AFML-TR-72-13

MANUFACTURING METHODS FOR HIGH PERFORMANCE GRAFTED-POLYETHYLENE BATTERY SEPARATORS

Vincent D'Agostino
Joseph Lee

FINAL TECHNICAL REPORT AFML-TR-72-13.

AFML/LTF PROJECT NO. 360-0

MAY 1972

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

PREPARED UNDER
CONTRACT F33615-70-C-1193

BY

R A I · RESEARCH CORPORATION
HAUPPAUGE. L.I.. NEW YORK 11787

FOR

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

EC

291

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

RAI Research Corporation
225 Marcus Boulevard
Hauppauge, L.I., New York 11787

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP
N/A

3. REPORT TITLE
Manufacturing Methods for High Performance Grafted - Polyethylene Battery Separators.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Final Report - September 1, 1970 March 30, 1972

5. AUTHOR(S) (First name, middle initial, last name)
Vincent D'Agostino, Joseph Lee

6. REPORT DATE
May 1972

7a. TOTAL NO. OF PAGES

7b. NO. OF REFS
12

8a. CONTRACT OR GRANT NO.
F-33615-70-C-1193

b. PROJECT NO.
396-0

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
FR-396-0

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
RAI 429, AFML-TR-72-13

APPROVED FOR PUBLIC RELEASE. DISTRIBUTION UNLIMITED.

[redacted] ng

Details of illustrations in this document may be better studied on microfiche

NSORING MILITARY ACTIVITY
Air Force Materials Laboratory
Air Force Systems Command
Wright Patterson AFB, Ohio 45433

13. ABSTRACT

This work on the development of new and improved manufacturing methods, controls, equipment and processes was directed toward the generation of methacrylic acid-grafted-polyethylene film for use as a superior alkaline battery separator material. This material is of interest to the Air Force as a means of significantly increasing the life and performance of secondary Ni/Cd and Ag/Zn batteries and thus accomplishing meaningful cost savings.

Technology was developed to permit design of equipment for large scale production of the separator material. Pilot equipment for each phase was constructed and operated to establish optimum operating conditions and to determine process controls. Limitations on processing steps such as, film extrusion, crosslinking, grafting, washing, converting, packaging and preliminary and final specifications for raw materials, in-testing processing and the end product were established. A preliminary plant layout for a manufacturing capability of 1,000,000 ft^2/year and product costs are predicted.

All objectives of the program were successfully accomplished. The process and product reliability and consistancy was demonstrated by producing 20,000 feet of product.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Battery, Alkaline						
Separators						
Manufacture of: battery separators crosslinked polyethylene.						
Radiation Grafting						
Crosslinking						
Processing of: grafted separators crosslinked film.						

AFML-TR-72-13

MANUFACTURING METHODS FOR HIGH PERFORMANCE GRAFTED-POLYETHYLENE BATTERY SEPARATORS

Vincent D'Agostino
Joseph Lee

FINAL TECHNICAL REPORT AFML-TR-72-13.

AFML/LTF PROJECT NO. 360-7

MAY 1972

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

PREPARED UNDER
CONTRACT F33615-70-C-1193

BY

R A I RESEARCH CORPORATION
HAUPPAUGE, L.I., NEW YORK 11787

FOR

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

MANUFACTURING METHODS FOR HIGH PERFORMANCE GRAFTED-POLYETHYLENE BATTERY SEPARATORS

Vincent D'Agostino
Joseph Lee

NOTICES

When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

Do not return this copy unless return is required by security considerations, contractual obligations, or notice on a specific document.

Due to the nature of this manufacturing contract, materials and supplies obtained from specific manufacturers are noted by name. In some instances manufacturers are noted even when their product did not meet our specific needs. It should not be construed that use of a particular manufacturer's product would signify no other source or that rejection would signify anything other than the fact that the product in question did not meet our particular application requirements when used under the specific conditions applied.

FOREWORD

This report was prepared by RAI Research Corporation, Hauppauge, L.I., NY 11787, under USAF Contract F-33615-70-C-1193, Project 396-0. This work was administered by the Air Force Materials Laboratory, Manufacturing Technology Division, Fabrication Branch, and under the technical direction of Charles Tanis, Senior Project Engineer.

This report covers work conducted from 1 December 1970 through 30 January 1972 and is submitted in partial fulfillment of the contract. The manuscript was released by the author in January 1972 for publication as a technical report.

This program was conducted under the Commercial Products Department of RAI Research Corporation. Personnel who cooperated in the program and in the preparation of this were: S.J. Arditti, Administrative Director; V.F. D'Agostino, Program Director; Dr. Joseph Lee, Sr. Polymer Chemist; Robert Coyle, Electrochemist; Preston Keusch, Sr. Chemical Engineer; Joseph Santisi, Product Engineer; Edward Spacek, Mechanical Engineer; and Edward Zito, Engineer Assistant. This technical report is catalogued by RAI Research Corporation as Report No. RAI 429.

This project has been accomplished as a part of the Air Force Manufacturing Methods Program, the primary objective of which is to develop on a timely basis, manufacturing processes, techniques and equipment for use in economical production of USAF materials and components.

Your comments are solicited on the potential utilization of the information contained herein as applied to your present and/or future production programs. Suggestions concerning additional manufacturing methods development required on this or other subjects will be appreciated.

This technical report has been reviewed and is approved.

JRMarsh

JACK R. MARSH
Chief, Fabrication Branch
Manufacturing Technology Division

ABSTRACT

This work on the development of new and improved manufacturing methods, controls, equipment and processes was directed toward the generation of methacrylic acid-grafted-polyethylene film for use as a superior alkaline battery separator material. This material is of interest to the Air Force as a means of significantly increasing the life and performance of secondary nickel-cadmium and silver-zinc alkaline aircraft batteries and thus accomplish meaningful cost savings.

Technology was developed to permit design of equipment for large scale production of the separator material. Prototype or pilot equipment for each phase was constructed and operated to establish optimum operating conditions and to determine process controls.

Limitations on processing steps such as, film extrusion, crosslinking, grafting, washing, converting and packaging were established.

Preliminary and final specifications were established for raw materials, testing processing and the end product. A preliminary plant layout for a production plant with a manufacturing capability of 1,000,000 ft^2/year and product costs are predicted.

All objectives of the program were successfully accomplished. The process and product reliability and consist~~a~~ency was demonstrated by producing 20,000 ft^2 of material which the Air Force will utilize in a large, exhaustive battery test program. The cost reduction objective of the program was achieved.

TABLE OF CONTENTS

Preceding page blank

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Cont'd)

LIST OF ILLUSTRATIONS (Cont'd)

Figure Page

LIST OF ILLUSTRATIONS (Cont'd)

LIST OF TABLES

Tables Page

LIST OF TABLES (Cont'd)

LIST OF TABLES (Cont'd)

1.0 INTRODUCTION

The purpose of this program was to develop manufacturing methods, controls, equipment, quality controls parameters and processes expressly directed toward the efficient generation of reliable, low cost grafted polyethylene separator film for high-performance aircraft alkaline type batteries.

To accomplish the above, the program was divided into nine separate tasks. The separation of the manufacturing process into distinct tasks was an outgrowth of a previous development contract wherein the salient steps in the process to prepare the grafted membrane were established on a limited scale.

Before discussing in detail the establishment of the manufacturing methods the basic procedure for preparing the grafted membrane is outlined to permit an understanding of the sequence necessary to prepare the separator.

A. Polyethylene resin selected on the basis of its molecular weight distribution is extruded as a lay-flat film to one mil ± 0.10 mil tolerance.

B. The film, which is made from a low density polyethylene Bakelite DFD-0602 resin, is then crosslinked using a high energy electron accelerator.

C. Next, the crosslinked film is interwound on a three inch core using a paper mesh spacer and then placed in a solution of methacrylic acid/benzene/carbon tetrachloride and swelled to equilibrium.

D. The reaction vessel with the polyethylene film and solution is then placed in a radiation vault, exposed to Cobalt 60 gamma radiation and thereby grafted.

E. After completion of the grafting cycle the roll is removed from the reaction container and the film is separated from the interlayer spacer.

F. The grafted film is subsequently washed in water (90-95°C) to remove homopolymer formed during the radiation and converted from the acid to the salt form by reaction in 5% KOH solution at 90-95°C.

G. The converted membrane is washed in water to remove residual homopolymer and alkali, dried, slit to size and packaged after removing samples for testing.

Process details have been omitted as have the quality control procedures since these will be dealt with under the specific tasks.

In order to adapt the above procedure, manufacturing methods and processes were to be developed along with specifically designed quality controlled techniques and equipment to assure an acceptable finished item. In the adaptation of the above process all quality control starts with incoming raw materials and is carried through each processing step. Wherever possible, new and improved non-destructive testing techniques were evaluated to quality control and characterize the final product.

The program was divided into the following nine work tasks which originally had the following objectives:

Task Number One: Radiation Facility Design, Construction and Acceptance.

This task required design of a cobalt 60 source to best insure uniform dosimetry for irradiation of a new large reactor designed for grafting the film solution mixture at a dose rate of about 10,000 rads/hour.

Task Number Two: Base film Scale-up.

Two sources of supply were to be secured to produce one mil film to a tolerance of ± 10%. Procedures for measuring the gauge of the incoming film on a continuous basis were to be established for possible inline control.

Task Number Three: Crosslinking of Film.

A continuous process for crosslinking film from task number two was to be developed. The necessary equipment to perform this operation was to be constructed and evaluated. A "continuous run" of at least 50,000 feet of uniformly crosslinked film had to be made to establish costs and procedures.

Task Number Four: Preparation of Film for Grafting.

The importance of the diffusion of monomer throughout the roll of film during irradiation requires absolute uniform winding under minimum tension. Various methods for winding the film such as center winding and surface winding were to be evaluated. The diffusion of monomer through the roll as a function of time and temperature had to be established to insure optimum swelling conditions to an equilibrium value.

Task Number Five: Design of Film Reactor.

The radiation grafting reactor was to be designed to permit reaction of five thousand square feet of film in a single reactor. The design included auxiliary equipment necessary to control the thermal environment, the monomer concentration and distribution of solution. The reactor and/or the film roll was to rotate during the radiation cycle to insure a uniform dose.

Task Number Six: Film Grafting.

The grafting reaction was to be established using the reactor designed in task five. Grafting parameters were to be determined as required to establish and optimize dose, dose rate, temperature, reaction time (this is a function of dose rate), concentration of monomer and chain transfer agents. After optimization was established "full scale operation runs" had to be made to demonstrate manufacturing techniques and controls. At least twenty thousand square feet of membrane was to be made and delivered to the Air Force to demonstrate achievement of a true production process.

Task Number Seven: Grafted Film Processing.

This task required design, construction and integration of one complete pilot plant line to process grafted film from task six. The line was to include provisions for heating, removal of homopolymer, conversion of the membrane to the salt form, removal of alkali, drying, slitting and packaging. Also required under this task was construction of auxiliary equipment to remove the reaction vessel from the vault, remove the membrane from the reactor and subsequently separate the membrane and interlayer.

Task Number Eight: Quality Assurance Testing.

The scope of this task was to establish and/or select tests to control incoming raw material, in-process parameters and final product quality.

The following characteristics of the membrane were to be evaluated in selection of tests for quality control of the final product:

a) AC and DC resistance.

b) Exchange capacity

c) Moisture content

d) Uniformity of graft at various depths in the roll

e) Zinc penetration (Hull test)

f) Silver and zinc diffusion

g) Cycle life

h) Membrane expansion characteristics

i) Tensile strength

Task Number Nine: Reports.

Monthly, quarterly and final engineering reports were to be submitted in sufficient detail to permit duplication of the manufacturing process. Included in the final report would be a preliminary design and plant layout for a production capacity of approximately 1,000,000 square feet/year of separator and an economic analysis of costs.

2.0 DEVELOPMENT OF MANUFACTURING PROCESS

2.1 TASK NUMBER ONE: RADIATION FACILITY, DESIGN CONSTRUCTION AND ACCEPTANCE

The preliminary design of the radiation vault was undertaken by R A I Research prior to the initiation of this manufacturing process development program. The design, construction, licensing and safety features associated with this task are given below.

2.1.1 Radiation Vault and Reaction Position

The radiation vault was designed to permit integration of the Cobalt 60 source and cask, designed under the contract, with the large membrane reactor required to process 5000 square feet of membrane per run. Provision was made for free access of monomer from outside the vault into the reaction vessel by means of stainless steel feed lines which were set in the east wall of the vault. Ten lines were set in the south end of the east wall to permit feed of monomer, nitrogen gas and air, and electrical lines for monitoring radiation dose and five temperature probes in the membrane reactor vessel.

The plan view of the vault is given in Figure 2-1. Figure 2-2 indicates the position of the reaction vessel and feed throughs plus the positioning of the required pumps, heating and monitoring equipment on the outside of the vault. Originally a filtering unit was included and monomer leaving the vault was filtered to remove homopolymer. The colloidal nature of the homopolymer precluded this approach since the filtering screens were easily clogged.

2.1.2 Design of Cobalt 60 Source and Development

The Cobalt 60 source was designed as two 4.135 inch capsules of 7000 curies ± 10%. The outside diameter of the capsules is 0.920 inches. The active source length is 3.70 inches and the active diameter is 0.80 inches. The active slugs are individually double sealed and then

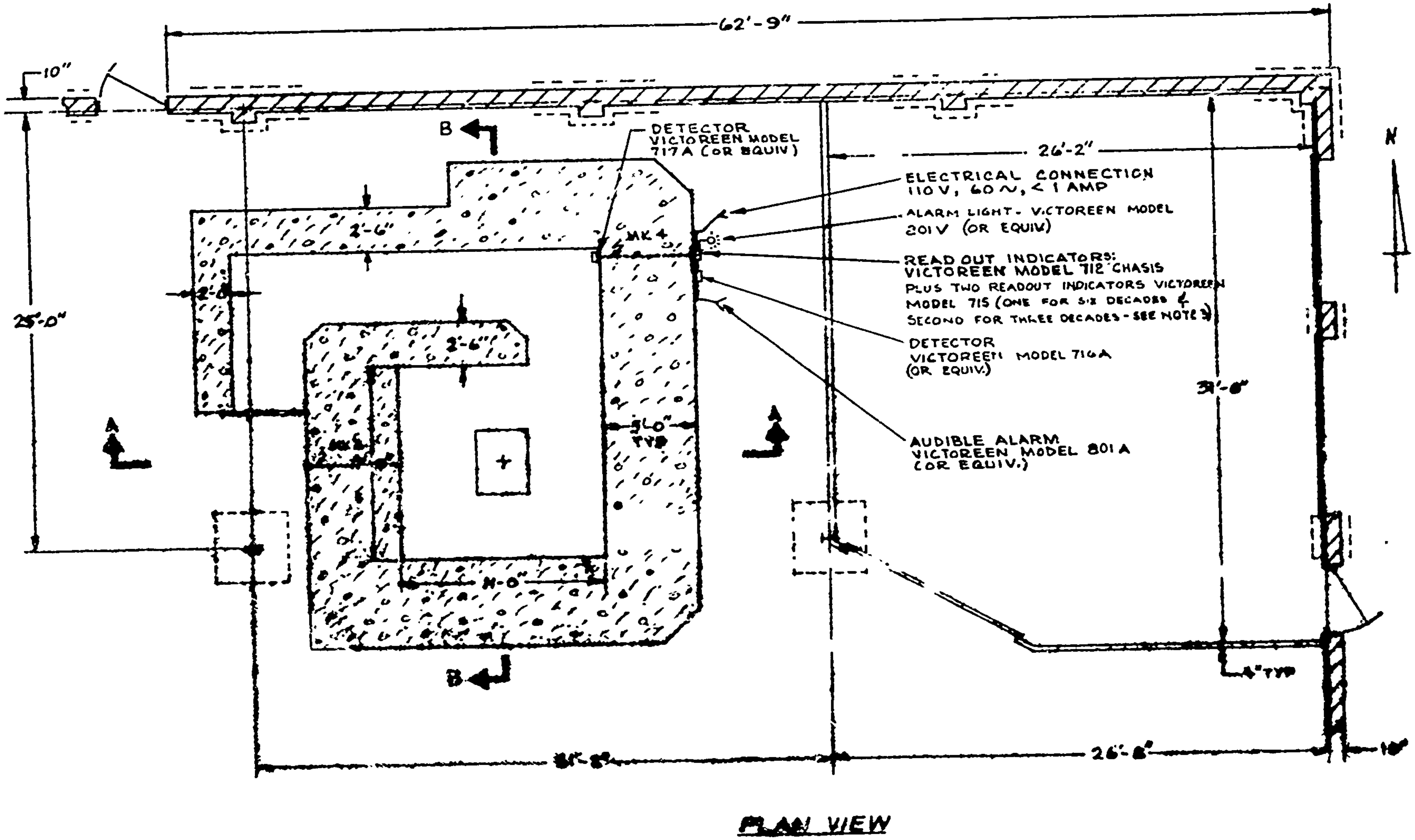


Figure 2-1 Plan View of Radiation Vault

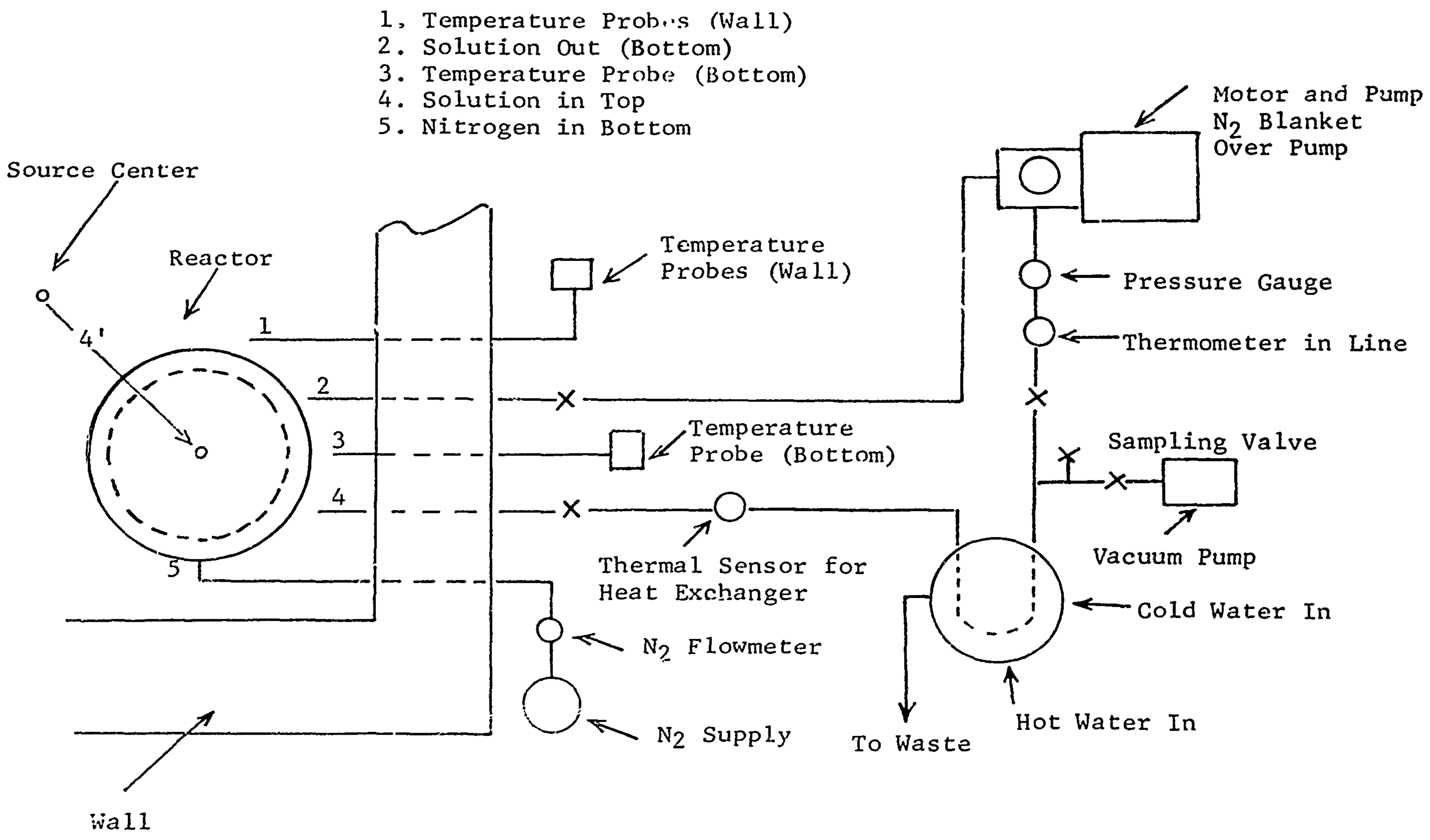


Figure 2-2 Reactor Position in Vault and Controls

again sealed in a twelve inch stainless tube. An active source is placed at both the top and bottom of the twelve inch pencil separated by a stainless spacer. Drawings and detail specification are not included in this report since they are quite extensive and do not constitute pertinent manufacturing information. The configuration, i.e. two slugs at either end of a 12 inch pencil was chosen since this form was calculated to yield a uniform radiation field of approximately 10,000 rads/hour at a distance of four feet from the source center. The source pencil was mounted onto a source holder assembly which in turn was attached to a modified lead plug. This plug is an integral part of the cask housing the active pencil.

