6.22	5.90
2 SI-0,2	37.4	50.3	47.7	0.38	0.38	0.38	5.96	6.20	5.82
	35.5	54.0	44.9	0.38	0.38	0.36	5.94	6.10	5.74
2 SI-1,3	33.5	45.5	45.7	0.36	0.36	0.38	5.84	6.08	5.76
	33.2	45.4	41.1	0.36	0.36	0.38	6.00	6.24	5.90
2 SI-1,4	34.4	48.3	45.2	0.36	0.36	0.38	6.00	6.24	5.90
	34.8	47.5	45.7	0.36	0.36	0.36	6.00	6.22	5.86
2 SI-2,5	41.0	55.6	57.0	0.36	0.38	0.38	6.00	6.36	6.00
	39.0	50.2	58.0	0.36	0.38	0.38	6.40	6.26	5.86
2 SI-2,6	37.3	49.4	52.5	0.36	0.36	0.38	6.00	6.14	5.72
	35.8	45.6	50.5	0.36	0.36	0.38	5.96	6.14	5.68
2 NO-0,1	58.8	96.7	83.4	0.36	0.40	0.38	6.00	6.30	6.04
	60.9	93.6	84.7	0.38	0.38	0.38	6.00	6.34	6.06
2 NO-0,2	61.6	94.2	97.4	0.38	0.40	0.44	6.00	6.30	6.04
	60.5	92.9	98.4	0.38	0.40	0.40	6.02	6.26	6.00
2 NO-1,3	56.5	86.5	99.1	0.38	0.40	0.38	5.98	6.44	6.06
	56.8	88.7	88.9	0.38	0.40	0.38	5.94	6.42	6.00
2 NO-1,4	54.6	87.8	83.4	0.36	0.40	0.40	5.96	6.44	6.14
	59.2	91.1	90.1	0.38	0.40	0.42	6.00	6.52	6.14
3 NI-0,5	46.4	69.0	84.8	0.36	0.38	0.36	6.00	6.16	5.94
	55.3	79.8	70.7	0.36	0.38	0.36	6.08	6.42	6.30
3 NI-0,6	55.2	90.6	84.7	0.38	0.40	0.38	5.94	6.52	6.58
	60.5	100.3	95.7	0.38	0.40	0.38	5.94	6.52	6.58

TABLE 5

DIMENSIONAL ANALYSIS OF SAMPLES BEFORE AND AFTER STERILIZATION (Cont'd)

	Weight, mg			Width, inches			Length, inches		
	Before Sterilization		After Sterilization	Before Sterilization		After Sterilization	Before Sterilization		After Sterilization
Sample	Dry	Wet**	Wet*	Dry	Wet**	Wet*	Dry	Wet**	Wet*
3 NI-1, 7	55.4	83.6	82.5	0.38	0.38	0.38	5.96	6.34	6.08
	55.2	76.8	73.5	0.38	0.38	0.38	6.02	6.32	6.00
3 NI-1, 8	51.7	76.6	84.0	0.38	0.36	0.38	5.94	6.42	6.10
	55.2	85.9	89.1	0.38	0.38	0.38	6.04	6.42	6.10
3 SO-0, 1	58.5	60.9	98.4	0.38	0.40	0.38	6.00	6.56	6.04
	56.5	147.2	102.1	0.38	0.40	0.38	6.04	6.46	6.08
3 SO-0, 2	55.5	93.8	101.4	0.34	0.40	0.40	5.88	6.40	6.06
	56.1	96.0	96.0	0.34	0.40	0.42	5.98	6.50	6.16
3 SO-1, 3	44.1	71.7	72.5	0.36	0.40	0.40	6.04	6.54	6.02
	52.0	86.8	85.2	0.34	0.38	0.40	5.92	6.54	6.34
3 SO-1, 4	54.0	95.0	97.3	0.36	0.40	0.40	5.94	6.54	6.34
	55.0	94.9	89.9	0.36	0.40	0.42	6.02	6.60	6.30
4 N-0, 5	50.0	94.8	88.6	0.28	0.34	0.34	5.08	5.66	5.32
	48.8	96.6	91.9	0.30	0.38	0.34	5.10	5.86	5.48
4 N-0, 6	-	67.7	59.9	-	0.36	0.34	-	3.98	3.32
	50.0	110.5	103.8	0.32	0.40	0.36	5.50	6.34	5.92
4 N-1, 7	51.5	87.5	79.1	0.36	0.40	0.40	6.00	6.54	6.18
	51.4	84.7	77.5	0.36	0.40	0.40	5.94	6.56	6.18
4 N-1, 8	52.8	95.8	85.5	0.36	0.40	0.40	6.00	6.76	6.20
	52.1	82.6	78.6	0.36	0.42	0.40	5.96	6.50	6.14

* 36 hours at 145°C in 40 wt% KOH

** 19 hours in 40 wt % KOH at room temperature

APPENDIX A

NOMENCLATURE

NOMENCLATURE

Sample Nomenclature

Film samples that were removed for sterilization were staggered so that the analysis of each roll would be indicative of the entire width of the roll.