A chimney assembly was designed and constructed to guide the modified plug and active source simply by raising the plug up into the chimney. The top of the plug contained a lug to which a 3/16 inch stainless wire cord was connected. At the top of the chimney a flange was constructed to prevent accidental removal of the plug and source pencil from the guide tube. A microswitch was also installed in the flange at a preset distance from the top to aid in positioning the source. The guide tube design has operated very satisfactorily and is easily maintained. Leak testing is easily accomplished either by removing the tube and wiping the walls or by sampling the tube in place. A cover has also been designed for the top of the guide tube to prevent contamination of the tube. Details are given in Figure 2-3.

The source lifting mechanism is shown in Figure 2-4. A winch located on the east wall of the vault is connected to the lug on top of the source plug by a stainless wire cord. The source is raised to the desired height by means of the winch. Attendant safety requirements include radiation detectors, warning lights and horns to indicate the source being raised, and door lock mode. Visual alarms and a relay activated lock which secures the door when the source is raised, i.e. is in the active position, is operated by a microswitch which releases the lock only when the source is down (i.e. inactive mode). Figure 2-5 and 2-6 indicate safety circuits operative to signal various conditions. In addition, an elaborate procedure using captive keys is in operation wherein the keys designed to permit activation of

18. # 4 40 UNC ¼ LG Rd/Hd Slotted Scr.
17. Company Nameplate
16. Dowel Pin 3/8 Dia. x 1½ LG Stl.
15. Capsule C-132 For RAI
14. Spacer - Upper
13. Spacer - Lower
12. Jacking Tool
11. $\frac{3}{4}$ 10 UNC 3 LG Soc/Hd Scr. Stl. Cad. Pl.
10. $\frac{5}{16}$ 18 UNC ½ LG Flat/Hd Scr. St/Stl.
9. $\frac{3}{4}$ 10 UNC 1¼ LG Soc/Hd Scr.Cad. Pl.
8. Leveling Pad 4x4x½ THK Stl.Pl.
7. Plug Modification
6. Skid Assy. #2
5. Skid Assy. #1
4. Cavity Shield Assy.
3. Source Holder Assy.
2. Chimney Assy.
1. Container Machining (F-127) Serial No.47

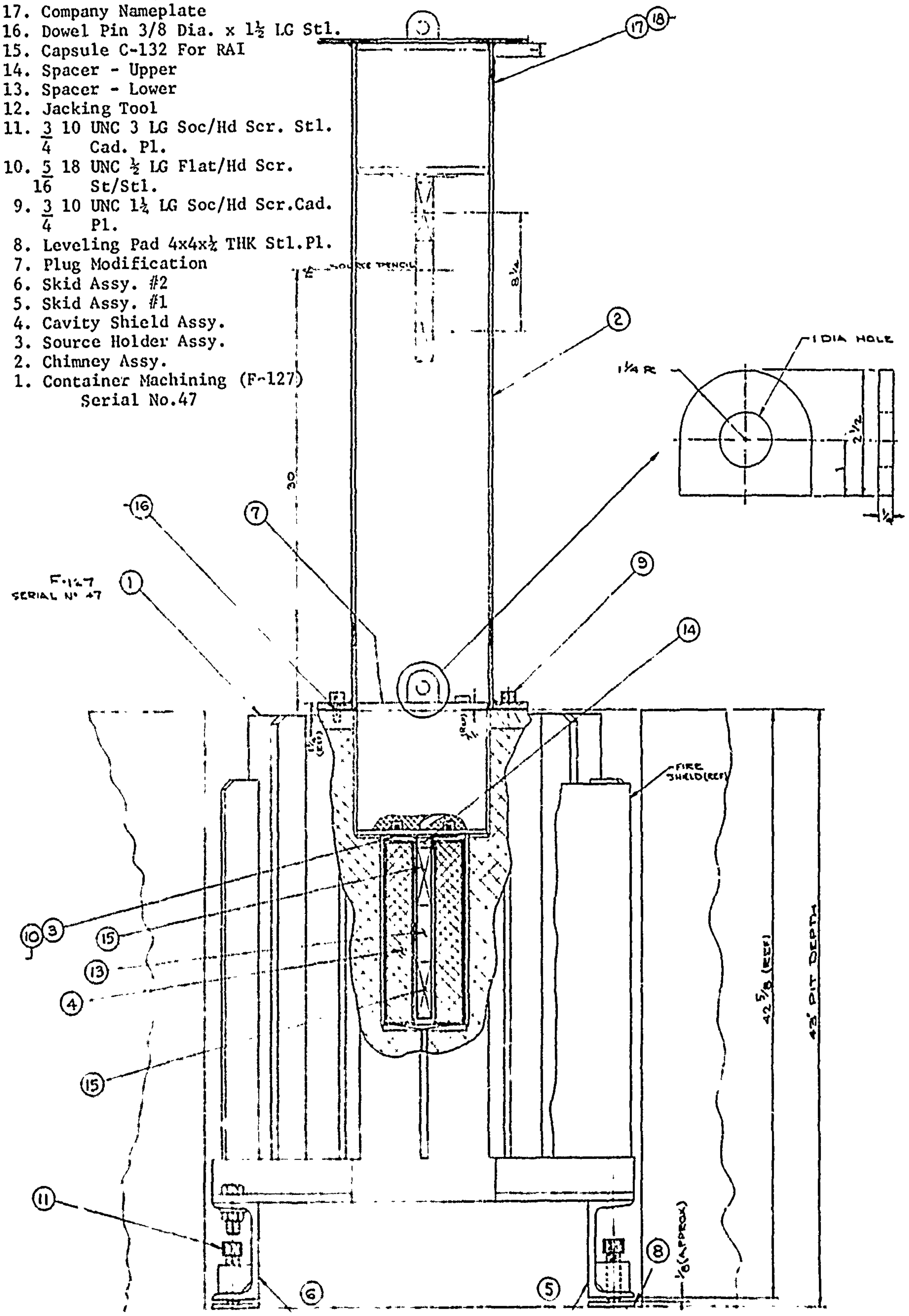


FIGURE 2-3 Cobalt 60 Source Cask and Guide Tube Assembly

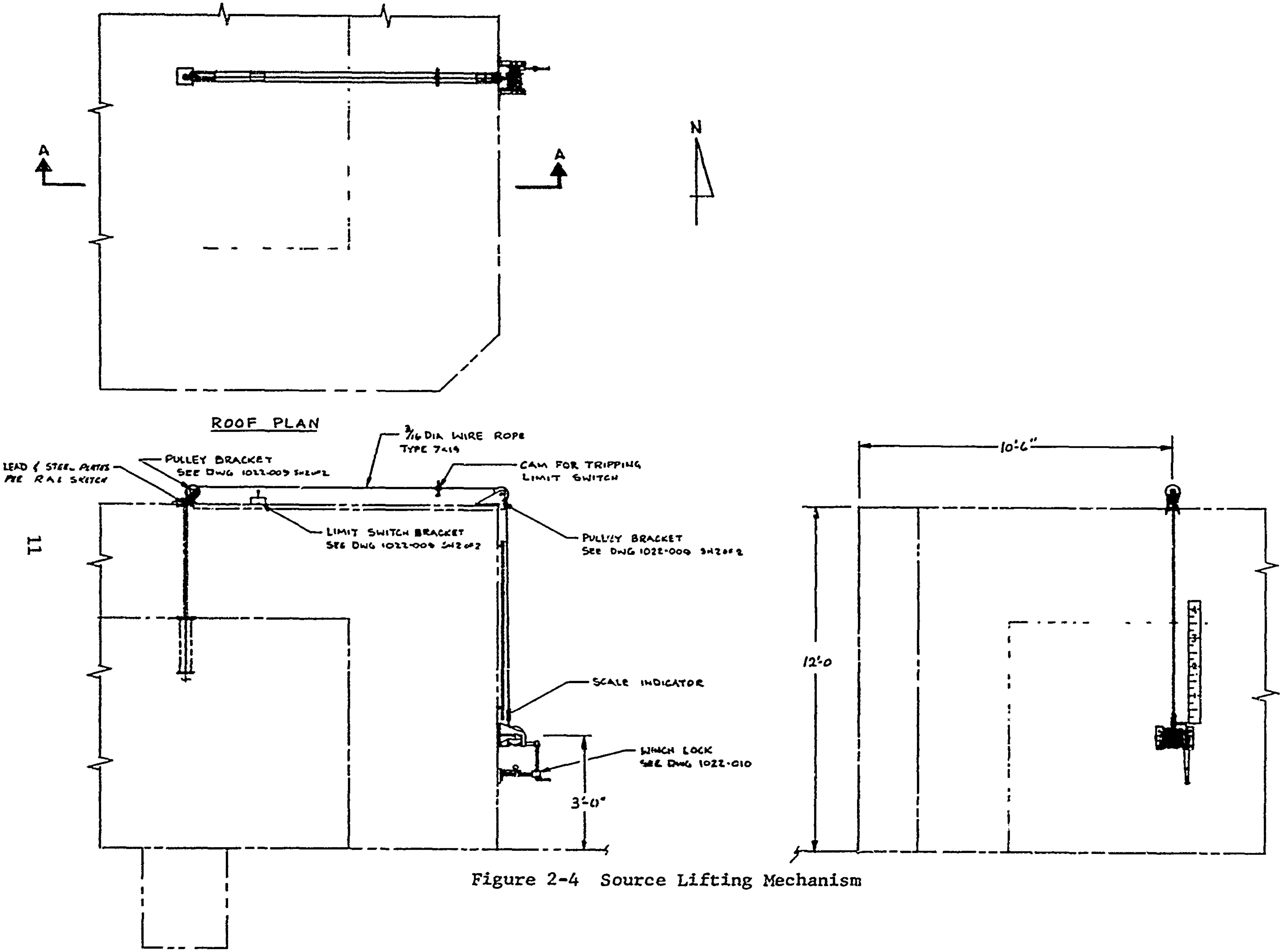
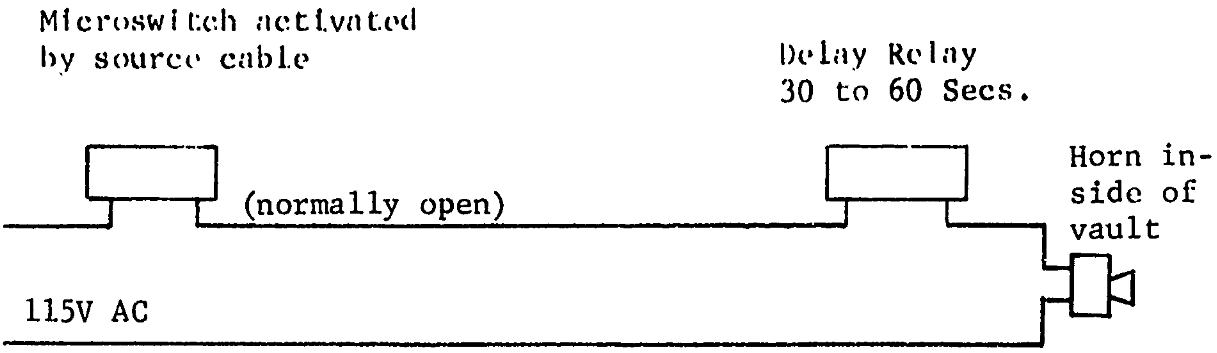


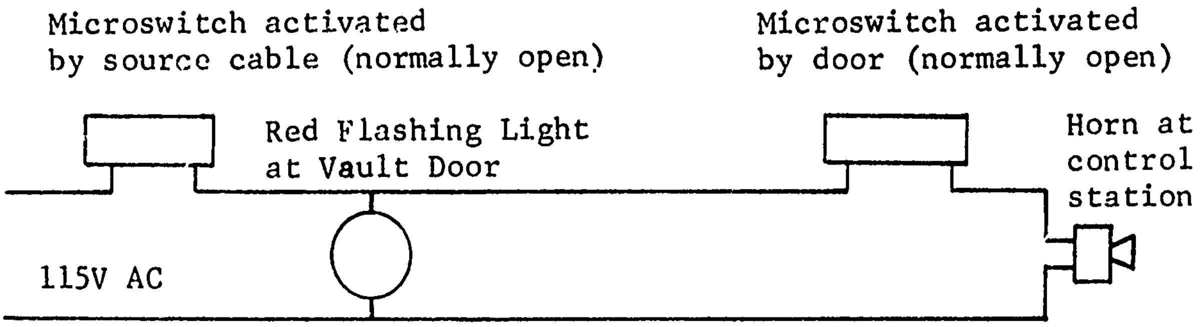
Figure 2-4 Source Lifting Mechanism

the source are also used to secure the doors to the vault. These keys are captive in the door in the open mode and can only be used in activating the source when the doors are closed. The specialty locks and keys can be obtained from I T E Imperial Corporation of N.Y.C., N.Y. They are designated, KIRK interlocks.

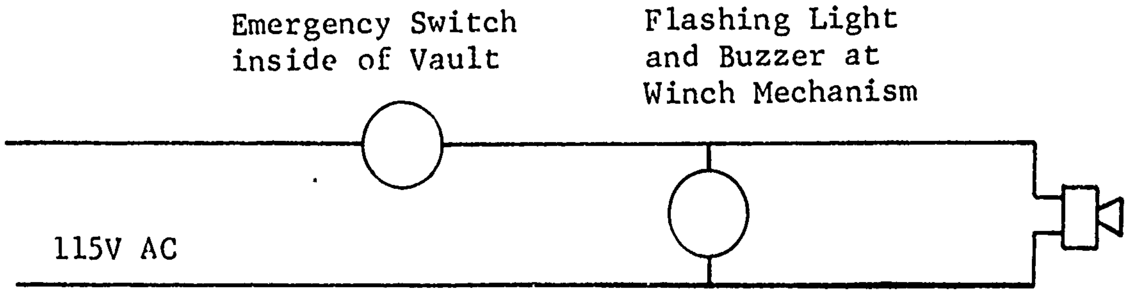
Safety precautions necessary in design of the radiation vault were made to conform to Industrial Code Rule 38 of the Radiation Protection Bulletin as issued by the Department of Labor of The State of New York. These are indicated in Table 2-1. It is sufficient to note that the vault area is completely fenced in and operated only by experienced, licensed personnel and all licensing requirements to operate the vault are in force.



Ready Deployment Alarm System



Door Mode and Warning Light System



Emergency Alarm System

Figure 2-5 Radiation Warning Systems

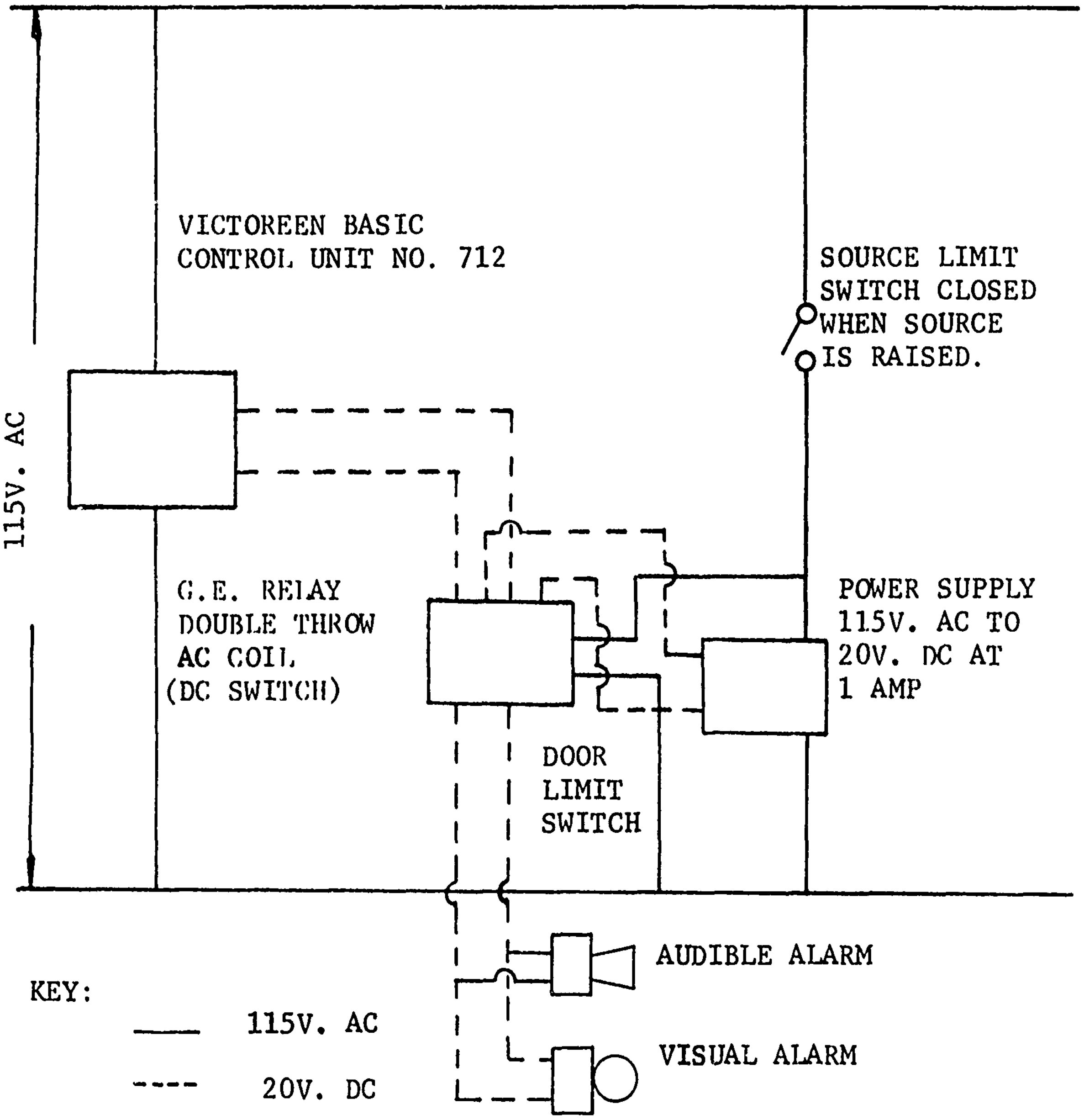


Figure 2-6 Radiation Alarm System

TABLE 2-1

RADIATION VAULT WARNING AND SAFETY FEATURES

1. **Radiation Detectors**

   A. Victoreen in vault-Model 717A (Figure 2-7) Range 1-10^6 millirads/hour.
   B. Victoreen on east wall monitor Model 716A Range 0.1-100 millirads/hour
   C. GM survey meters

2. **Warning Horns - Audible Alarms**

   A. If the dose in vault exceeds a preset level, 1A activates a horn.
   B. If dose outside vault exceeds a preset level (1.5 mr) 1B activates a horn.
   C. A horn inside vault activates when the source is being raised.
   D. A panic switch in the vault activates a horn outside the vault. This is for emergency use and is necessary to prevent the source from being raised with someone in the vault.
   E. If the source is being raised and the door is not secured a horn is automatically sounded.

3. **Locks**

   A. The main door to the vault is locked and contains a panic bar inside the vault to override the lock.
   B. A second gate door to the vault area is locked. The key to this is captive open.
   C. When the source is up a microswitch operates a bolt which secures the gate, preventing accidental entrance even with a key.
   D. Two locks are maintained on the winch source lifting mechanism. One lock is opened only by the key to the gate lock which is available only when the gate is locked. A second lock can only be opened by the radiation safety monitor's key.

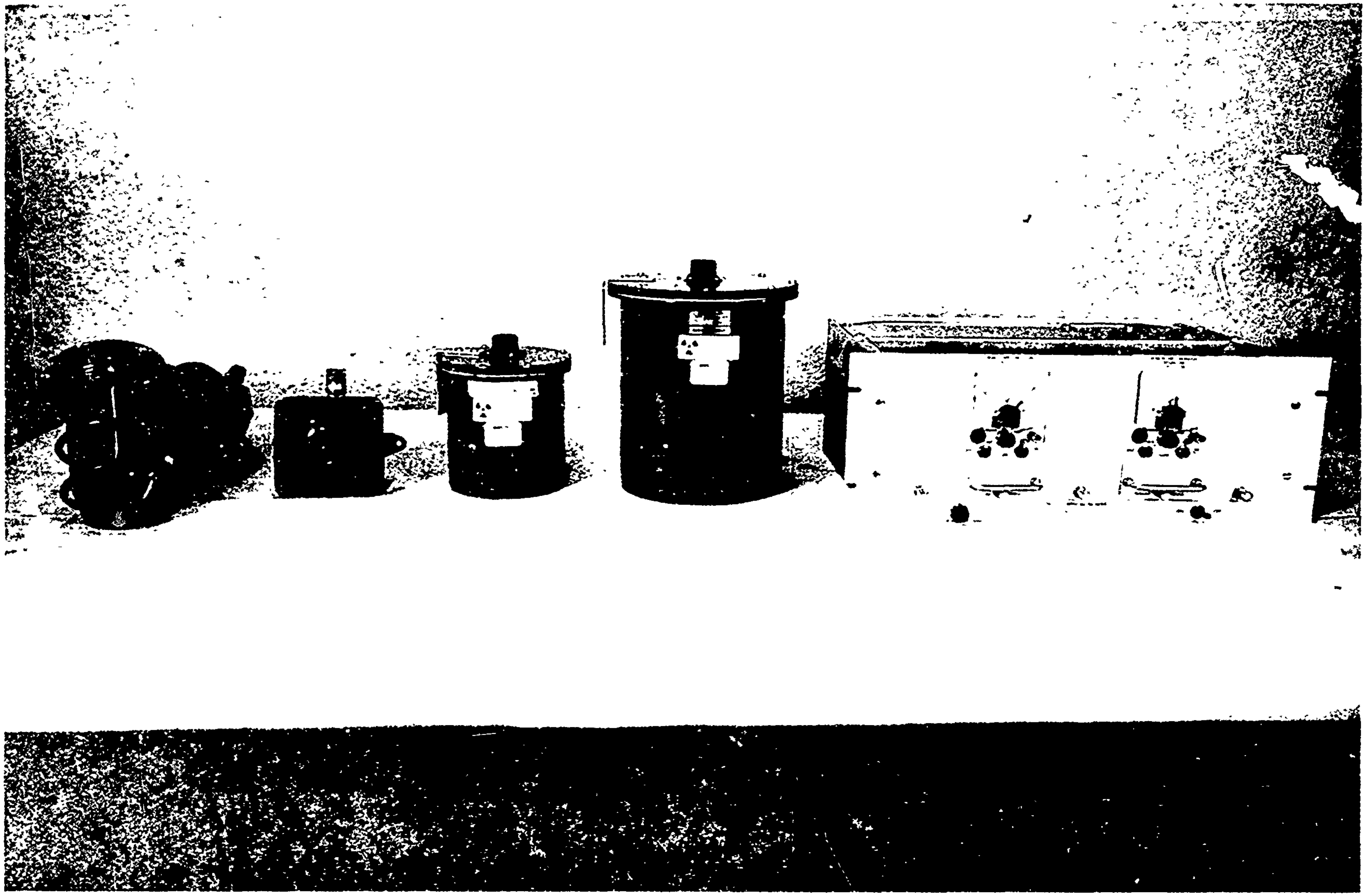


Figure 2-7 Radiation Monitoring Equipment

4. Visual Alarms

A. A flashing red light above the door to the radiation vault is on when the source is in an active position.

B. A light near the source raising mechanism indicates that the electrical system is operative.

C. A height indicator light is also by the source mechanism and indicates when the source is at a preset height.

2.1.3 Dosimetry

The dosimetry of the colbalt 60 source was measured according to ASTM D-1671-59T, "Absorbed gamma radiation dose in the Fricke dosimeter". Only one section of the vault where the film reactor is located has been plotted. The dosimetry data determined is given in Table 2-2. This data was taken with the source 27 inches above the floor.

TABLE 2-2

Dose-Distance Relationship Around the Cobalt-60 Source

Height Above Floor Inches	rads/hour Distance from the Source		
	48"	60"	85"
6	9900	7199	4061
10	10048	7308	4122
14	10105	7308	4122
18	10231	7308	4122
22	10231	7298	3950
26	10231	7298	3928
30	9980	7150	3900
34	9683	6995	3745
38	8960	6600	3690
42	7947	6212	3654

Details of calibration, calculations and the dosimetry in the film reactor are discussed in task 8.

2.2 TASK NUMBER TWO: BASE FILM SCALE-UP

2.2.1 Film Procurement

The separator developed under the research contract AF Contract No. AF33 (615)-3487 AFAPL-TR-69-57, 30 June 1969 "Silver-Zinc Electrodes & Separator Research" (1) preceding this manufacturing development effort substantiated the importance of using a polyethylene resin having a narrow molecular weight distribution in preparing the base film. The resin, Bakelite DFD-0602, was found under the previous contract to contain little low molecular weight fractions and was very efficiently crosslinked as evidenced by the gel fraction and crosslink density measured by the Mc values. The Mc value is a measure of the molecular weight between crosslinks and effectively measures crosslink density. These results are given in the final report noted in reference one above.

Based on those results, it was established that the Bakelite DFD-0602 resin would be used in preparing the base film. Thickness specification was set at 1.0 mil ± 10%. The film originally used during the research contract had been obtained from the Sea Space Corporation of Torrance, California. They had indicated at that time that they could on a special basis extrude one mil film to ± 5% absolute tolerance. Most manufacturers find a 10% tolerance on one mil a difficult specification to meet. The quantity of film required (100,000 to 200,000 square feet) constitutes little volume for most extruders; 1-2000 pounds of resin yields this quantity of film.

The Sea Space Corporation was contacted initially to supply film with a ± 5% gauge tolerance. Unfortunately this specialty extrusion group had gone out of business. Other companies were contacted originally to supply film with a ± 5% gauge tolerance. When it was found that no group would undertake making film to this tight a tolerance we reverted to the ± 10% tolerance as originally required by the contract. Even with this change, no extruder would guarantee results and an initial order for extrusion of 1000 pounds of resin was let to Shorline Industries Incorporated of Madison, Connecticut on a best efforts basis.

The resin was purchased from Union Carbide and qualified using Gel Permeation Chromatography, for determination of the molecular weight distribution; infrared, for evaluation of the presence of carbonyl; and density. After acceptance of the resin by R A I Research Corporation it was released to the extruder. Shorline Industries Incorporated has available a beta ray thickness unit to measure film gauge tolerance, however, they indicated that they check gauge tolerance with a Federal Products film micrometer. This is similar to in-house equipment used to check film tolerance.

The film was to be prepared by blown extrusion as a fifty inch tube which would give a 25 inch wide lay-flat. This form was chosen after initial results from task 3 indicated that 2 mil film could be irradiated most efficiently. The width of the film was limited by the width of the electron beam which would be used to crosslink the film. The maximum beam width with the Radiation Dynamitron is 26 inches. By processing film as a 25 inch lay-flat, it is possible to produce 4 feet of crosslinked film for each linear foot of travel of the film past the electron beam.

The crosslinked film could not be processed in the subsequent winding and grafting steps as a 25 inch lay-flat. After crosslinking, it was intended to slit the film one half inch on each end and on center to give twelve inch wide film.

Film extruded by Shorline Industries Incorporated was checked for guage tolerance and rejected. The maximum thickness was 1.10 mils and a minimum gauge of 0.85 mils was found. The average deviation was 1.0 ± 8% but the absolute variation on a spot-to-spot basis was +10, -15 percent. If the low gauge fraction was isolated in a single area of the tube length the film could be qualified by slitting the low gauge section. This could not be done, however, since the 0.85 mil section varies in location around the tube diameter.

Two other companies indicated they would accept a purchase order to extrude film to ± 10% provided a minimum of 10,000 pounds of resin were ordered. This could not be done within the budget limitations of the contract but does indicate a source of supply for extruded film after manufacture of the separator in larger quantities is established. These companies are the Edison Plastic Company of Edison, New Jersey and the Pollack Paper Company of Texas.

A second order for film was placed with the Phillips Joanna Company of Ladd, Illinois. This company extruded qualified resin as 25 inch lay-flat tubing using blown extrusion techniques. Approximately 12,000 linear feet of tubing was placed on each of nine rolls on 3 inch diameter heavy duty cores. The film received from the Phillips Joanna Company was acceptable. The gauge of this film was within specification when evaluated using a Federal Products film gauge. One section of some rolls fell to 0.85 mil. Since this low gauge section ran the length of the tubing it could be easily removed after crosslinking. The majority of the film fell between 0.92 and 1.00 mils.

When the film qualified here was crosslinked it was found that the film was not uniformly rewound. This resulted in film which had to be laboriously rewound to obtain neat bundles prior to slitting. The extensive labor involved in this operation required a change in the procedure. Subsequent to the completion of the contract, film was again obtained from the Phillips Joanna Company. This time the film was extruded as a 25 inch lay-flat tube and slit by the extruder, one half inch on each end and on center. This material has not been crosslinked to date but it is anticipated that no difficulty will result from pre-slitting the film prior to crosslinking and a substantial labor savings will result from this procedural change.

2.2.2 Thickness Measurement Equipment

Film obtained from the extruder was qualified in-house by means of a Federal Products gauge (Model #0-21). This gauge was standardized against a magnetic induction gauge using a 0.85 mil standard metal foil. The micrometer reading was 0.83 mils, i.e. only 0.02 mil deviation. (Note the difference between 0.8 and 0.9 mils is estimated to the nearest tenth.) Spot checks were made of each crosslinked roll. This is a non-destructive test but depends on samplings to qualify the film since all the extruded film could not be tested.

There are a number of companies making equipment to determine thickness on a continuous basis. The cost of this equipment is quite high ranging to $17,000 for beta ray gauges. Three companies manufacturing equipment for continuously recording gauge tolerance are:

1) Microwave Instrument Company
Corona, Del Mar, California.

This equipment operates on the principle of microwave interference and could determine the thickness of film. It is questionable if this method could be used to determine better than 0.5 mil thickness. The application of this unit for determination of moisture content of film on a continuous basis is practiced generally. It also appears possible that the percent graft of the film on a continuous basis could be determined by the application of the microwave spectrum. Samples of film, grafted and ungrafted, were prepared and evaluated by Microwave Instrument Company. The results were inconclusive and were not pursued due to the high cost and speculative nature of possible results.

2) Trapedo Division of
LFE Corporation
300 Northern Blvd.
Great Neck, N.Y.

These people manufacture standard beta-ray gauges. This equipment can be used to measure thickness on a continuous basis. t actually measures mass rather than thickness so that though it could be used to measure incoming film which is uniform, it could not measure the final product which is a "composite" of polyethylene methacrylic acid salt and water.

3) Electronic Control Division
Indev Incorporated
Pawtucket, R.I.

This instrument operates on the basis of variable inductance and measures thickness directly. The unit can measure to ± 0.00004 inch accuracy which is within our limits. The total device consists of measuring unit and control console. The sensing unit can traverse the film web automatically and record thickness variations as the film travels perpendicular to the transverse direction. The cost of this equipment is approximately $12,000.

Because of cost and time limitation none of the above procedures could be directly evaluated. The procedure used appears to be adequate in qualifying film for our requirements. Gross differences in gauge thickness are not likely to occur based on the extrusion procedure. Even if one assumes a variation of 10% in base film thickness the maximum contribution this can make to resistance decreases as the resistance of the film decrease. Separator material made under the original research contract had a resistance of 50-65 milliohms/in^2. A 10% variation could result in ± 6.5 milliohms/in^2.Separator as made under this manufacturing contract has a resistance of 35 milliohms/in^2 and a 10% variation in gauge would result in no more than 3.5 milliohms/in^2. Therefore, as the resistance of the film decreases the absolute gauge tolerance becomes less severe.

2.3 TASK NUMBER THREE: CROSSLINKING OF FILM

2.3.1 Introduction

The importance of crosslinking in development of superior battery separators was demonstrated under the research contract preceding this manufacturing development effort (1). Under that contract the prime importance of the resin used in preparing the polyethylene film and the method of crosslinking were clearly related to the extent and uniformity of crosslinking.

It is well known that with electron radiation the dose received by a film varies with the thickness of the material into which the electrons are traveling (2). Thus, it is possible when a parallel beam of fast electrons impinges on the surface of matter, that the energy absorbed per gram of matter may be greater at a depth below the surface. This effect is not due to any increase in ion density along the electron track, but merely results from the scattering of the initial parallel beam. After scattering, the electrons are moving, on the average, obliquely to the forward direction of the beam, and leave more energy behind in a thin layer of matter which is normal to the beam direction.

The relationship of dose deposited at various depths using an electron accelerator can be determined by placing cellophane dosimeters at various depths in the material being irradiated and evaluating the change in the absorption of blue cellophane dosimeters. Testing to determine the dose-depth relationship of the Radiation Dynamics Incorporated Dynamitron accelerator and comparison of these results with a theoretical curve for 1 Mev electrons is given in Figure 3-1. Data as determined on stacked packs of film is given in Table 3-1. This data was obtained from reference one and is used to show; (1) the actual radiation dose received by the film deviates from the theoretical curve. This deviation is due to experimental conditions and machine characteristics. (2) the reproducibility of results is good when all machine parameters and positioning of the materials to be irradiated are fixed. (3) the technique of irradiation of stacked packed films yields only a small portion of usable irradiation film. In Table 3-1 (1st irradiation) only the 19th to 37th layers of crosslinked film is ± 5 M rads and in the 2nd irradiation only the 33rd to 68th layers are within acceptable tolerance levels.

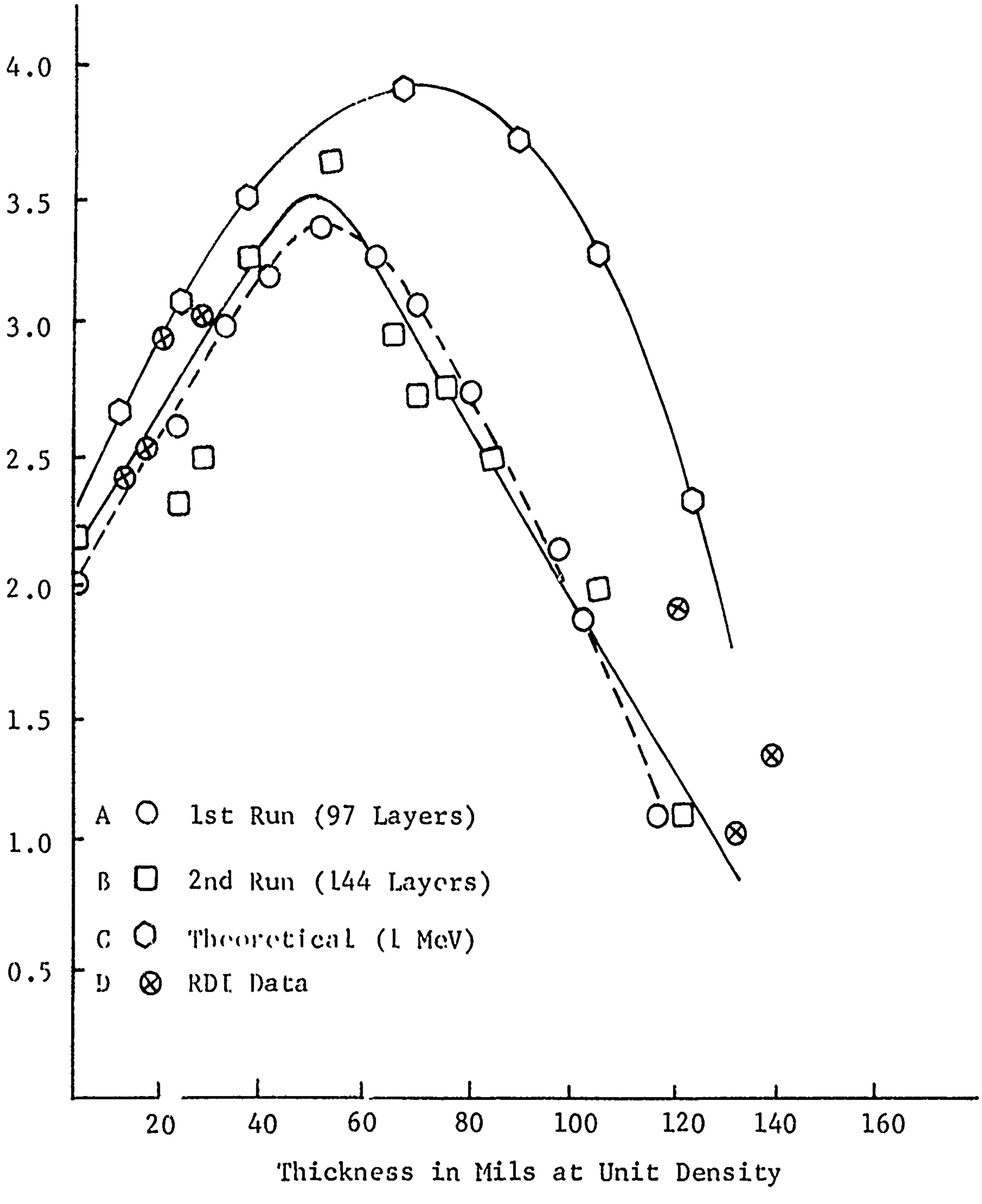


Figure 3-1 Theoretical and Actual Dose-Depth Curves

TABLE 3-1

Dose-Depth Relationship Stacked Packs of Crosslinked Films

Data From 1st Irradiation (97 Layers)

Layer No.	Corrected(a)(b) Depth (Mils)	Dose Per Pass Mrads	Total Dose Mrads	Gel %
1	23.81	2.64	73	72
10	33.01	3.00	84	89
19	42.56	3.22	90	90
28	51.96	3.35	94	91
37	62.16	3.30	92	88
46	70.42	3.10	87	84
55	80.16	2.74	77	87
67	97.46	2.20	62	86
79	104.76	1.66	47	81
85	110.27	1.35	38	78
91	116.76	1.08	30	74
97	122.61	0.84	24	66
Data From 2nd Irradiation (144 Layers)				
1	23.81	2.35	65.8	
5	27.96	2.50	70.0	
15	38.41	3.25	91.0	
20	42.30	3.35	93.8	
30	53.96	3.65	102.2	
40	64.36	2.95	82.6	
45	69.76	2.70	75.6	
50	74.76	2.80	78.4	
60	84.76	2.50	70.0	
65	90.16	2.25	63.0	
80	106.76	2.00	56.0	
98	123.76	1.15	32.2	
126	-	0	0	
141	-	0	0	

(a) The average film thickness was 1.13 mils for a nominal 1.0 mil material

(b) The electron prior to impinging on the film penetrates
1.2 mil titanium window
2.6 inches of air and
3.6 mils of polyethylene (i.e., the bag)
This is equivalent to 22.76 mils of unit density; the depth of film = layer number x average thickness x .922 + 22.76

A simple procedural modification which was adapted assured uniform crosslinking of all the film irradiated and reduced the deviation to less than 2.3%. This procedure involved irradiating the half penetration thickness of the corrected depth dose curve to one half the required dose and then reversing the packaged film, back to front, and irradiating again for one half the required dose. The total dose received by the stack of film using this technique is illustrated in Figure 3-2. As shown in the solid curve, the surface dose at the first layer of the stack corresponds to about 60% of the maximum dose at the 73rd layer of the film, which is as would be expected from the theoretical dose-depth relationship. The dotted curve represents the total dose imparted to the whole stack of film, which now is almost a perfect straight line. The dose received was calculated to be 89 ± 2 Mrads. The linearity of the curve reflects the uniformity of the dose received.

The irradiation dose given was also related to the gel content and the Mc value. As crosslinking progresses the linear polyethylene is converted to a three dimensional structure which is then insoluble in the common solvents for uncrosslinked polyethylene. The techniques for determination of gel content and Mc values are given in a subsequent section of this report. The Mc value is calculated according to the method of A. Charlesby (3).

Using the modified crosslinking technique, 2,000 feet of film was prepared. A cost analysis of this method, which required an extensive amount of labor and time to permit cooling of the film package after each 5 megarads of exposure, indicated a cost of in excess of 20 cents per square foot. Obviously this was not satisfactory. A careful review of the crosslinking procedure also indicated that uniform usable film might be obtained by continuous crosslinking if the film was festooned in front of the electron beam. If this technique were to be used it would be critical to control film speed, make provisions for dissipation of heat, provide a nitrogen atmosphere and control winding and unwinding of the film remotely. To obtain design data a prototype had to be constructed and film had to be irradiated on a continuous basis.