In order to trace these samples which were removed for sterilization, the following nomenclature was employed:

The sample rolls to be irradiated were placed on the turntables in positions labeled North and South, as shown in Figure 1. The numerical prefix before North and South, as shown in Table 1, designates the run number. Each sample which was regrafted (with the exception of 4 North and 4 South) was divided in half and the suffix Outer (O) and Inner (I) added, as shown in Table 2. The Inner (I) represents the inner half of the roll. The Outer (O) represents the outer half of the roll. It will be noted that sample rolls 4 North and 4 South do not carry the Outer and Inner designations.

The fourth term represents the position from which samples were removed for sterilization and analysis. This position designation refers to the longitudinal location along the roll as well as the location with respect to the width of the roll. The zero (0) represents the upper half of the inner end of the roll, and one (1)

represents the lower half of the outer end of the roll. One exception to this sterilized sample designation appears below, under 2-South Inner.

The fifth term, appearing only in sterilized sample designations, indicates the specific sterilization chamber which was used. Designations of samples shipped to the Sponsor are shown below.

2-North Inner (2 NI) - No analysis. See counterpart 2 NO.

2-North Outer (2 NO) - Two one-foot samples removed for analysis.
Sample labeled 2 NO-0, removed from inner end (next to aluminum rod).
Sample labeled 2 NO-1, removed from outer end of roll.

2-South Inner (2 SI) - Three one-foot samples removed for analysis.
Sample labeled 2 SI-0, removed from inner end (next to aluminum rod), upper one-third of film.
Sample labeled 2 SI-1, removed ten feet from inner end, middle one-third of film.
Sample labeled 2 SI-2, removed from outer end of roll, bottom one-third of film.

2-South Outer (2 SO) - No analysis. See counterpart 2 SI.

3-North Inner (3 NI) - Two one-foot samples removed for analysis.
Sample labeled 2 NI-0, removed from inner end (next to aluminum rod).
Sample labeled 2 NI-1, removed seventeen feet from inner end.

3-North Outer (3 NO) - No analysis. See counterpart 3 NI.

3-South Inner (3 SI) - No analysis. See counterpart 3 SO.

3-South Outer (3 SO) - Two one-foot samples removed for analysis.
Sample labeled 3 SO-0, removed from inner end (next to aluminum rod).
Sample labeled 3 SO-1, removed from outer end of roll.

3-North Outer/3 South Outer (3 NO/3 SO) - Unidentified portions of 3 NO/3 SO.

4-North (4 N) - Two one-foot samples removed for analysis.
Sample labeled 4 N-0, removed from inner end (next to aluminum rod).
Sample labeled 4 N-1, removed from outer end of roll.

4-South (4 S) - No analysis. See counterpart 4 N.

APPENDIX B

JPL ADVANCED DEVELOPMENT

ENGINEERING NOTE

No. 342011

EXHIBIT I TO PURCHASE ORDER NO. CA-384805

C O P Y

JPL ADVANCED DEVELOPMENT

Dated: 11/1/65
Revised: 12/8/65

ENGINEERING NOTE

No. 342011

FABRICATION OF BATTERY SEPARATOR MATERIAL FROM MODIFIED POLYETHYLENE

1.0 Purpose

This document describes the procedure for the fabrication of modified polyethylene to be used as a separator material for a heat sterilizable battery.

2.0 Scope

This document includes an extract of a report describing the preparation of small quantities of the desired separator material. It will be incumbent upon the user of the procedure to scale the quantities to the desired levels.

3.0 Procedure

The general preparative procedure for small quantities is as follows:

3.1 A 30-foot strip of uncrosslinked polyethylene film is rolled into a helix with a strip of absorbent paper toweling.

3.2 A glass test tube 6.7 cm. in diameter and 46 cm. high is filled with 1,000 cc. of a solution of divinylbenzene in methanol.

3.3 The roll is immersed in the test tube and allowed to equilibrate for 24 hours.

3.4 Next, the test tube is placed on a rotating platform in a Cobalt-60 source for the appropriate period of time.

3.5 The test tube is then removed from the source, the sample unrolled, and the paper discarded.

3.0 Procedure (Continued)

3.6 The film is rinsed with benzene for a resident time of about 30 sec. and rerolled in fresh paper toweling.

3.7 A test tube is then filled with 1,000 cc. of an acrylic acid-benzene solution and the roll immersed therein for 24 hours.

3.8 The test tube is then irradiated again in the Cobalt-60 source.

3.9 Next, the sample is removed; washed in 5% KOH at 80°C for 1 hour, then washed in water at 80°C for 1 hour and then dried in paper toweling.

C
O
P
Y

TABLE 1

Solution concentrations, doses and dose rates are listed below:

Crosslinking Solution	Dose Rate (Mrads/hr)	Total Dose (Mrads)	Grafting Solution	Dose Rate (Mrads/hr)	Total Dose (Mrads)	Base Polymer Density
1.0% DVB 1.0% Benzene 98% Methanol	0.025	0.55	25% Acrylic Acid 70% Benzene 5% CCl_4	0.021	1.430	0.917

TABLE 2

Divinylbenzene	Cat. No. DX2403 - Metro Scientific, Inc., Carle Place, Long Island, New York
Methanol	Cat. No. A-411 - Fisher Scientific Co., Fairlawn, New Jersey
Benzene	1° Nitration Grade - Peerless Oil & Chemical Co., Long Island, New York
Acrylic Acid	Glacial Acrylic Acid - Rohm & Haas Co., Philadelphia, Pa.
Carbon Tetrachloride	Reagent Grade Cat. No. C-187 - Fisher Scientific Co., Fairlawn, New Jersey
Sterilization Chambers	304 Stainless Steel Pipe Nipple, 12" long, 3" diameter, threaded on both ends; 304 Stainless Steel Cap for 3" I.D. pipe - 150 lb. class.

It is not required that the materials be obtained from the suppliers which are listed. However, it is necessary that equivalent materials be used.

C
O
P
Y

WIRE

Southwest Research Institute
Attention: Dr. John T. Goodwin
Subject: Purchase Order CA 384805.

April 6, 1966

As a result of recent conversations, we are considering changing the subject purchase order as follows:

1. In the engineering Note 342011, after paragraph 3.9, ADD...

> "Paragraphs 3.7 through 3.9 may be repeated once if the Specifications of A.2.1 in the Statement of Work cannot be satisfied by a single grafting."

2. In the Statement of Work ADD to the first paragraph the following sentence...

> "Absorbent paper toweling to be used in the JPL process shall be furnished by JPL."

3. DELETE paragraph a.1.II., and REPLACE it by the following sentence...

> "Measurements on the material shall be performed in a manner that assures uniformity."

4. After paragraph E.1., ADD the following phrase as paragraph E.2. ...

> "...absorbent paper toweling in quantities as needed."

5. In paragraph a.2.V.A., DELETE the sentence...

> "This cycle shall be repeated two (2) additional times."

Change the last sentence to read...

> "At the end of the cycle, the samples shall be removed and tested in accordance with paragraphs A.2.I. through III."

WIRE (Continued)

6. The period of performance will be extended by 45 days.

It is my understanding that the above will have no effect on the existing purchase order price. Please confirm this and advise if the above changes are agreeable with you.

/s/ H. E. Patterson
Senior Contract Negotiator
Jet Propulsion Lab.

C
O
P
Y

APPENDIX C

HIGH-LEVEL RADIATION EFFECTS FACILITY

HIGH-LEVEL RADIATION EFFECTS FACILITY

INTRODUCTION

Southwest Research Institute has available two "hot" cells for radiation effects research and development. This facility is located in the Aerospace Propulsion Research building and available to assist government and industry in research programs that require high-intensity Cobalt-60 irradiation or studies of post-irradiation effects. The cells were designed to handle 100,000 curies of Cobalt-60; additional shielding will permit the installation to house 1,000,000 curies of Cobalt-60. With minor modifications and additions the laboratory can also accommodate research programs utilizing gaseous or liquid radioisotopes and contaminated or contaminating materials.

DESCRIPTION OF EXISTING FACILITY

Figure 1 is a photograph of the front of the two hot cells. Figures 3 - 6 show details of construction of the cells. Each cell is 9 feet by 15 feet in floor plan with a 13 foot high ceiling. Entrance to each is through a hydraulically operated eight-ton magnetite concrete access door 3'0" wide by 6'4" high. The doors are lowered into a floor well to eliminate the psychological hazard of walking beneath a large suspended weight. A left rod in the center of each door opening leaves sufficient opening

for passage of personnel; when equipment is moved in or out of the cell, the left rod is unthreaded within a few minutes and withdrawn into the walls.