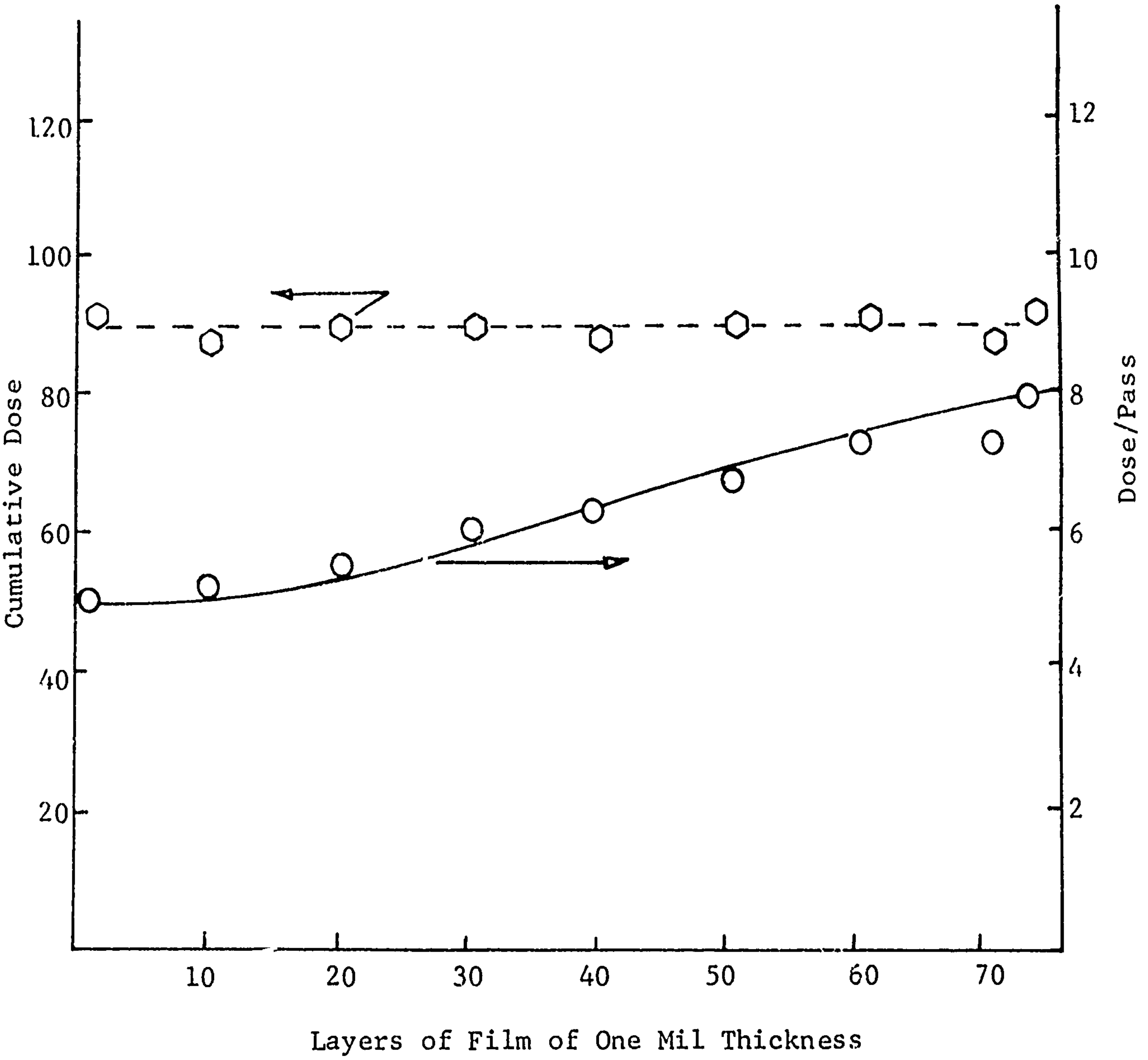


Figure 3-2 Uniformity of Crosslinking Obtained by Modified Technique

2.3.2. Initial Irradiation Data

In general, the effective thickness of a film of a given density that can be irradiated is dependent upon the energy of the irradiating electrons. Typical dose-thickness curves for industrial accelerators at various electron energies is shown in Figure 3-3. The characteristic maxima observed are due to electrons continuously losing energy by interacting with the matter through which it is passing and to the high momentum electrons (such as those that have just entered the material). These have much less of a tendency to back-scatter. This results in the ionization or dose relationships with thickness being non-uniform. It has been firmly established that 60% of the maximum absorbed radiation dose is absorbed at the surface of film being irradiated and this dose increases to a maximum within the material. The position of the maxima is dependent on the density of the material being irradiated (3).

For crosslinking we are interested in the effective thickness the electron beam sees in processing the film. Since the beam is diverging and the electrons are slowed down by the air gap between layers of film being irradiated the effective thickness varies with the particular configuration of the film during irradiation. The effective thickness may be visualized in three configurations, (1) as a solid slab (2) as a number of separate one mil sheets each touching or (3) as a number of films of various thickness each separated by an air gap.

Configurations (1) and (2) are equivalent; configuration (3), however, gives different effective thicknesses. The effective thickness is mainly dependent upon the way the individual thicknesses of film comprising the total effective thickness are arranged and the air gap distance between individual thicknesses. This is due to attenuation caused by spreading of the beam and absorption. In general, different effective thicknesses will be obtained for different arrangements of configuration (3), i.e. different arrangements of film thickness and air gaps.

Conditions: 1.5 MeV, Current 8.0 ma

3.0 MeV, Current 1.0 ma

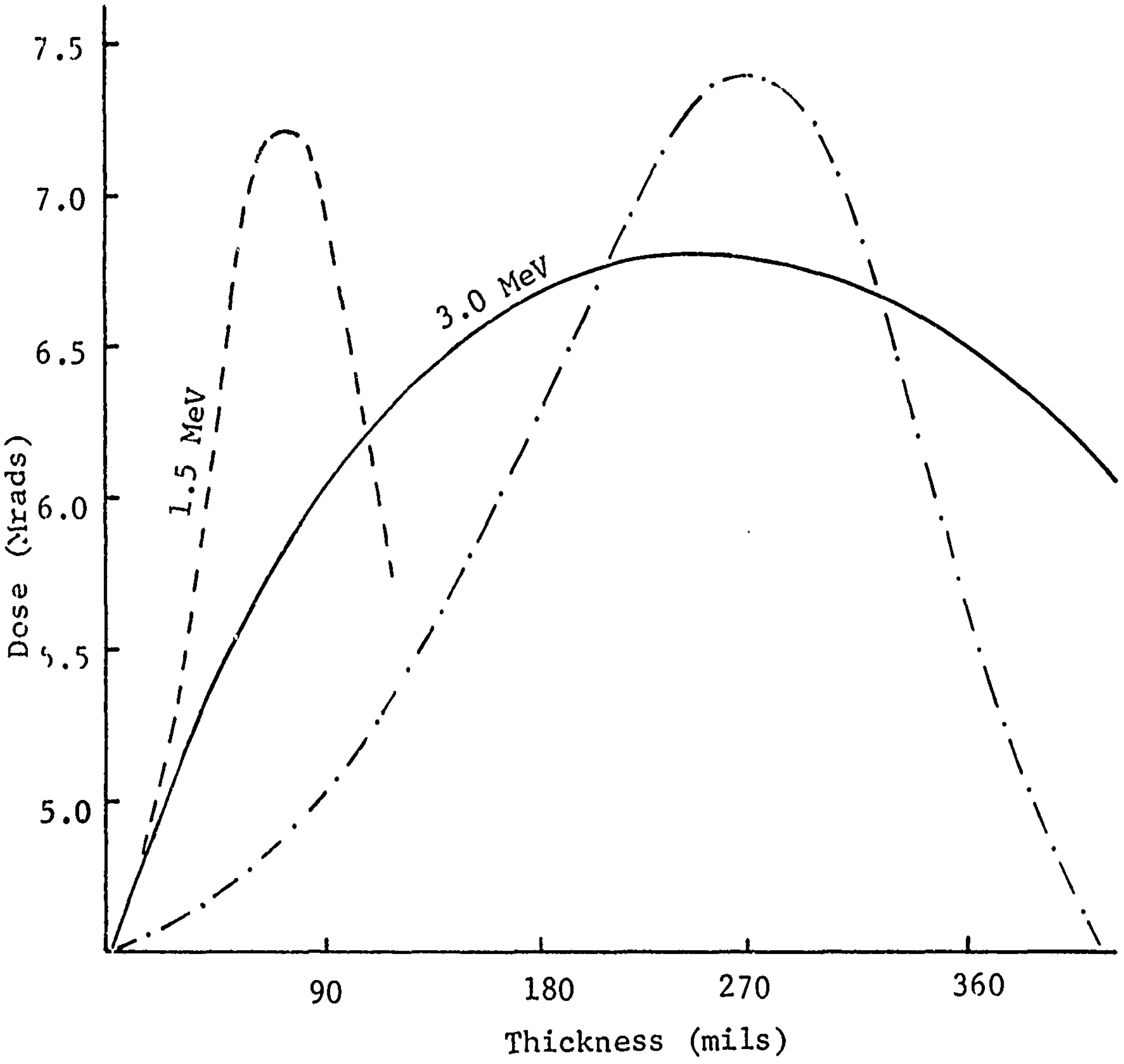


Figure 3-3 Actual Dose-Depth Distribution for Electrons Passing Through Polyethylene with Electron Energy as a Parameter

In light of the above, a series of runs were performed prior to design of the prototype crosslinking unit to establish a method to continuously irradiate the base film. Sets of 33 layers of 1, 2 and 3 mil films, equally spaced 1 inch apart on racks, (Figure 3-4) were passed in front of the horn of an electron accelerator at a linear speed of 8.25 ft/min and exposed to electrons having 1.4 MeV energy. Blued dyed cellophane dosimeters were placed on each layer of film to measure the dose each layer received. The dose attained was determined by the change in optical density of the cellophane dosimeters after irradiation as measured with a Beckman spectrophotometer.

The dose received as a function of thickness for each of the three arrangements of configuration three is presented in Tables 3-2 to 3-4 and Figures 3-5 through 3-7. These tables also give the cumulative dose that would be attained if the film were to travel continuously through a given number exposures or "thicknesses" within the field of the beam. The rate of travel of the film needed to attain a total dose of 90 Mrads in going through a given number of layers is also tabulated. These values could be calculated since the dose received is inversely proportional to the rate of travel of the film through the field of the beam. The speeds are plotted in Figures 3-8 through 3-10 as a function of the cumulative thickness for films of 1, 2 and 3 mil gauge. From these three curves it was then possible to plot the speed necessary to obtain a dose of 90 Mrads as a function of film thickness for a given number of layers of film. These curves are shown in Figure 3-11.

2.3.3 Irradiation Data from Prototype

The data in Tables 3-2 through 3-4 and Figures 3-5 through 3-7 shows the specific dose of each film layer for the three particular arrangements of configuration (3). It is seen that each arrangement shows a characteristic peak a few layers into the "pack" where there is an optimum energyback-scatter combination. Figures 3-8 through 3-10 show that as the film traverses through an increasing number of film layers the velocity needed to obtain 90 Mrads increases. This is true since the exposure time in the beam increases as the number of layers increase if the rate of travel were constant. Although the velocities needed to attain a given dose for each of the three arrangements are relatively close, Figure 3-11, which is a plot of velocity as a function of arrangement, shows that with the two thickness (2 mil) arrangement the highest film velocity is possible.

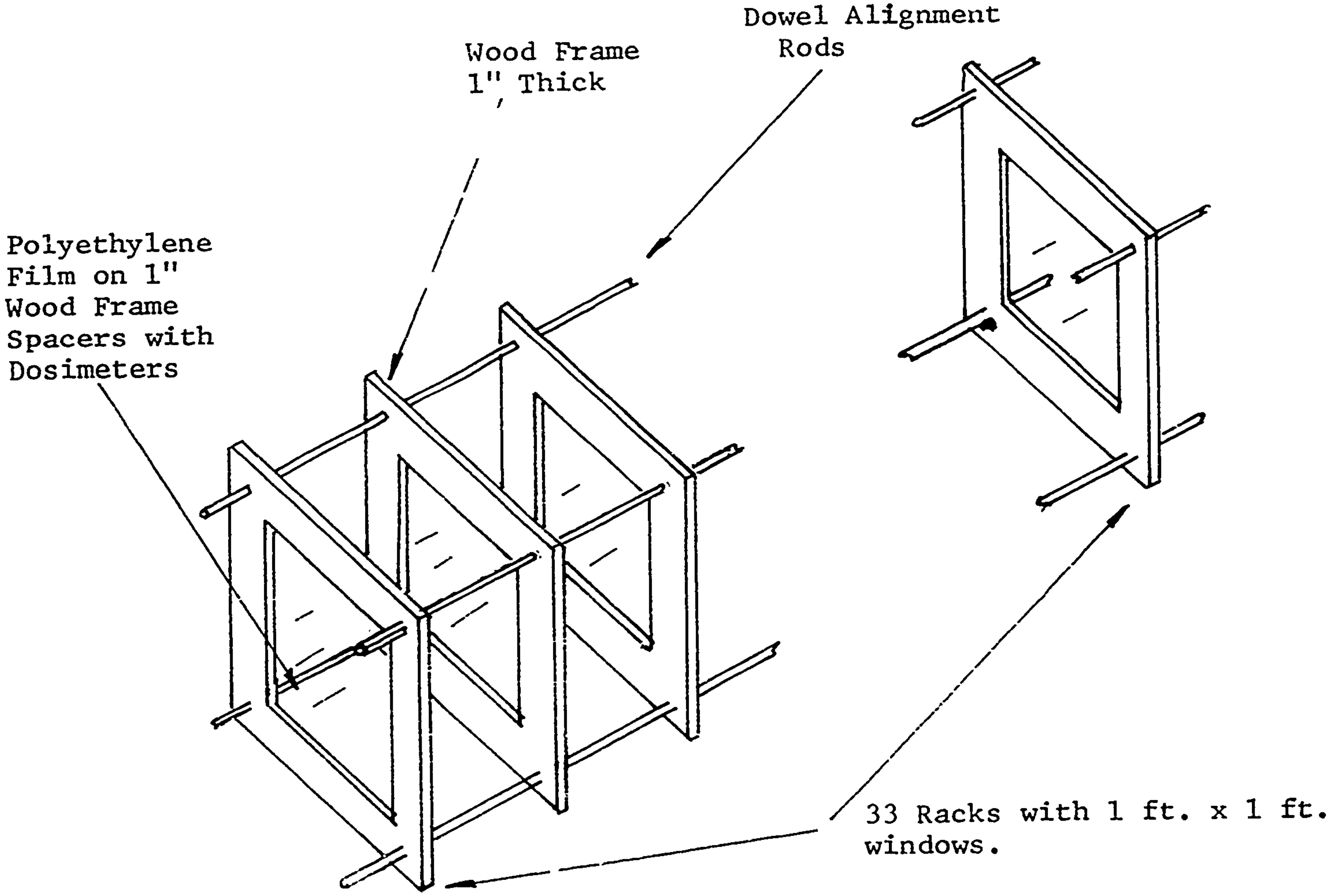


Figure 3-4. Wood Frame Holders for Irradiating Film.

TABLE 3-2

Dose Data with thickness for 33 layers of 1 mil film spaced 1 inch apart[a]

Film Thickness #	Film Thickness cumulative (mil)	Distance (in)	Dose (Mrads)	Cumulative Dose (Mrads)	v (ft/min)
1	1	6	4.83	4.83	.443
2	2	7	5.12	9.95	1.242
3	3	8	5.17	15.12	1.387
4	4	9	5.02	20.14	1.847
5	5	10	4.83	24.97	2.226
6	6	11	4.64	29.61	2.715
7	7	12	4.44	34.05	3.122
8	8	13	4.25	38.30	3.512
9	9	14	4.01	42.31	3.880
10	10	15	3.86	46.17	4.234
11	11	16	3.72	49.89	4.575
12	12	17	3.53	53.42	4.899
13	13	18	3.38	56.80	5.209
14	14	19	3.24	60.04	5.506
15	15	20	3.09	63.13	5.789
16	16	21	2.95	66.08	6.060
17	17	22	2.75	68.83	6.312
18	18	23	2.61	71.44	6.551
19	19	24	2.51	73.95	6.781
20	20	25	2.37	76.32	6.998
21	21	26	2.22	78.54	7.202
22	22	27	2.13	80.67	7.397
23	23	28	1.98	82.65	7.579
24	24	29	1.93	84.58	7.756
25	25	30	1.84	86.42	7.925
26	26	31	1.79	88.21	8.089
27	27	32	1.79	90.00	8.253
28	28	33	1.74	91.74	8.413
29	29	34	1.74	93.48	8.572
30	30	35	1.69	95.17	8.727
31	31	36	1.40	96.57	8.855
32	32	37	1.35	97.92	8.979
33	33	38	1.35	99.27	9.103
34	34	39	1.30	100.57	9.222

[a] Irradiation conditions:

Energy	1.4 MeV
Current	8.0 ma
Velocity	8.25 ft/min.

Velocities calculated by

$$v = 8.25 \frac{D(t)}{90}$$

where D(t) is the cumulative dose at a given layer

TABLE 3-3

Dose Data with thickness for 33 layers of 2 mil film spaced 1 inch apart[a]

Film Thickness #	Film Thickness cumulative (mil)	Distance (in)	Dose (Mrads)	Cumulative Dose (Mrads)	v (Ft/min)
1	2	6	4.97	4.97	0.456
2	4	7	5.16	10.13	0.929
3	6	8	5.31	15.44	1.415
4	8	9	5.31	20.75	1.902
5	10	10	5.12	25.87	2.371
6	12	11	4.87	30.74	2.818
7	14	12	4.62	35.36	3.241
8	16	13	4.37	39.73	3.641
9	18	14	4.17	43.90	4.024
10	20	15	3.97	47.87	4.388
11	22	16	3.87	51.69	4.738
12	24	17	3.68	55.37	5.075
13	26	18	3.53	58.90	5.399
14	28	19	3.38	62.28	5.704
15	30	20	3.18	65.46	6.000
16	32	21	3.08	68.54	6.282
17	34	22	2.93	71.47	6.551
18	36	23	2.73	74.20	6.801
19	38	24	2.63	76.83	7.042
20	40	25	2.48	79.31	7.270
21	42	26	2.38	81.69	7.488
22	44	27	2.24	83.93	7.643
23	46	28	2.14	86.07	7.889
24	48	29	1.99	88.06	8.072
25	50	30	1.89	89.95	8.245
26	52	31	1.84	91.79	8.413
27	54	32	1.74	93.53	8.573
28	56	33	1.64	95.17	8.723
29	58	34	1.54	96.71	8.864
30	60	35	1.44	98.15	8.996
31	62	36	1.34	99.49	9.119
32	64	37	1.29	100.78	9.237
33	66	38	1.19	101.97	9.347

[a] Irradiation conditions:

Energy 1.4 MeV
Current 8.0 ma
Velocity 8.25 ft/min

Velocities calculated by

$$v = 8.25 \frac{D(t)}{90}$$

where D(t) is the cumulative dose at a given layer

TABLE 3-4

Dose Rate with thickness for 33 layers of 3 mil film spaced 1 inch apart[a]

Film Thickness #	Film Thickness cumulative (mil)	Distance (in)	Dose (Mrads)	Cumulative Dose (Mrads)	v (ft/min)
1	3	6	5.12	5.12	0.470
2	6	7	5.32	10.44	0.957
3	9	8	5.43	15.87	1.455
4	12	9	5.43	21.30	1.953
5	15	10	5.27	26.57	2.436
6	18	11	5.02	31.59	2.897
7	21	12	4.76	36.35	3.333
8	24	13	4.50	40.85	3.745
9	27	14	4.75	45.10	4.136
10	30	15	3.99	49.09	4.502
11	33	16	3.79	52.88	4.849
12	36	17	3.53	56.41	5.173
13	39	18	3.38	59.79	5.483
14	42	19	3.17	62.96	5.773
15	45	20	3.02	65.90	6.050
16	48	21	2.87	68.85	6.314
17	51	22	2.76	71.61	6.567
18	54	23	2.61	74.22	6.806
19	57	24	2.51	76.73	7.036
20	60	25	2.41	79.14	7.257
21	63	26	2.25	81.39	7.463
22	66	27	2.15	83.54	7.661
23	69	28	2.05	85.59	7.849
24	72	29	1.95	87.54	8.027
25	75	30	1.84	89.38	8.196
26	78	31	1.74	91.12	8.356
27	81	32	1.64	92.76	8.506
28	84	33	1.54	94.30	8.647
29	87	34	1.43	95.73	8.778
30	90	35	1.38	97.11	8.905
31	93	36	1.28	98.39	9.022
32	96	37	1.18	99.57	9.131
33	99	38	1.13	100.70	9.234

[a] Irradiation conditions:

Energy	1.4 MeV
Current	8.0 ma
Velocity	8.25 ft/min

Velocities calculated by

$$v = 8.25 \frac{D(t)}{90}$$

where D(t) is the cumulative dose at a given layer.