In front of the hot cells is a working area of 1000 square feet for the preparation of unirradiated specimens and for test equipment to be used in conjunction with the hot cells.

The cobalt is stored in the wall between the cells (Figure 6) and can be transported into either or both cells for irradiation of test materials. The cobalt storage room is approximately a four-foot cube. The doors for closing off the cobalt storage area are constructed of the same material as the access doors. They are also hydraulically moved, but they rise when opened instead of dropping into the floor. The cobalt is transported on two steel dollies guided by tracks in the floor. The movements of the dollies and the doors are, of course, remotely controlled and electrically interlocked for safety.

The operators' wall consists of 42 inches of magnetite concrete (244 lbs/ft^3), and will provide operational shielding with a million-curie source. The viewing windows (Figure 2), one to each cell, are conventional zinc bromide construction with three inches of nonbrowning glass on the source side, 37 inches of optical-grade zinc bromide, and two inches of laminated plate glass on the viewer's side. The window on the source side is 48 inches wide by 42 inches high, and on the

operators' side it is 48 inches wide by 22 inches high. These windows are two of the largest ever built and offer a superb undistorted view of the cell area.

A special pair of Central Research Laboratory Model 8 manipulators are available for operation in either cell (Figure 2). These manipulators have a 45-inch "Z" travel and a longer arm in the hot cell than on the operator's side. Motorized side and forward separation are built into these manipulators to facilitate operations in front of the viewing window.

In addition to the manipulator holes above the viewing window, two additional holes are installed in the wall to the side of and above the viewing window to allow the manipulators to be relocated. An "A" frame is used to relocate the manipulators. This operation takes about ten minutes. Relocation allows the movement of the manipulators to cover the entire cell area. Adequate access holes for utilities, pressure connections, instrumentation, and electrical leads are provided near the floor line and just below the ceiling line. The utility and instrumentation leads pass through corkscrew-shaped conduits encased in plugs of high density material. This eliminates line-of-sight radiation through the utility connections. Figure 6 shows the location of the manipulator holes and utility access holes. One of the cells is equipped with a motorized chain hoist for lifting heavy objects.

Each cell is ventilated with a complete change of air every minute. A high quality commercial air filter is used on the inlet side, and on the outlet side an identical air filter is used ahead of a Cambridge absolute air filter. A blower is located on the suction side to keep the cell itself at a negative pressure. This insures that in the event of some catastrophic accident in the cell, cobalt dust could not spread to the personnel area.

Each cell is equipped with a high-level radiation monitor. The radiation monitors are interlocked with the access doors for safety protection of the personnel operating the caves. In addition, there are two radiation monitors in the preparation room.

A pit is provided in the floor of one of the cells for temporary disposal of radioactive wastes.

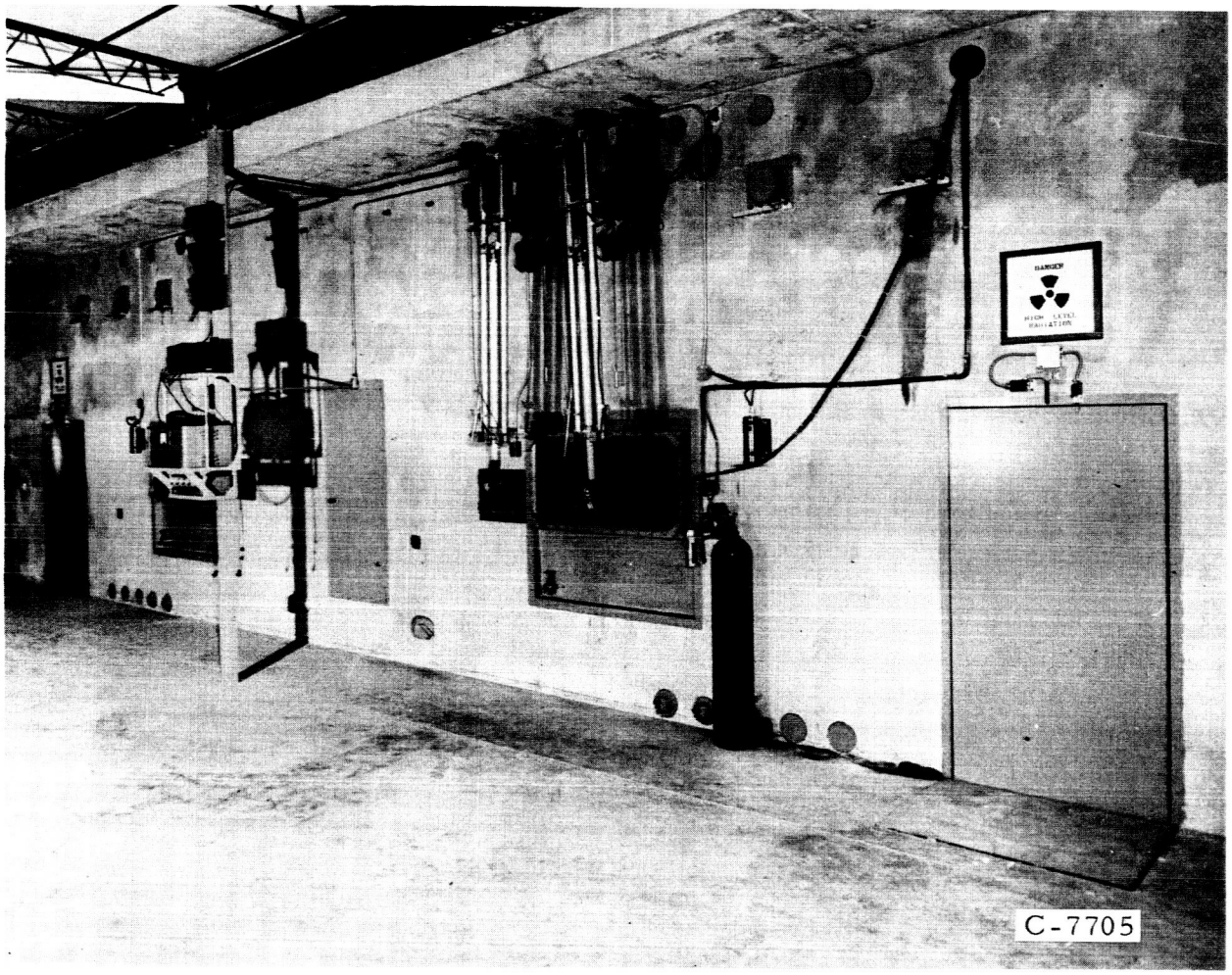


FIGURE 1. FRONT VIEW OF HOT CELLS

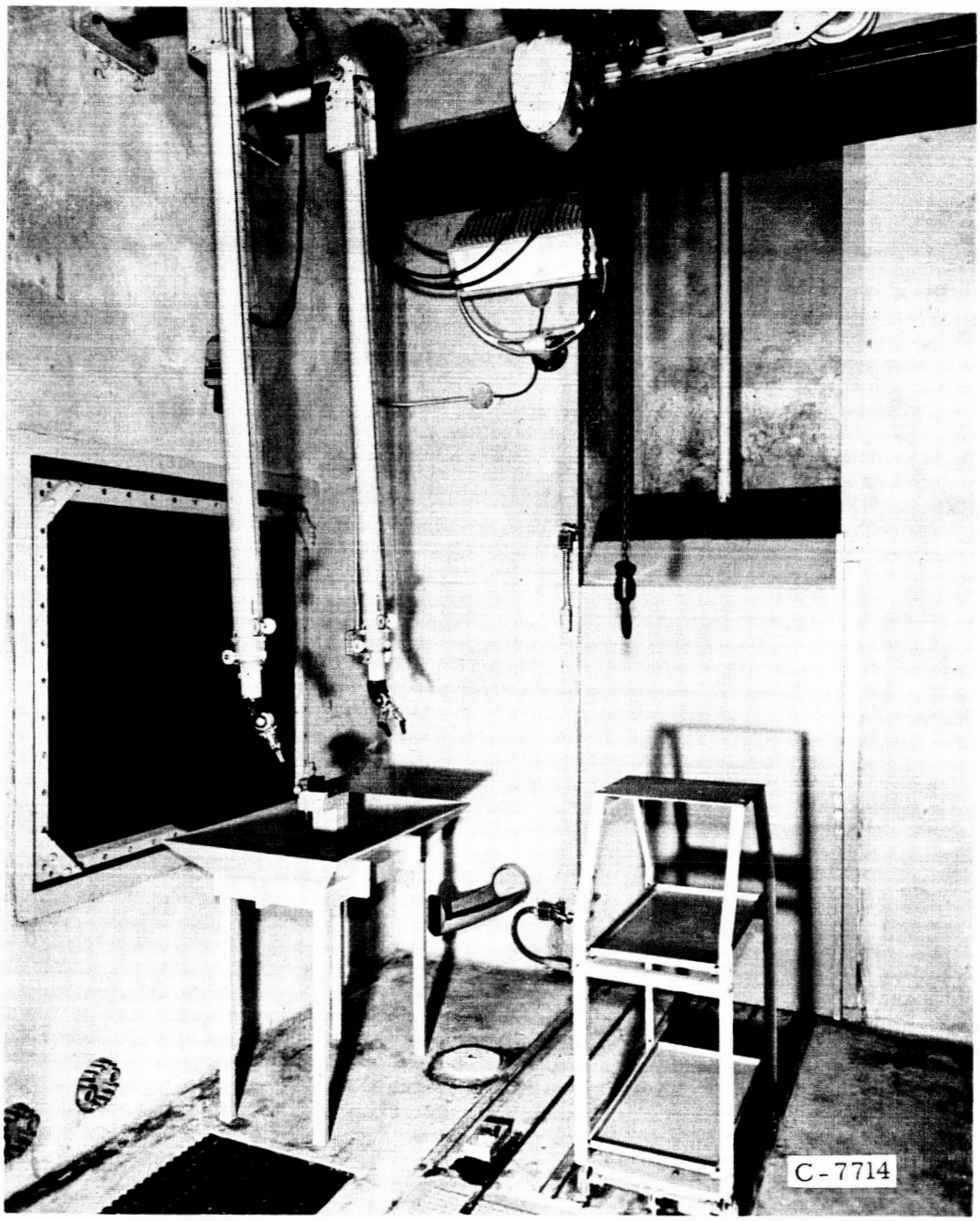
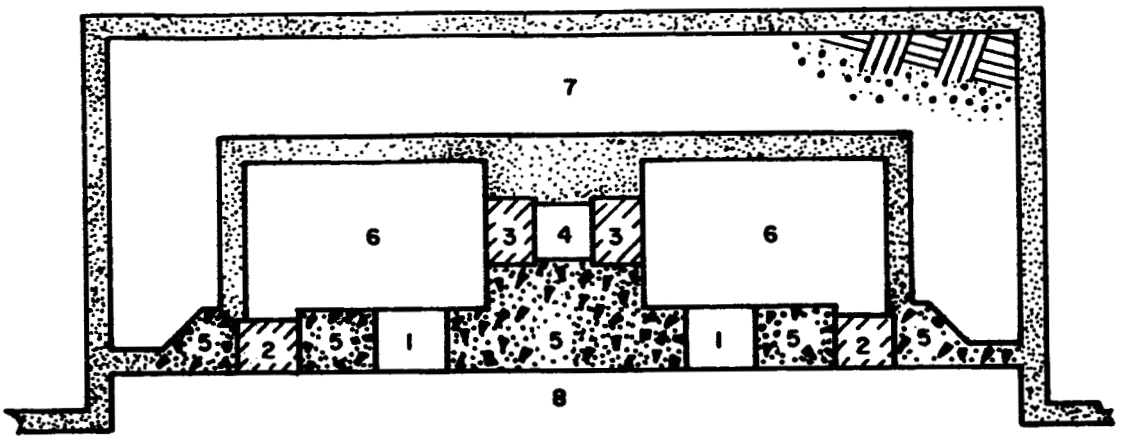


FIGURE 2. INTERIOR OF RIGHT HAND CELL



1. ZINC BROMIDE WINDOW
2. ACCESS DOORS (CAST IRON CHIP)
3. STORAGE DOORS (CAST IRON CHIP)
4. COBALT STORAGE AREA
5. MAGNETITE ORE CONCRETE, FRONT WALL
6. EXPOSURE CELL
7. EARTH FILL
8. OPERATING AREA