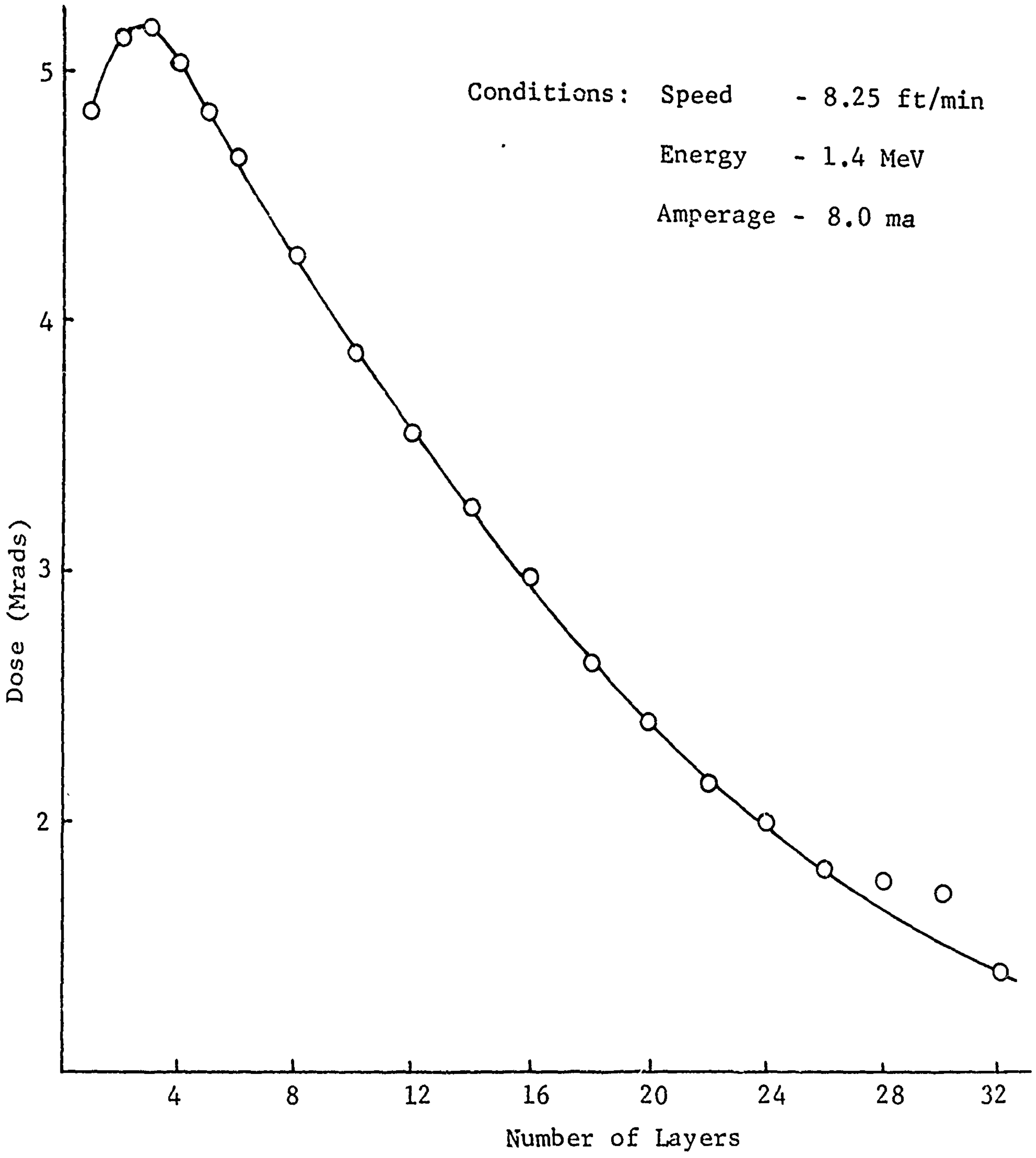


Figure 3-5 Dose Layer Curve for Arrangement of 1 Mil Film Spaced 1 Inch Apart Passing an Electron Beam

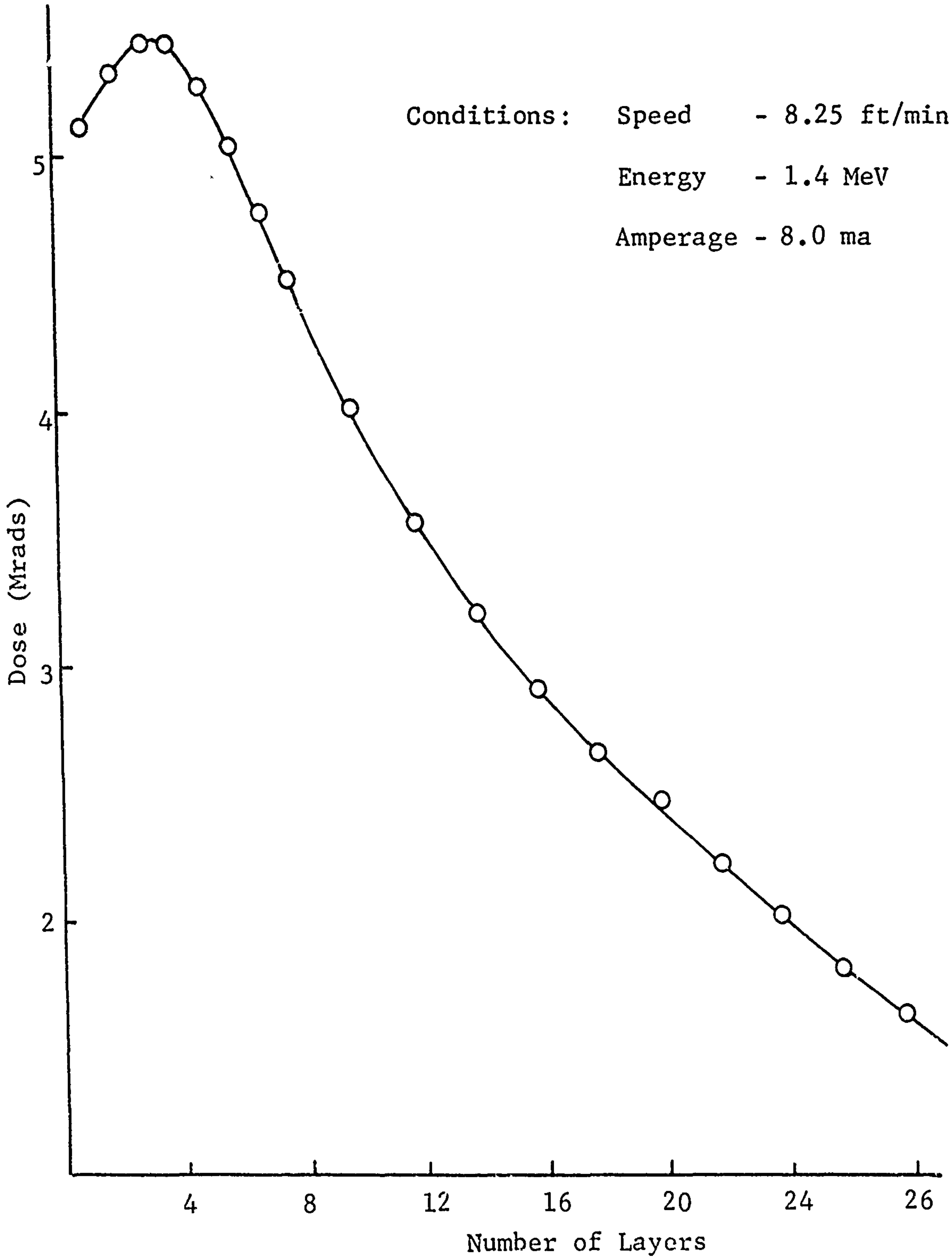


Figure 3-6 Dose Layer Curve for Arrangement of 2 Mil Film Spaced 1 Inch Apart Passing an Electron Beam

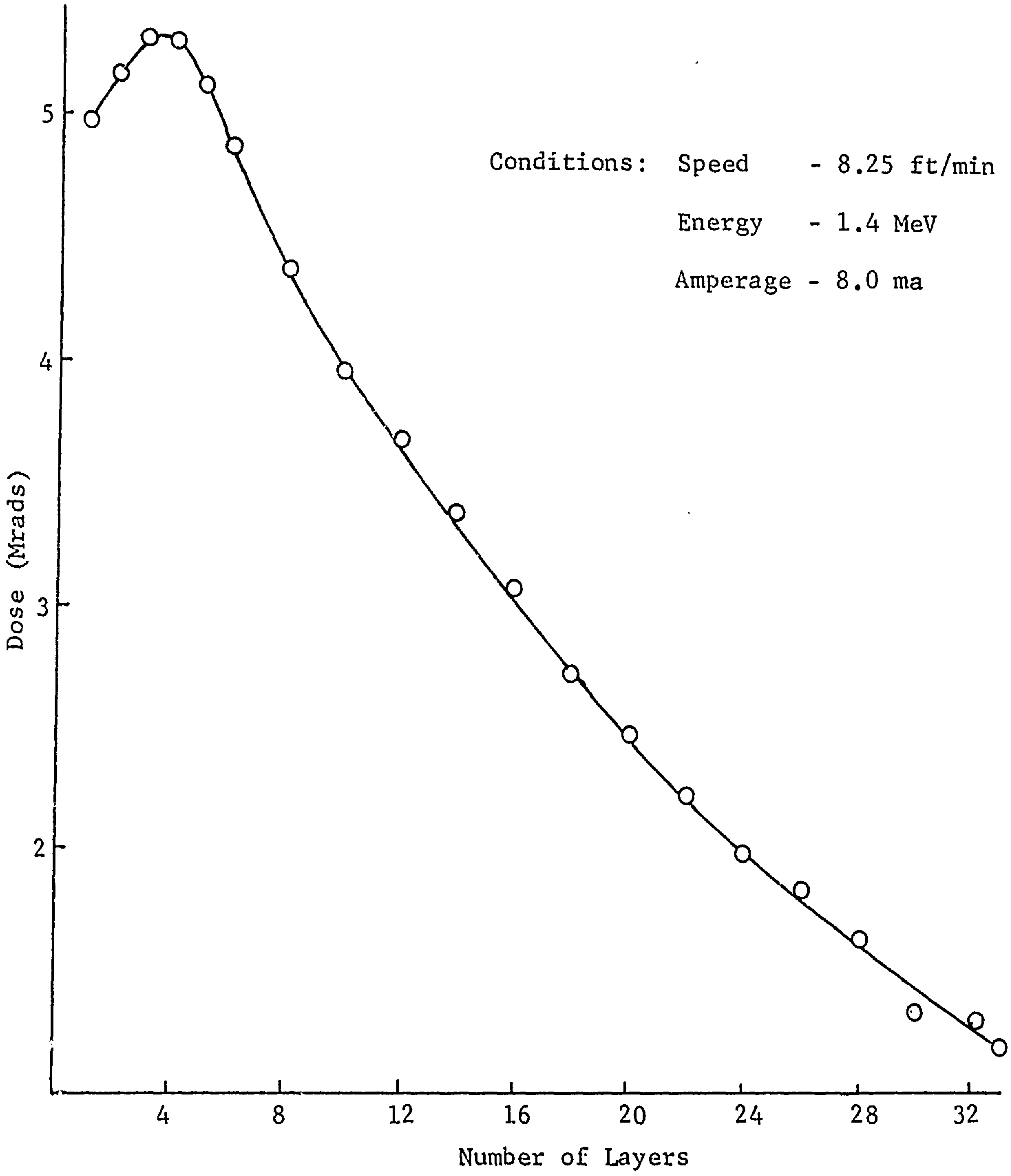


Figure 3-7 Dose Layer Curve For Arrangement of 3 Mil Film Spaced 1 Inch Apart Passing an Electron Beam

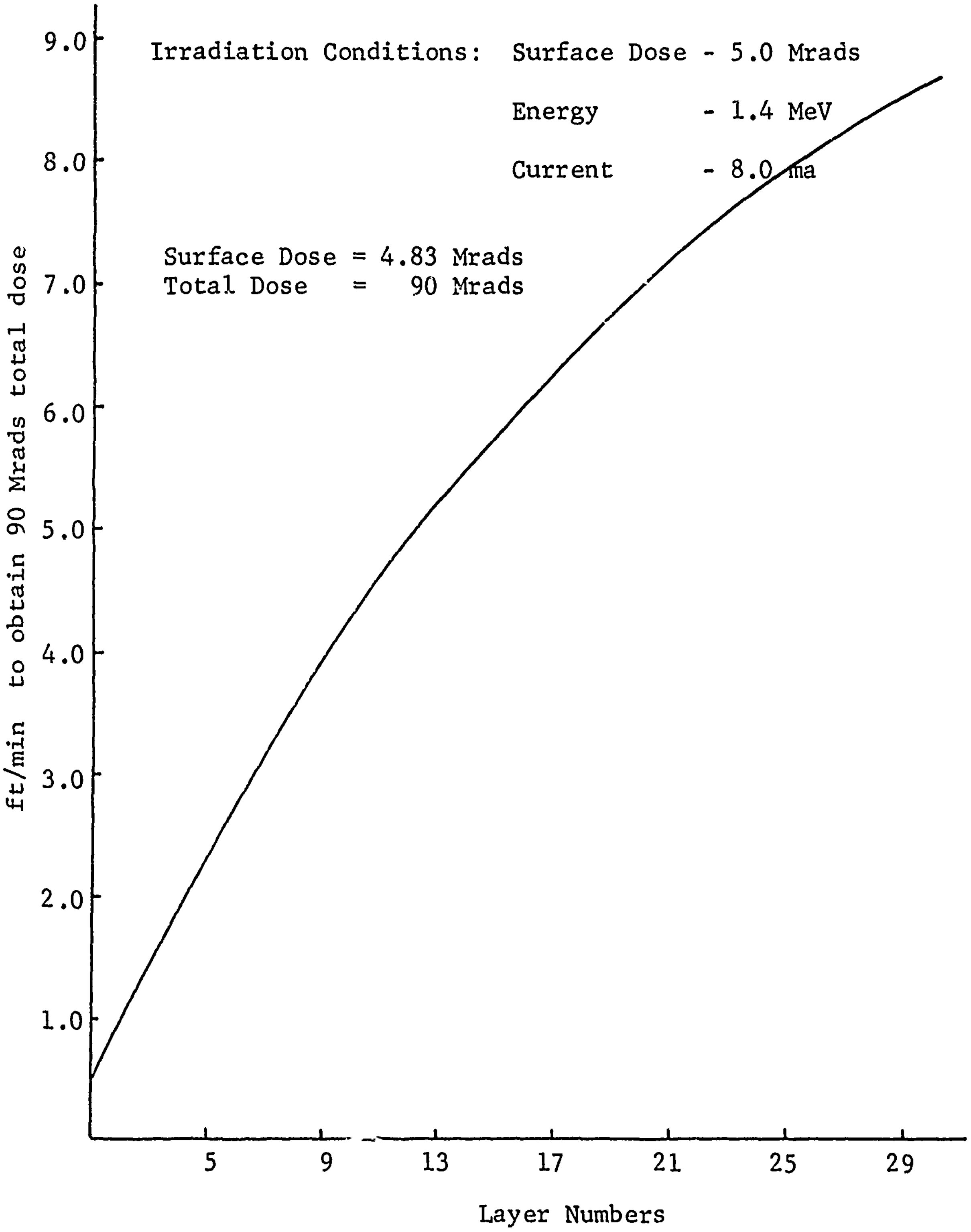


Figure 3-8 Film Velocity Needed For Travel Through a Given Number of Layers For 1 Mil Film With Layers Spaced 1 Inch Apart

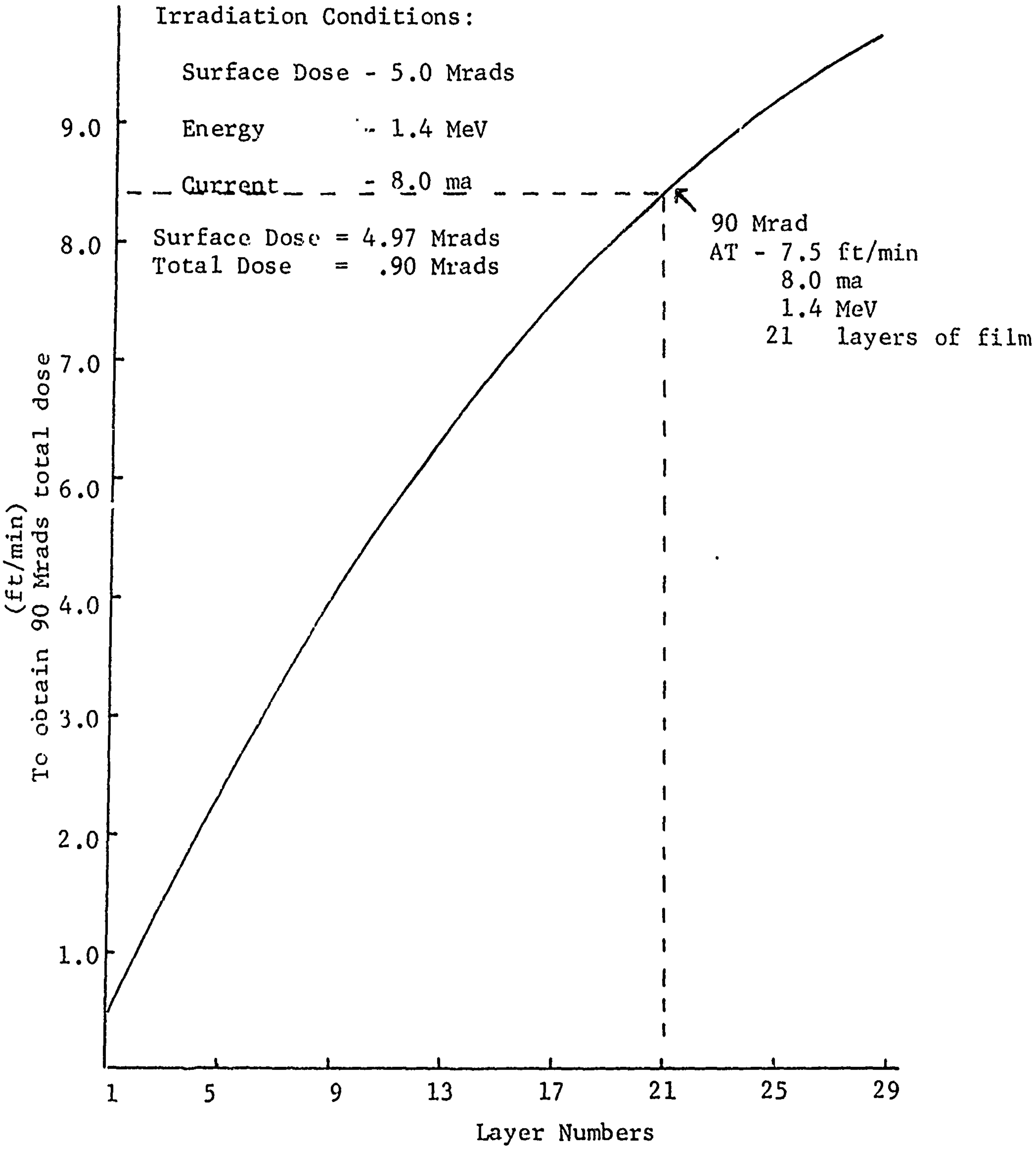


Figure 3-9 Film Velocity vs Number of Layers Required to Obtain 90 Mrads Total Dose For 2 Mil Film Spaced 1 Inch Apart