FIGURE 3. PLAN VIEW OF CELLS

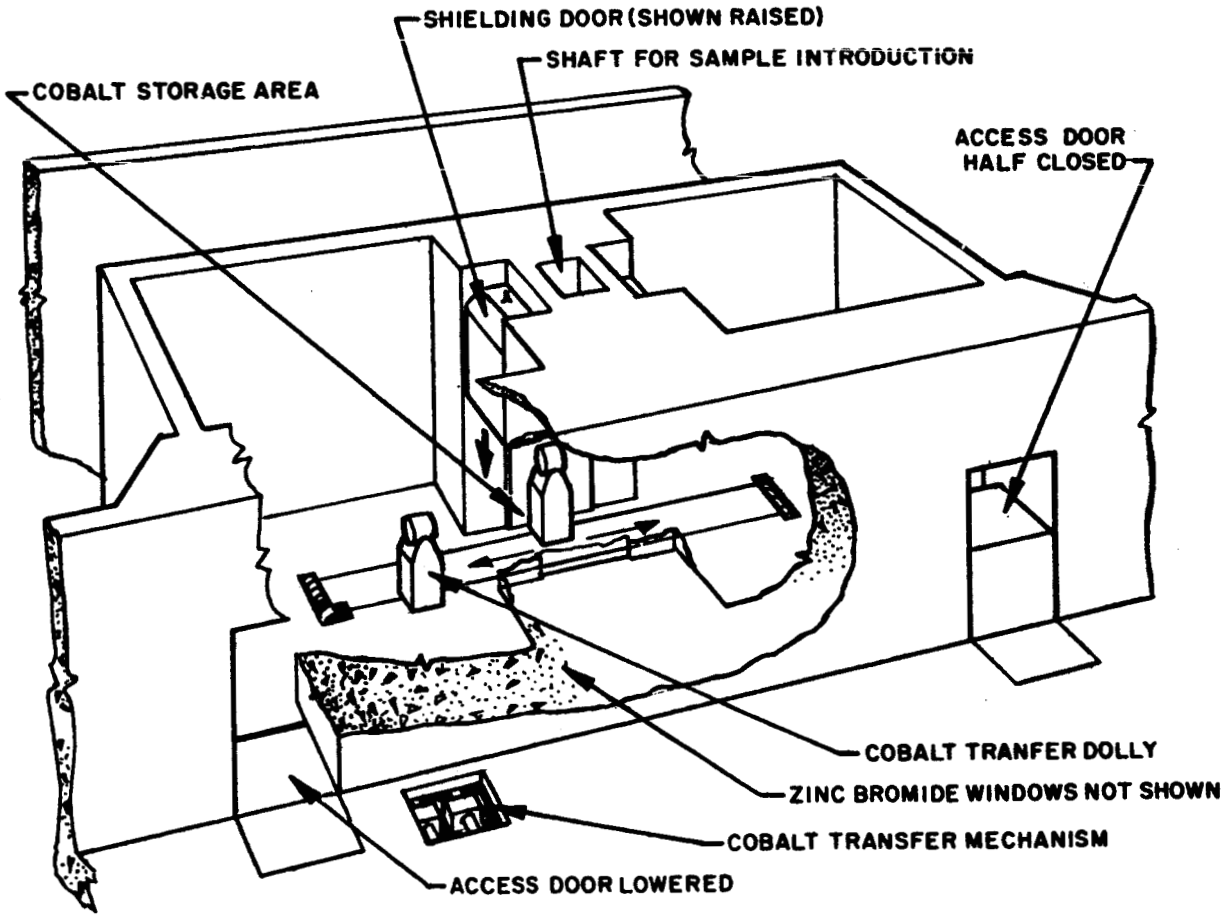


FIGURE 4. PERSPECTIVE OF CELL ARRANGEMENT

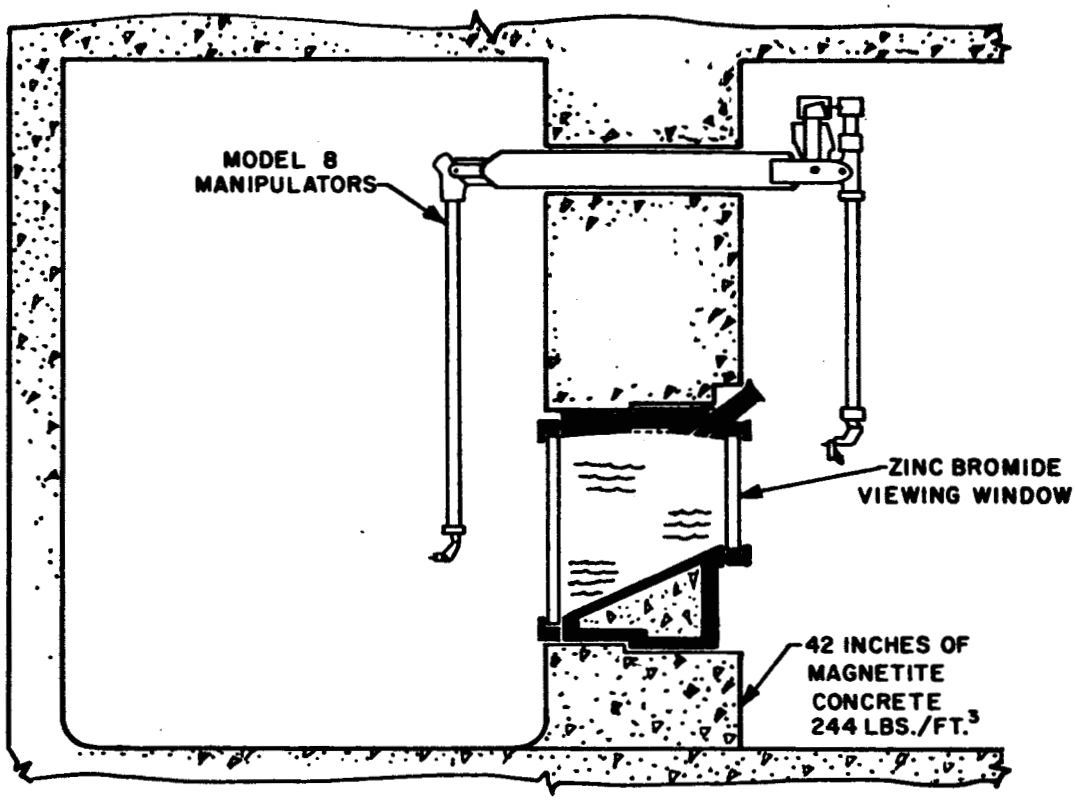


FIGURE 5. SECTION THROUGH CELL WALL

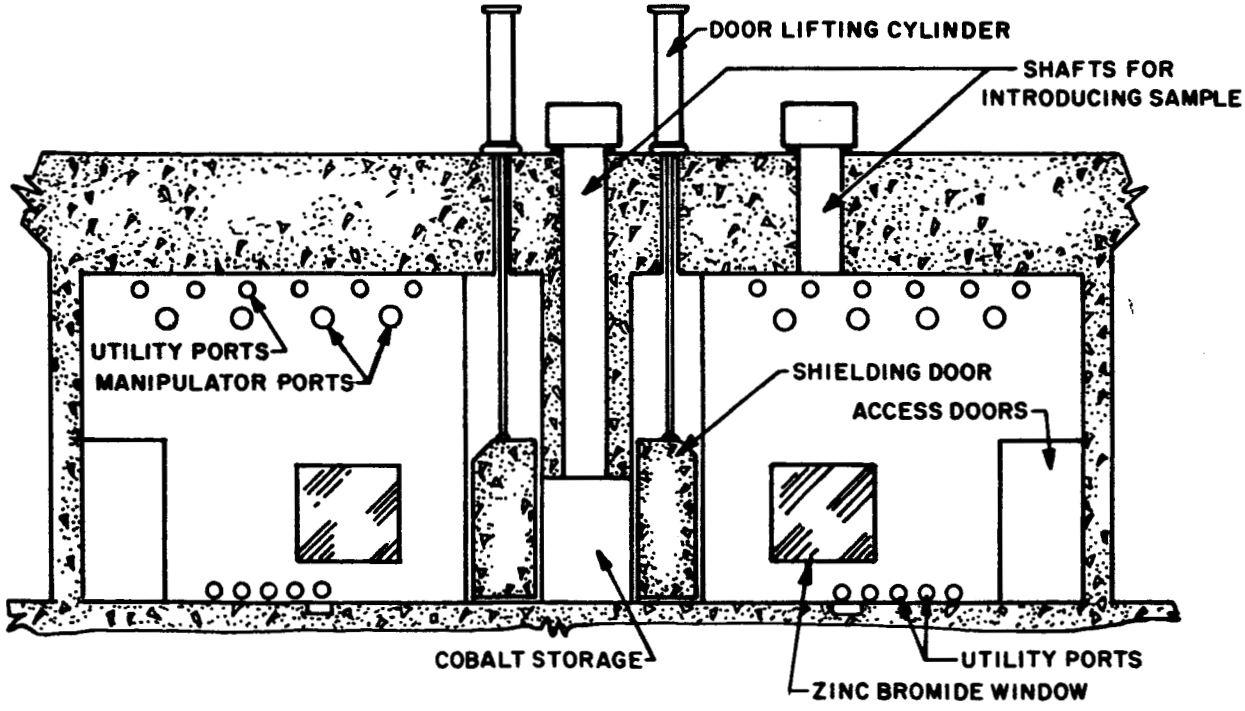


FIGURE 6. SECTION THROUGH CELLS
LOOKING AT OPERATOR'S SHIELDING WALL