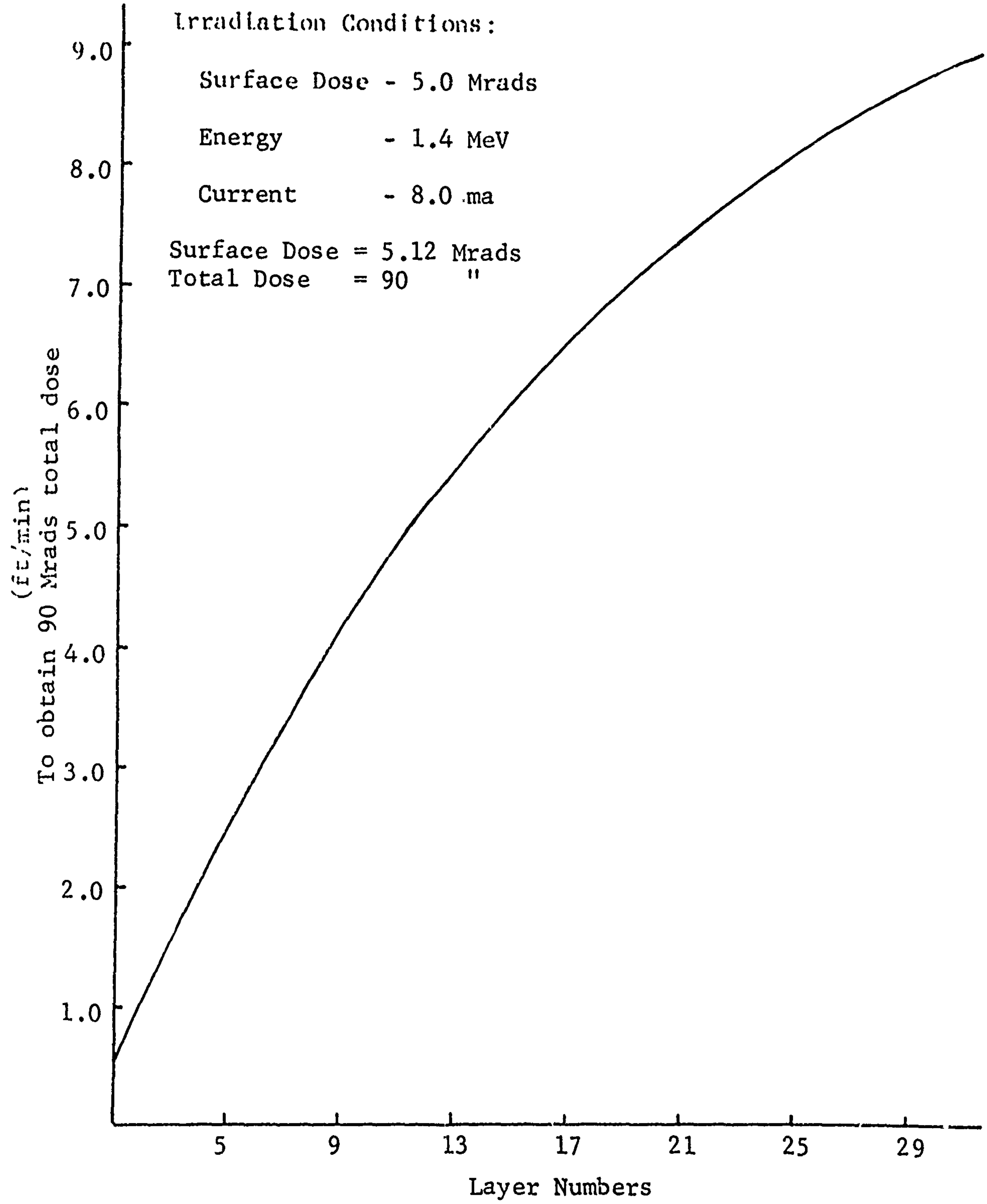


Figure 3-10 Film Velocity vs Number of Layers to Obtain 90 Mrads Total Dose For 3 Mil Film Spaced 1 Inch Apart

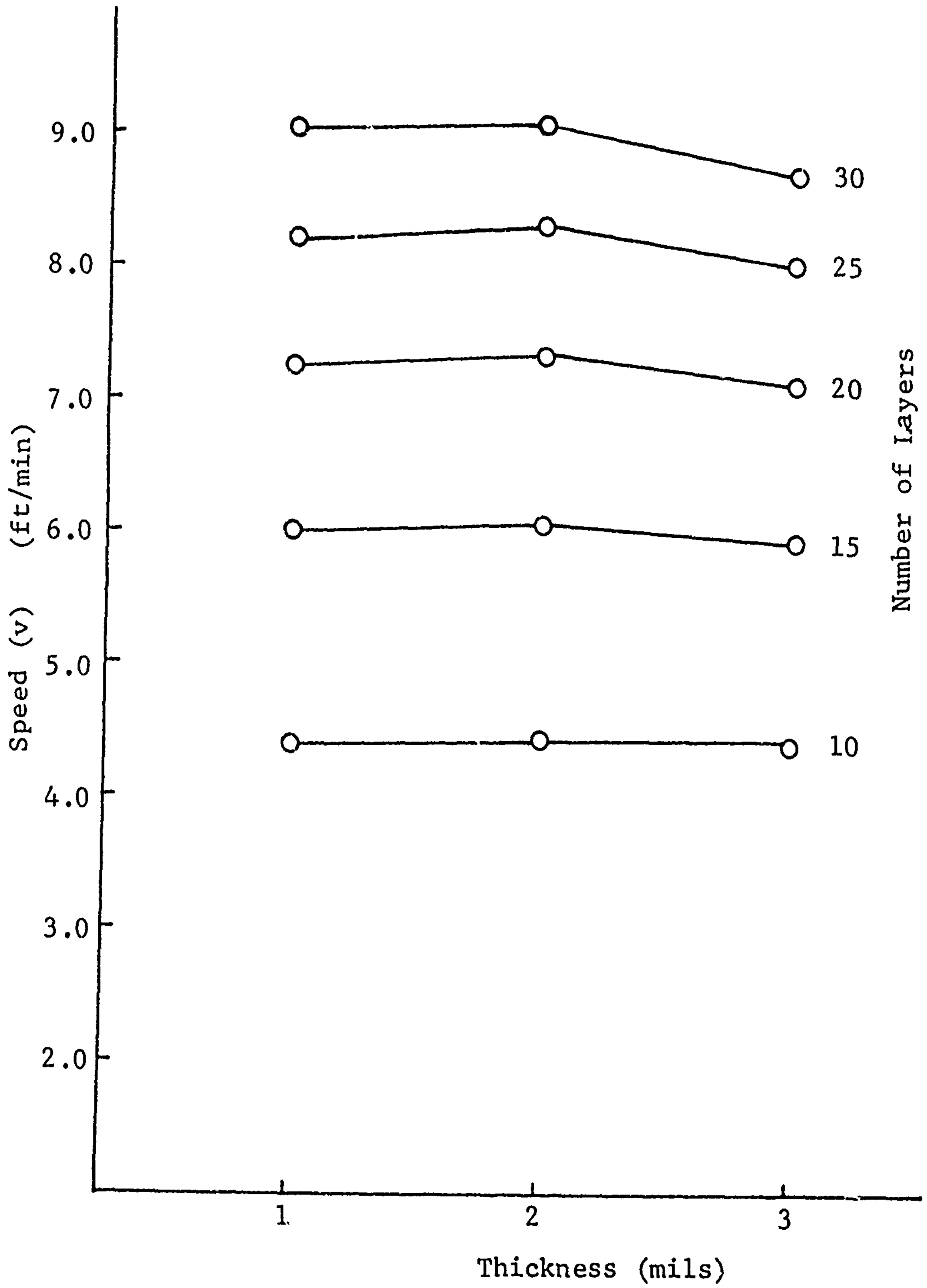


Figure 3-11 Speed vs Film Thickness With Number of Layers as a Parameter to Achieve 90 Mrads Total Dose

Using this preliminary data a prototype crosslinking unit for continuous irradiation was constructed. The unit is shown in Figure 3-12 and Figure 3-13. The first continuous irradiation run was performed using this unit. Figure 3-14 shows the unit in place and the electron beam scan horn of the electron accelerator.

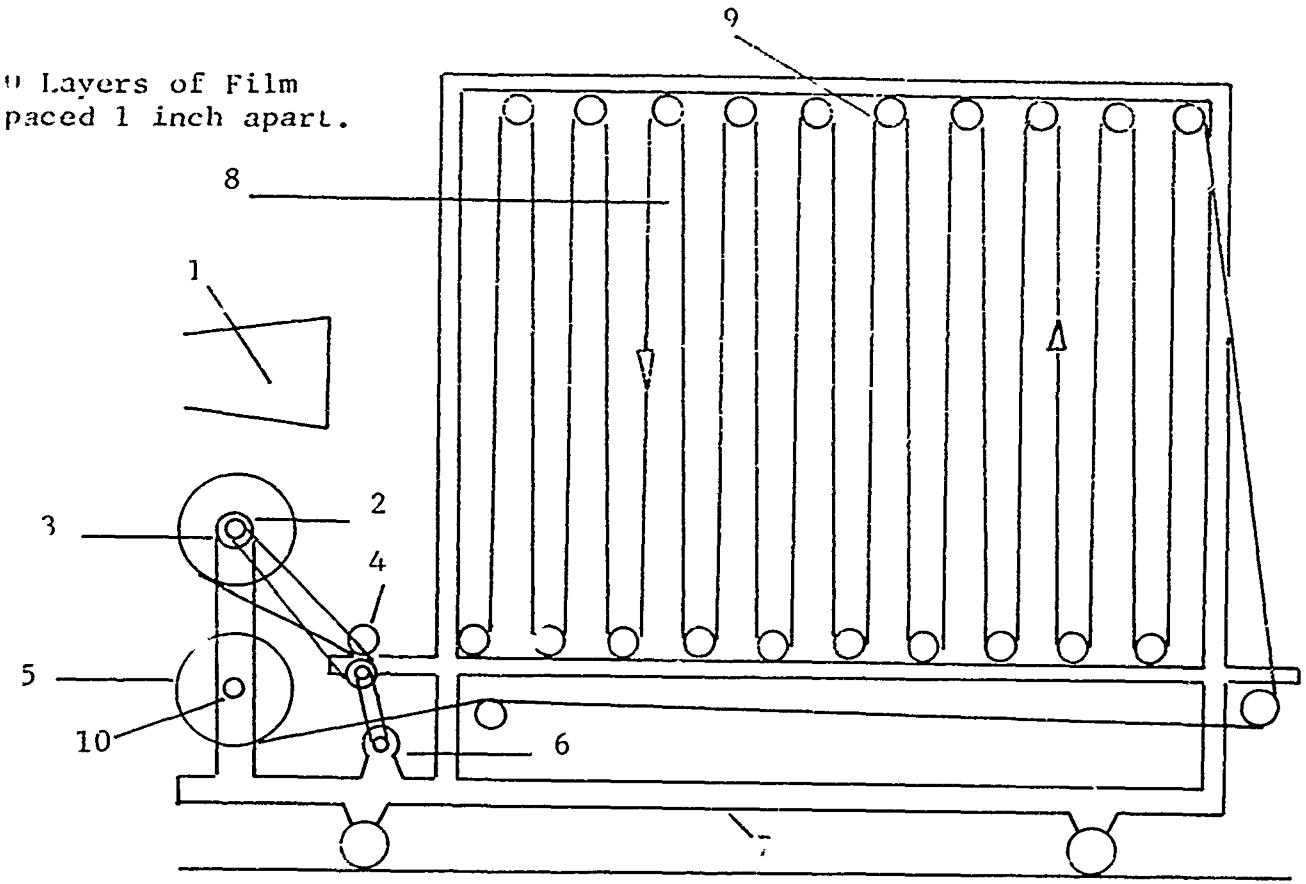
Constant speed of the film through the prototype was maintained by the use of driven nip rollers. The unirradiated film first enters the field of the beam at the furthermost position from the beam and then continuously goes through the other positions by means of the festooned rollers, each time picking up additional dosage. The purpose of the first continuous irradiation run was twofold:

1) to determine if using this basic design film could be continuously processed under actual irradiation conditions; and

2) to establish dosimetry data on different film configurations for subsequent design of the production unit.

The initial irradiation substantiated the feasibility of the design. Film was festooned in front of the beam for 15 minutes at 7.0 feet per minute. The electron accelerator beam current was set at 8.0 ma and the voltage used was 1.35 MeV. Under these conditions no heat problem developed and the irradiation of double layers of film did not result in film blocking. The design was ideal since the top rollers were spaced well above the beam and no enclosure was provided to permit heat build-up during irradiation. No nitrogen environment was maintained during these initial evaluations. The unit ran for only 15 minute intervals since it did not have provisions for remote control monitoring and film handling. During this short run the film "walked" (i.e. moved from the centered position on the rollers) and the tension control of the film was poor causing occasional stopage of the take-up rolls. These problems were eliminated in constructing the production crosslinking unit by employing tachometers on the driven nip rolls, the feed roll and the take-up rolls. The tachometers were connected via a cable to meters outside the radiation vault and feedback control was possible. By careful construction of the festooning unit, to insure parallel positioning of all rollers, use of low friction bearings, and installation of an electric eye edge guide, the film was kept centered.

20 Layers of Film
spaced 1 inch apart.



1. Electron beam
2. Clutch for drum
3. Rewind drum
4. Nip roller
5. Feed drum
6. DC Motor
7. 3" channel
8. Film
9. Rollers (variable nos.)
10. Brake

Figure 3-1 Schematic Diagram of Prototype for Continuous Irradiation Rig.

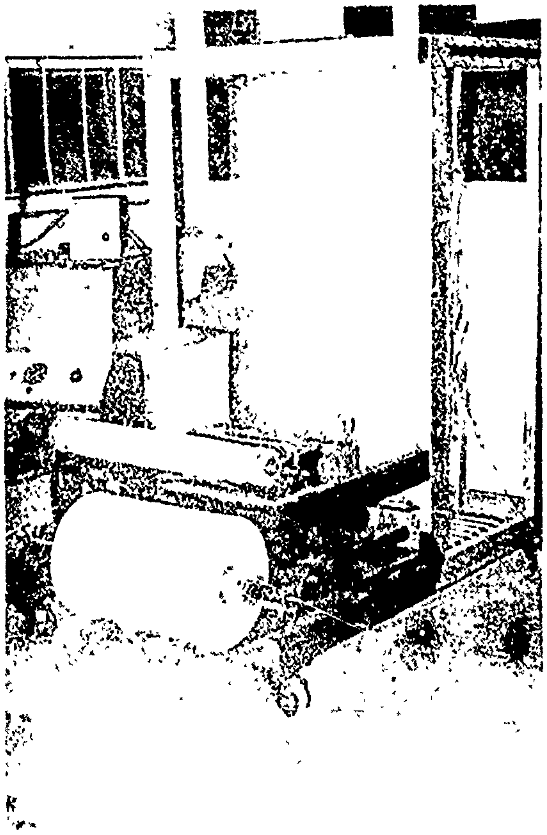


Figure 3-13 Continuous Irradiation Prototype

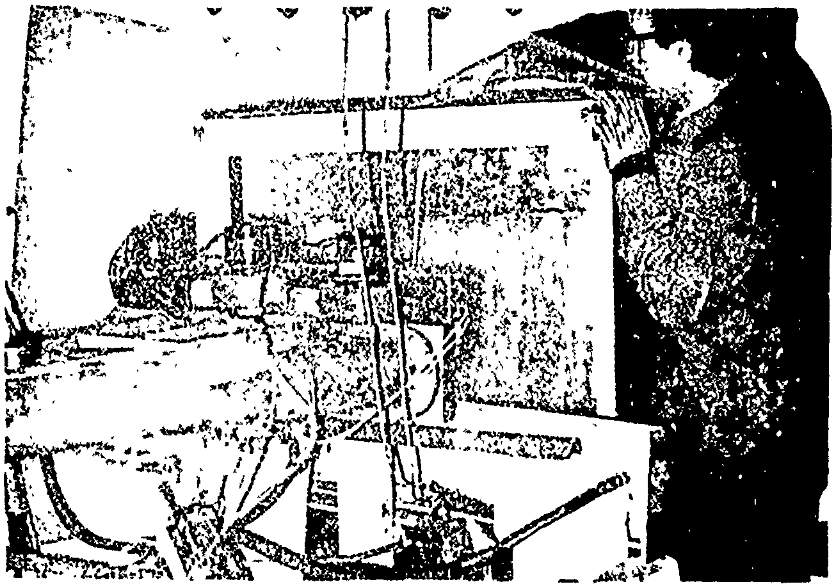


Figure 3-14 Continuous Irradiation Unit Placed in Front of RDI's Dynamatron Accelerator

Dosimetry data was taken during the initial evaluation on the three arrangements noted previously: i.e. one mil sheeting, one mil tubing (total thickness 2 mils) and 1.5 mil tubing (total thickness 3 mils). Each arrangement was run at 7.0 ft/min. The electron accelerator was set at 1.35 MeV energy, a beam current of 8.0 ma and a beam scan width of 24 inches. Blue dyed cellophane dosimeters were placed on the bottom of all the even numbered layers of film (from the 2nd to 20th) and on the top of the first layer of film (see schematic diagram, Figure 3-15). The film driving motor was then activated simultaneously with the electron beam. The film was allowed to travel so that each layer would pass the beam only once. The dose achieved for each layer was then determined by measuring the percent transmittance of the irradiated cellophane dosimeters at 625 mu wavelength on a Beckman spectrophotometer. The dose was then obtained from a standard curve (Figure 3-16). The doses received by each layer is given in Tables 3-5 through 3-7 and Figures 3-16 through 3-18. The total dose obtained for each film arrangement is found by adding the doses received in each layer. The total doses found were:

76.0 Mrads for 1 mil film
71.8 Mrads for 2 mil film
65.8 Mrads for 3 mil film

The result for the 3 mil is only a rough approximation since there was a great deal of scatter in the data obtained for this run (see Figure 3-19).

The dose received under the conditions applied was below the required 90 Mrads. To increase the total dose to 90 Mrads the beam current could be increased, the film speed reduced and/or the number of layers of film festoon in front of the beam could be increased.

To determine the increased current required, use was made of the fact that the dose received is directly proportional to the beam current. Therefore, the current I necessary for 90 Mrads is given by

$$I = I_o \frac{90}{D_o}$$

where I_o is 8.0 ma and D_o is the dose found at 8.0 ma current. For the three situations evaluated the calculated current to give 90 Mrads was; 9.47 ma, 10.02 ma and 10.94 ma for 1, 2 and 3 mil thickness respectively.

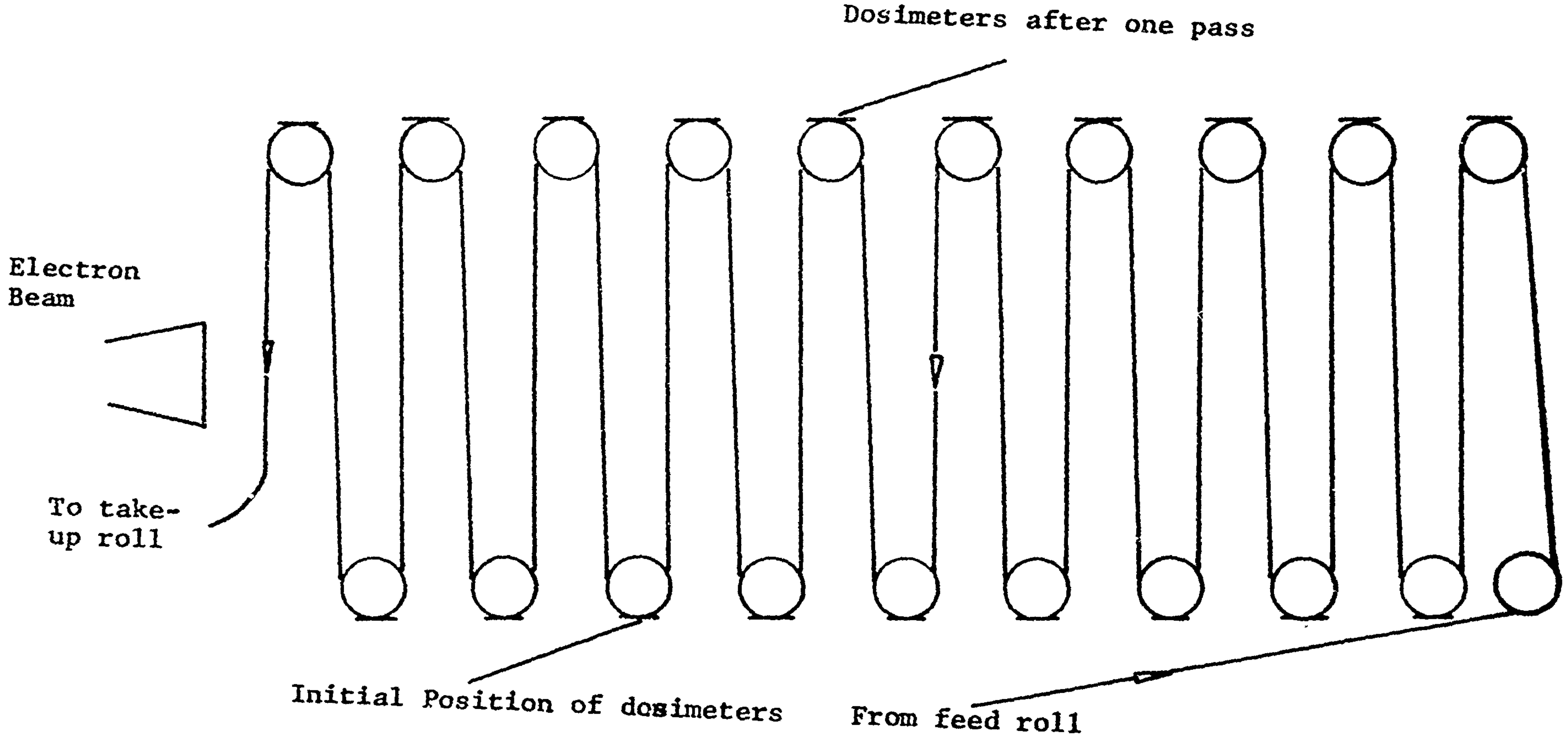
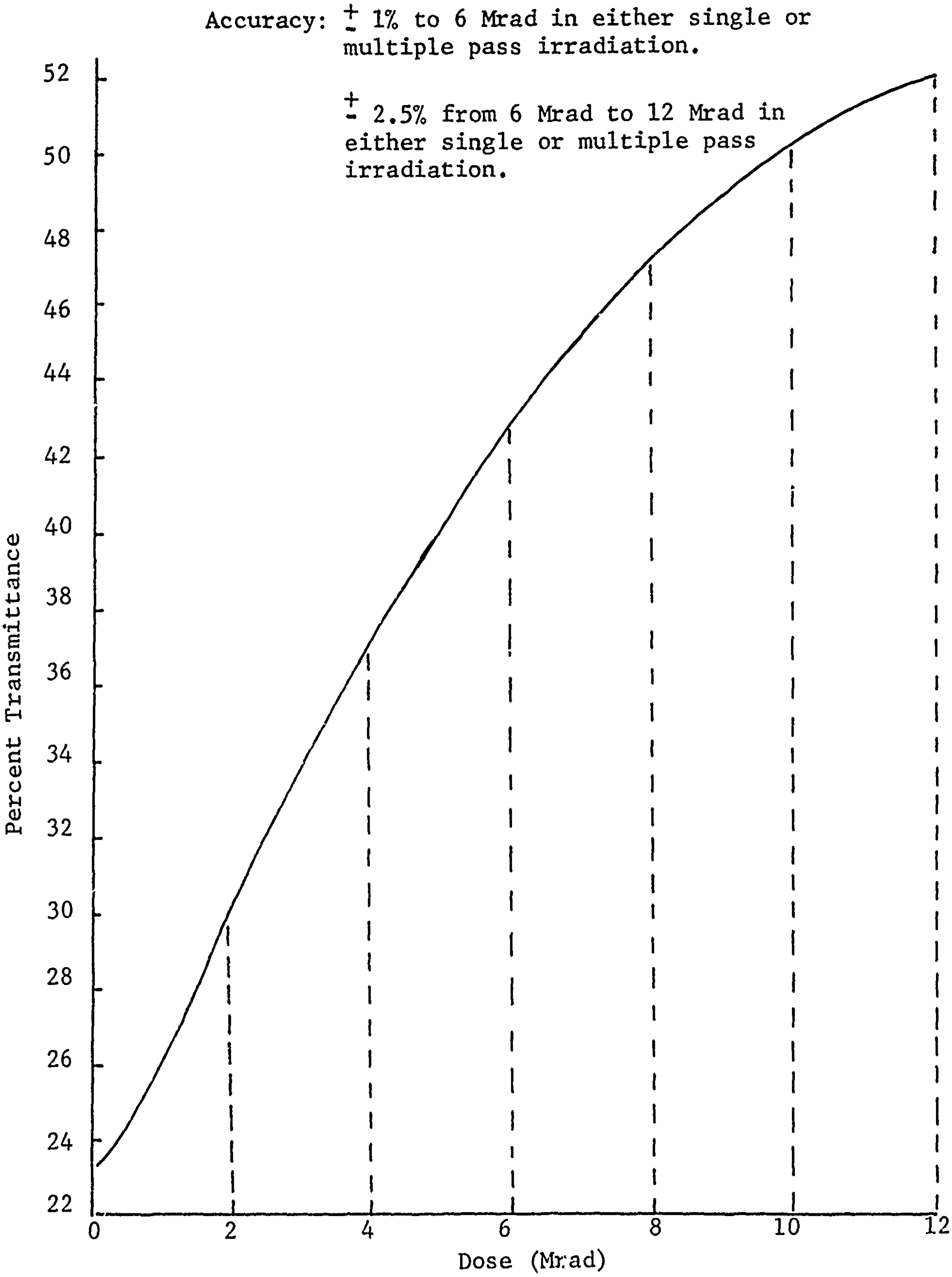


Figure 3-15 Schematic For Dosimetry



Accuracy: ± 1% to 6 Mrad in either single or multiple pass irradiation.

± 2.5% from 6 Mrad to 12 Mrad in either single or multiple pass irradiation.

Figure 3-16 Dosimetry Calibration Curve

TABLE 3-5

Dose obtained in a given layer for 1.0 mil film traveling at 7.0 ft/min across the electron beam

Beam Conditions: Scan - 24 in.
Current - 8 ma
Energy - 1.35 MeV

Layer No.	% Trans-mittance	Dose (Mrads)	% Trans-mittance	Dose (Mrads)	% Trans-mittance	Dose (Mrads)	Average Dose (Mrads)
1	39	4.5	39	4.5	38.5	4.0	4.43
2	39	4.5	39	4.5	38.5	4.0	4.43
3	-	-	-	-	-	-	-
4	39	4.5	38.5	4.3	37.5	4.0	4.27
5	-	-	-	-	-	-	-
6	38	4.17	38	4.17	37	3.8	4.05
7	-	-	-	-	-	-	-
8	37.5	4.0	36.5	3.7	37.5	4.0	3.90
9	-	-	-	-	-	-	-
10	38	4.17	37	3.8	36.5	3.7	3.89
11	-	-	-	-	-	-	-
12	37.5	4.0	37	3.8	37	3.8	3.87
13	-	-	-	-	-	-	-
14	37	3.8	36	3.5	36	3.5	3.60
15	-	-	-	-	-	-	-
16	35.5	3.42	35.5	3.40	35.5	3.42	3.42
17	-	-	-	-	-	-	-
18	34.5	3.0	35.5	3.42	34.5	3.0	3.14
19	-	-	-	-	-	-	-
20	36	3.5	35.5	3.42	33.5	3.42	3.44

TABLE 3-6

Dose obtained in a given layer for 2.0 mil film traveling at 7.0 ft/min across the electron beam

Beam Conditions: Scan - 24 in.
Current - 8 ma
Energy - 1.35 MeV

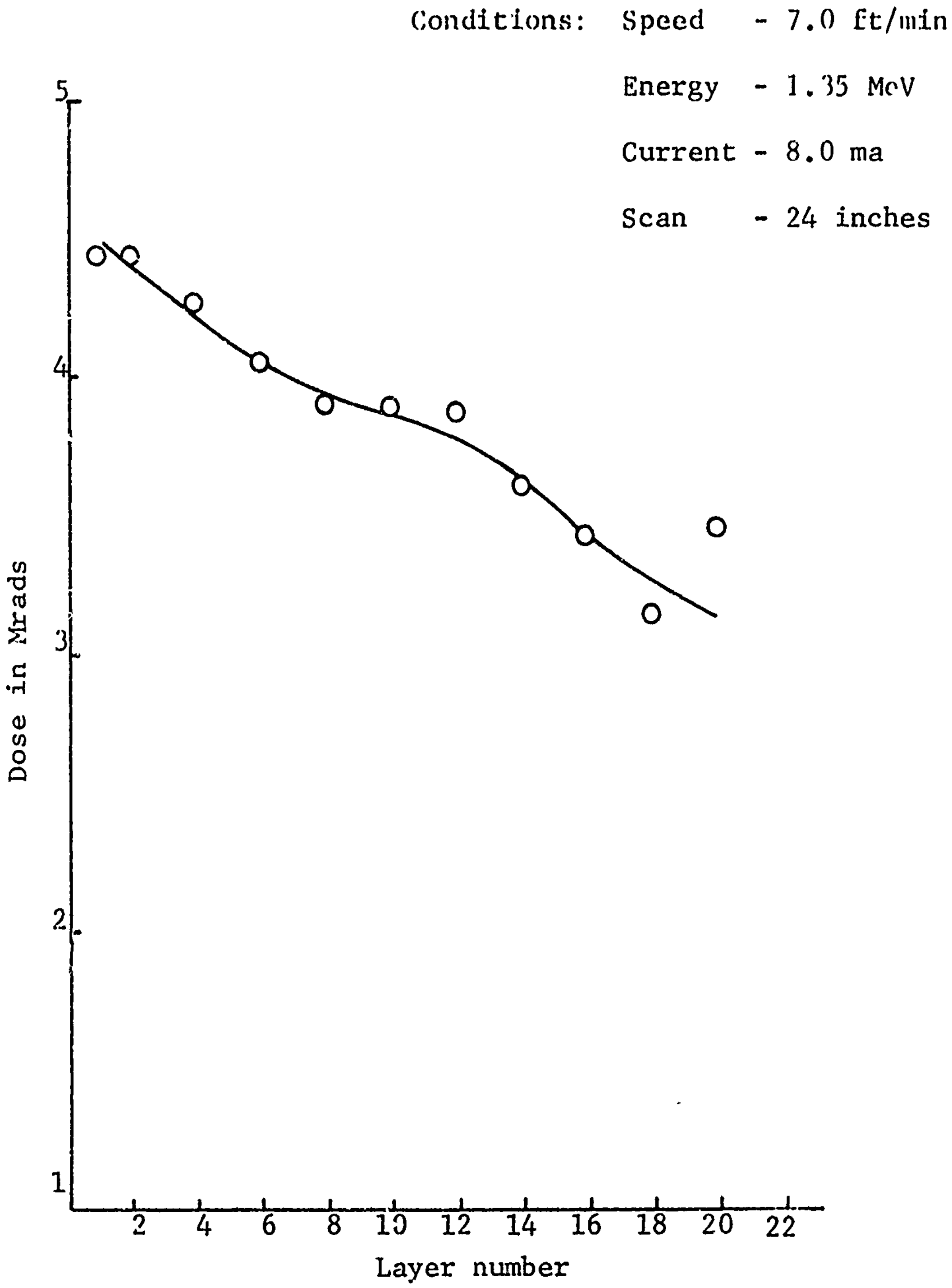
Layer No.	% Trans-mittance	Dose (Mrads)	% Trans-mittance	Dose (Mrads)	% Trans-mittance	Dose (Mrads)	Average Dose (Mrads)
1	39.0	4.5	38.0	4.17	38.0	4.17	4.23
2	39.0	4.0	38.5	4.3	38.5	4.3	4.36
3	-	-	-	-	-	-	-
4	36.5	3.75	35.5	3.5	36.5	3.75	3.67
5	-	-	-	-	-	-	-
6	37.5	4.0	38.0	4.17	38.0	4.17	4.11
7	-	-	-	-	-	-	-
8	35.0	3.25	33.0	2.65	32.0	2.4	2.77
9	-	-	-	-	-	-	-
10	36.0	3.5	38.0	4.17	36.0	3.5	3.72
11	-	-	-	-	-	-	-
12	35.5	3.42	36.0	3.5	36.0	3.5	3.47
13	-	-	-	-	-	-	-
14	35.5	3.42	35.0	3.25	33.0	2.65	3.11
15	-	-	-	-	-	-	-
16	35.0	3.25	35.0	3.25	34.0	2.9	3.13
17	-	-	-	-	-	-	-
18	33.0	2.65	35.0	3.25	34.5	3.0	2.97
19	-	-	-	-	-	-	-
20	34.0	2.9	34.0	2.9	33.5	2.75	2.85

TABLE 3-7

Dose obtained in a given layer for 3.0 mil film traveling at 7.0 ft/min across the electron beam

Beam Conditions:	Scan	-	24 in.
	Current	-	8 ma
	Energy	-	1.35 MeV

Layer No.	% Trans-mit-tance	Dose (Mrads)	% Trans-mit-tance	Dose (Mrads)	Average Dose (Mrads)
1	34.0	2.9	36.0	3.5	3.2
2	36.0	3.5	37.0	3.8	3.65
3	-	-	-	-	-
4	35.0	3.25	34.5	3.0	3.13
5	-	-	-	-	-
6	36.0	3.5	36.0	3.5	3.50
7	-	-	-	-	-
8	35.0	3.25	36.0	3.5	3.37
9	-	-	-	-	-
10	34.0	2.9	36.0	3.5	3.70
11	-	-	-	-	-
12	36.0	3.5	34.5	3.0	3.25
13	-	-	-	-	-
14	36.0	3.5	35.5	3.42	3.46
15	-	-	-	-	-
16	35.5	3.42	33.5	2.75	3.59
17	-	-	-	-	-
18	34.0	2.9	32.0	2.5	2.7
19	-	-	-	-	-
20	34.0	2.9	32.0	2.5	2.7



Conditions: Speed - 7.0 ft/min
Energy - 1.35 MeV
Current - 8.0 ma
Scan - 24 inches

Figure 3-17 Dose-Layer Curve For 20 Layers of One Mil Film

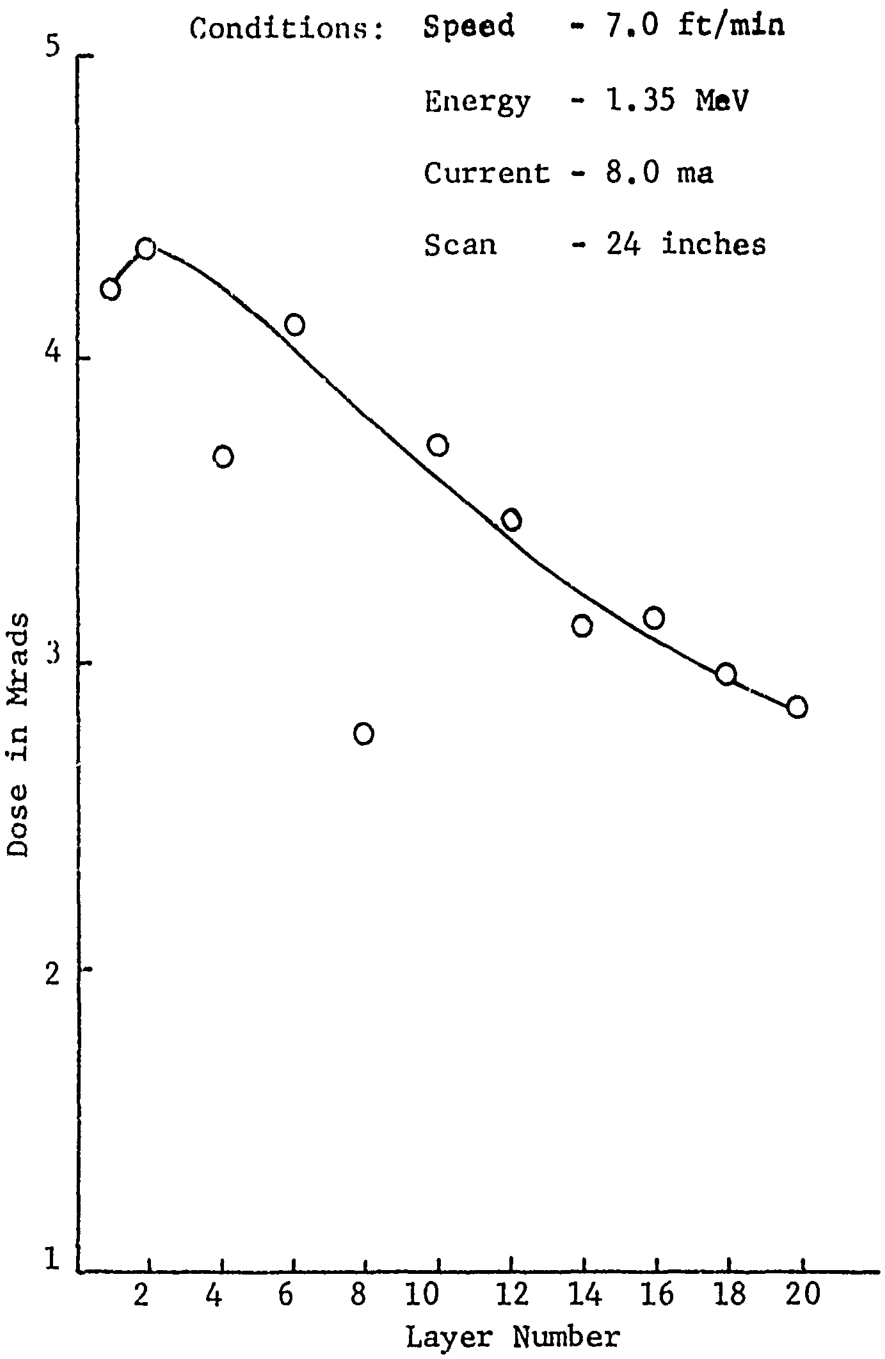


Figure 3-18 Dose-Layer Curve For
20 Layers of Two Mil Film.

Condition: Speed - 7.0 ft/min
Energy - 1.35 MeV
Current - 8.0 ma
Scan - 24 inches

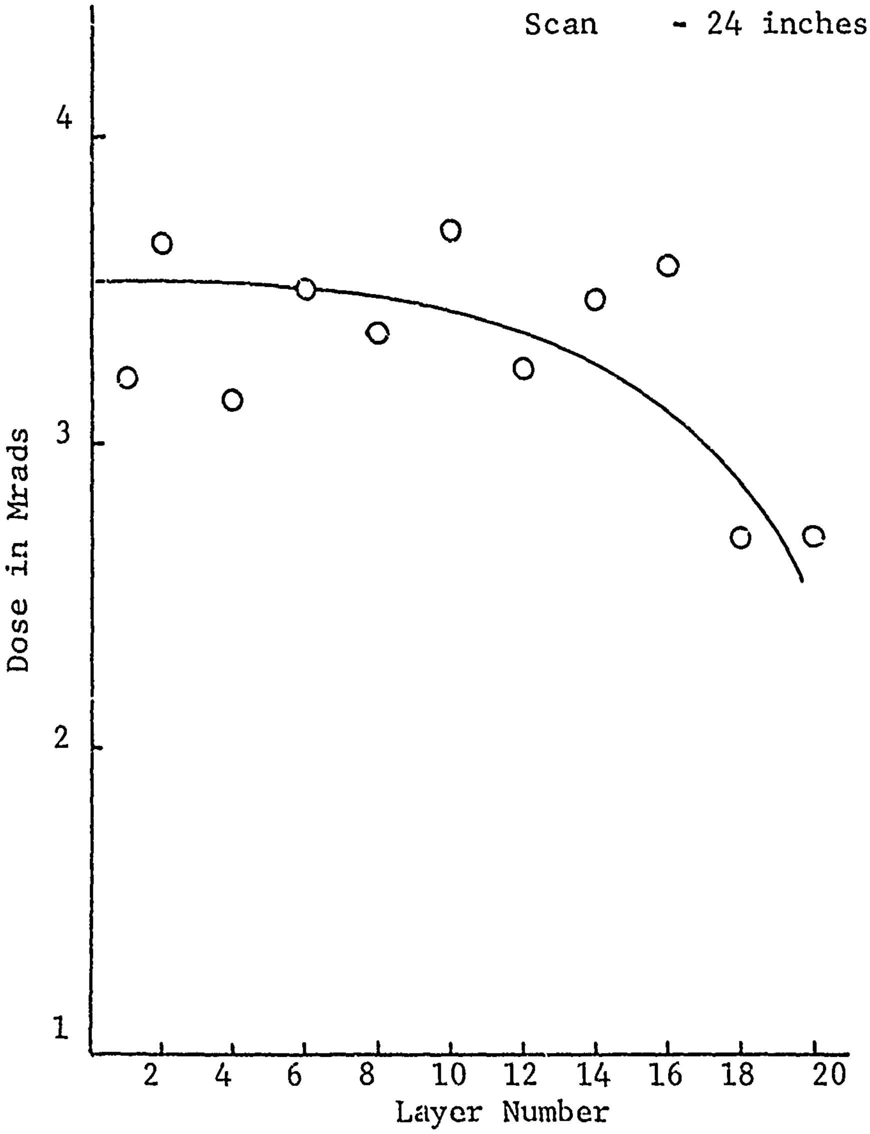


Figure 3-19 Dose-Layer Curve For 20 Layers of Three Mil Film

Since the total dose is also directly proportional to the residence time of the film in the field of the beam and hence inversely proportional to its velocity, the velocity may be decreased to achieve 90 Mrads. The required velocity for 90 Mrads is therefore:

$$v = v_o \frac{Do}{90}$$

where v_o = 7.0 ft/min, and v for 1, 2 and 3 mil films is:

5.91 ft/min for 1 mil film
5.58 ft/min for 2 mil film
5.12 ft/min for 3 mil film.

From this data estimated production rates for each arrangement should be:

5.91 ft/min x 1 = 5.91 ft/min
for 1 mil film

5.58 ft/min x 2 = 11.96 ft/min
for 2 mil film (2.1 mil layers)

5.12 ft/min x 3 = 15.36 ft/min
for 3 mil film (3.1 mil layers)

The third method of increasing the production rate would be to increase the length of travel, i.e. increase the number of times the film is festooned in front of the beam.

2.3.4 Alternate Radiation Source

Prior to design of the production unit for crosslinking polyethylene, a second electron accelerator facility was investigated. The accelerator was at Columbia Research Corporation of Gaithersberg, Md.. The accelerator produces at 2.5 MeV, 10 milliampere electron beam. Its high voltage power supply is essentially a cascade generator, operating on a frequency of 140 kH. The accelerator itself and the associated power supplies are located in a tower so that the beam is accelerated in a vertical direction and is spread on the ground floor by means of a "horn" that sweeps an area varying in width between 24 and 48 inches.

Doses were determined by methods similar to those used at RDI. In addition, radiation measurements have often been exchanged between Columbia Research and the National Bureau of Standards, where they are checked for absorbed dose by means of calormetric methods. Dosimetry measurements have been made at Columbia Research showing the dose-depth distribution for 2.5 MeV electrons (Figure 3-19) and the dose variation with length of their scan horn (Figure 3-20). This last curve shows that sheets of film with widths of up to about 28 inches may be uniformly irradiated. The increase of dose at the ends of the scan occurs because the beam is swept across the horn by an oscillating magnetic field and the beam does not instantly reverse when it reaches the end of the horn but has a slight dwell time there. The radiation setup at Columbia Research is physically adequate for the performance of the desired radiation.

Since this unit can give 2.5 MeV electrons a larger number of film layers can be penetrated by the beam. To evaluate this machines capability a crosslinking run was made at Columbia Research Corporation using the technique developed at RDI. This was done for one, two and three mil film spaced .8 inches apart. Since the beam energy was 2.5 MeV, irradiation of a 53 layer thickness of film was evaluated. This was passed under the beam at 7.0 ft/minute.

The first film layer was positioned one (1) inch from the face of the beam. The irradiation machine settings for all the runs were 2.5 MeV, 10 ma beam current and 33.5 inches scan width. Blue cellophane dosimeters were placed on top of each layer of film to measure the dose obtained at each layer while passing through the beam. Passing a set of layers of film across the beam at a given rate simulates the function of a continuous festooned irradiation rig. If the total dose is known by summing the doses for each layer, and if the velocity of travel of the film past the irradiation horn is known, it is possible to predict the film velocity necessary to impart 90 Mrads under the same condition by using the equations noted in the previous section.

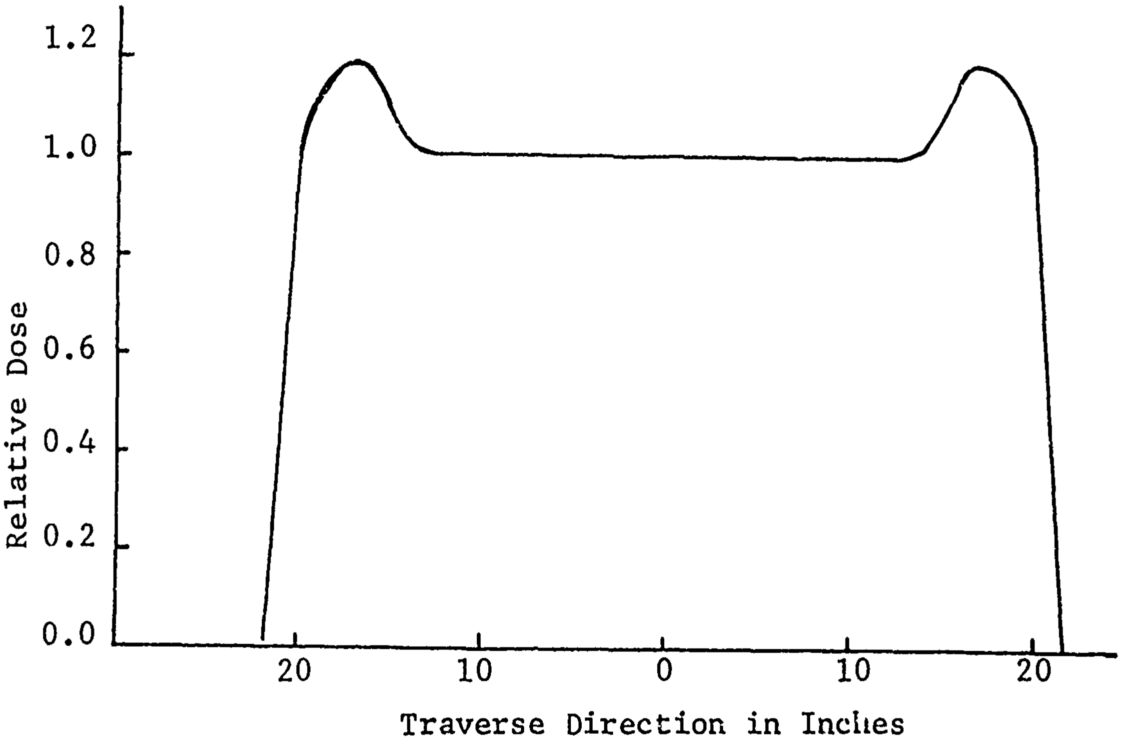


Figure 3-20 Relative Dose Vs Traverse Direction

The results of these runs are given in Tables 3-8 through 3-10 and Figures 3-21 through 3-23. Summing the doses of each layer and applying the velocity formula to determine the velocity necessary to give 90 megarads yields; 16.16 feet/minute, 15.19 feet/minute and 15.95 feet/minute for the one, two and three mil thick samples. Furthermore, since the beam width is 33.5 inches a 24 inch wide film can be irradiated. Therefore the production rate possible with this accelerator is; 33.52 feet/minute, 60.76 feet/minute and 95.70 feet/minute for one, two and three mil film.

A comparison of the production rates at both Columbia Research and Radiation Dynamics is given in Table 3-11 along with the estimated time it would take to produce 100,000 square feet of film irradiated to 90 Mrads.

The data given in Table 3-11 indicates that per day a significantly greater amount of crosslinked film could be produced by using the Columbia Research Facility. The rental cost and location of this facility, however, were such that the unit cost of film produced would be much greater. In addition, by using the RDI facility a second or third shift could attend the crosslinking without requiring subsistent or overtime labor costs. The fact that RDI is located in our immediate vicinity, the lower operating costs and the "experimental nature" of the first production run led us to select using this facility. In addition, R A I has used this electron accelerator and is familiar with its operation and sustained capability.

2.3.5 Irradiation Atmospheres

Tests conducted on film showed a distinct difference on crosslinking due to the atmosphere in which the polyethylene was irradiated. On most previous works used to synthesize separators, nitrogen atmospheres were used during the irradiation. In order to determine the effect of atmosphere (N_2 or air) on the base film, Bakelite DFD-0602 was irradiated in nitrogen and in air. A tensile test was then used to determine the modulus of elasticity of the material above its crystalline melting point. The modulus of elasticity above the crystalline melting point of a crosslinked material gives a measure of the crosslinking density of an irradiated material - the higher the modulus the higher the crosslinking density. The following data was found for the 1.0 mil Bakelite DFD-0602 film crosslinked to 90 Mrads:

TABLE 3-8

Data for Dose obtained in a given layer for 1.0 mil film traveling at 7.0 ft/min. across the electron beam.

Beam Conditions: Scan - 33.5 in.
Current - 10 ma
Energy - 2.5 Mev

Layer No.	% Trans-mit-tance	Dose (Mrads)	% Trans-mit-tance	Dose (Mrads)	Average Dose (Mrads)
1	43.5	5.4	41.0	4.8	5.1
2	44.0	5.5	45.0	5.3	5.7
4	49.0	7.3	49.0	7.3	7.3
6	47.5	6.7	45.0	5.8	6.3
8	44.0	5.5	46.0	6.2	5.9
10	42.5	5.2	46.5	6.3	5.8
12	41.0	4.8	43.0	5.3	5.0
14	43.5	5.4	43.5	5.4	5.4
16	44.5	5.7	44.0	5.5	5.6
18	39.0	4.2	40.5	4.6	4.4
20	39.5	4.3	38.0	3.9	4.1
22	41.0	4.8	42.5	5.1	5.0
24	40.0	4.5	39.5	4.3	4.4
26	36.5	3.5	39.0	4.2	3.9
28	38.0	3.9	37.0	3.7	3.8
30	37.5	3.8	36.5	3.5	3.7
32	35.5	3.3	36.0	3.4	3.4
34	36.5	3.5	35.5	3.3	3.4
36	34.0	2.8	35.5	3.3	2.6
38	34.0	2.8	33.5	2.7	2.8
40	33.5	2.7	33.5	2.7	2.7
42	33.0	2.5	33.5	2.7	2.6
44	33.5	2.7	33.0	2.5	2.6
46	33.0	2.5	Tape to small		2.5
48	32.0	2.3	32.0	2.3	2.3
50	32.0	2.3	32.0	2.3	2.3
52	31.0	2.0	31.0	2.0	2.0
53	31.0	2.0	31.0	2.0	2.0

TABLE 3-9

Data for Dose obtained in a given layer for 2.0 mil film traveling at 7.0 ft/min. across the electron beam.

Beam Conditions: Scan - 33.5 in.
Current - 10 ma
Energy - 2.5 MeV

Layer No.	% Transmittance	Dose (Mrads)	% Transmittance	Dose (Mrads)	Average Dose (Mrads)
1	41.0	4.8	42.0	4.8	4.8
2	44.0	5.5	44.0	5.5	5.5
4	43.0	5.3	42.0	5.0	5.2
6	43.5	5.4	45.0	5.8	5.6
8	43.0	5.3	45.0	5.8	5.5
10	43.0	5.3	44.0	5.5	5.4
12	42.5	5.2	39.0	4.2	4.5
14	41.0	4.8	43.0	5.3	5.1
16	39.0	4.2	42.0	5.0	4.6
18	40.0	4.5	42.0	5.0	4.8
20	38.5	4.0	39.0	4.2	4.1
22	37.5	3.8	42.0	5.0	4.6
24	38.5	4.0	40.5	4.6	4.3
26	38.0	3.9	40.0	4.5	4.2
28	37.5	3.8	36.5	3.5	3.7
30	36.0	3.4	36.5	3.5	3.5
32	35.5	3.3	35.0	3.1	3.2
34	35.0	3.1	35.0	3.1	3.1
36	32.0	2.2	32.5	2.4	2.3
38	33.0	2.5	33.0	2.5	2.5
40	33.0	2.5	33.5	2.7	2.6
42	32.0	2.2	32.5	2.4	2.3
44	31.0	2.0	31.5	2.1	2.1
46	31.0	2.0	29.5	1.6	1.8
48	30.0	1.8	30.0	1.8	1.8
50	29.0	1.5	27.5	1.0	1.3
52	30.5	1.9	29.0	1.5	1.7
53	29.5	1.6	28.0	1.2	1.4

TABLE 3-10

Data for Dose obtained in a given layer for 3.0 mil film traveling at 7.0 ft/min. across the electron beam.

Beam Conditions: Scan - 33.5 in.
Current - 10 ma
Energy - 2.5 MeV

Layer No.	% Transmittance	Dose (Mrads)	% Transmittance	Dose (Mrads)	Average Dose (Mrads)
1	41.0	4.8	45.0	5.8	5.3
2	44.9	5.8	44.0	5.5	5.6
4	45.5	6.0	46.5	6.3	6.2
6	47.5	7.0	47.0	6.5	6.8
8	46.5	6.3	48.5	7.2	6.7
10	45.5	6.0	45.5	6.0	6.0
12	--	--	45.5	6.0	6.0
14	46.0	6.2	45.0	5.8	6.0
16	45.0	5.8	44.5	6.0	5.9
18	44.0	5.5	44.5	6.0	5.8
20	41.5	4.9	42.0	5.0	5.0
22	41.0	4.8	37.5	3.8	4.3
24	40.0	4.5	39.5	4.3	4.4
26	38.5	3.3	35.5	3.3	3.3
28	36.0	3.4	37.5	3.8	3.6
30	35.0	3.1	38.0	3.9	3.5
32	37.0	3.7	36.0	3.4	3.6
34	35.0	3.1	33.5	3.3	3.2
36	32.5	2.4	34.0	2.8	2.6
38	33.0	2.5	30.0	1.8	2.2
40	32.5	2.4	32.5	2.4	1.2
42	29.5	1.6	30.5	1.9	1.8
44	31.0	2.0	30.5	1.9	2.0
46	31.0	2.0	29.0	1.5	1.8
48	30.5	1.9	30.0	1.8	1.9
50	29.5	1.6	29.0	1.5	1.6
52	29.0	1.5	28.5	1.3	1.4
54	30.0	1.8	29.5	1.6	1.7

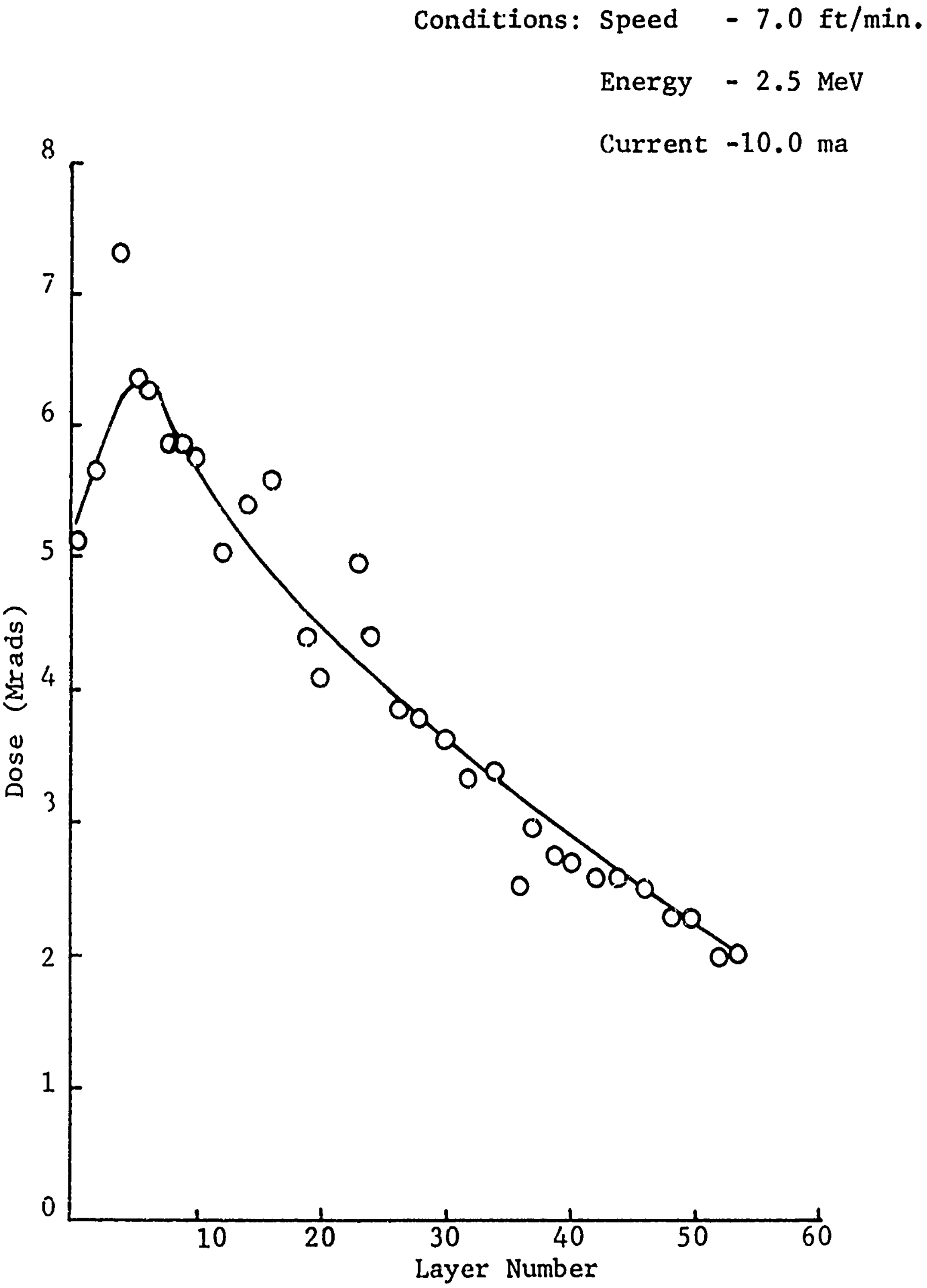


Figure 3-21 Dose Layer Curve for Arrangement of 1 Mil Film Spaced 0.8 Inch Apart Passing an Electron Beam.

Conditions: Speed - 7.0 ft/min.
Energy - 2.5 MeV
Current - 10.0 ma

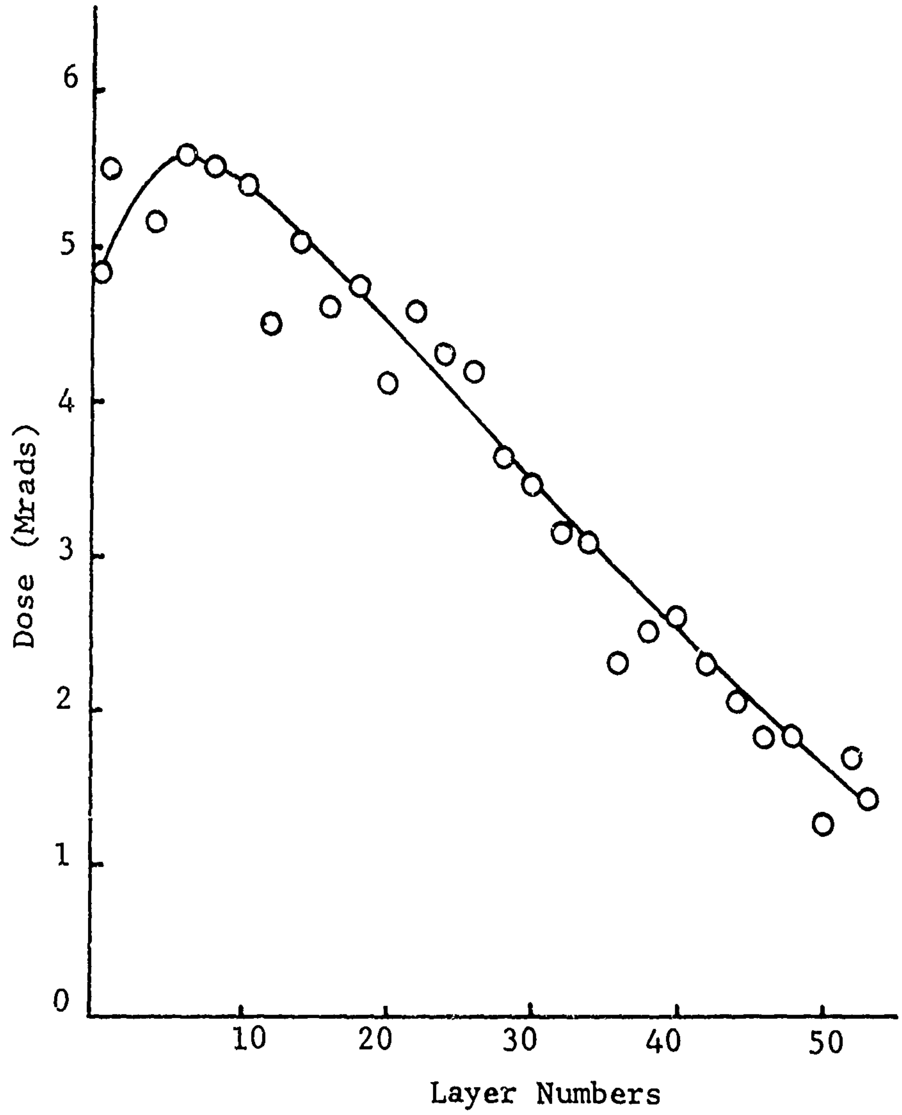


Figure 3-22. Dose Layer Curve for Arrangement of 2 Mil Film Spaced 0.8 Inch Apart Passing an Electron Beam.

Conditions: Speed - 7.0 ft/min.
Energy - 2.5 MeV
Current - 10.0 ma

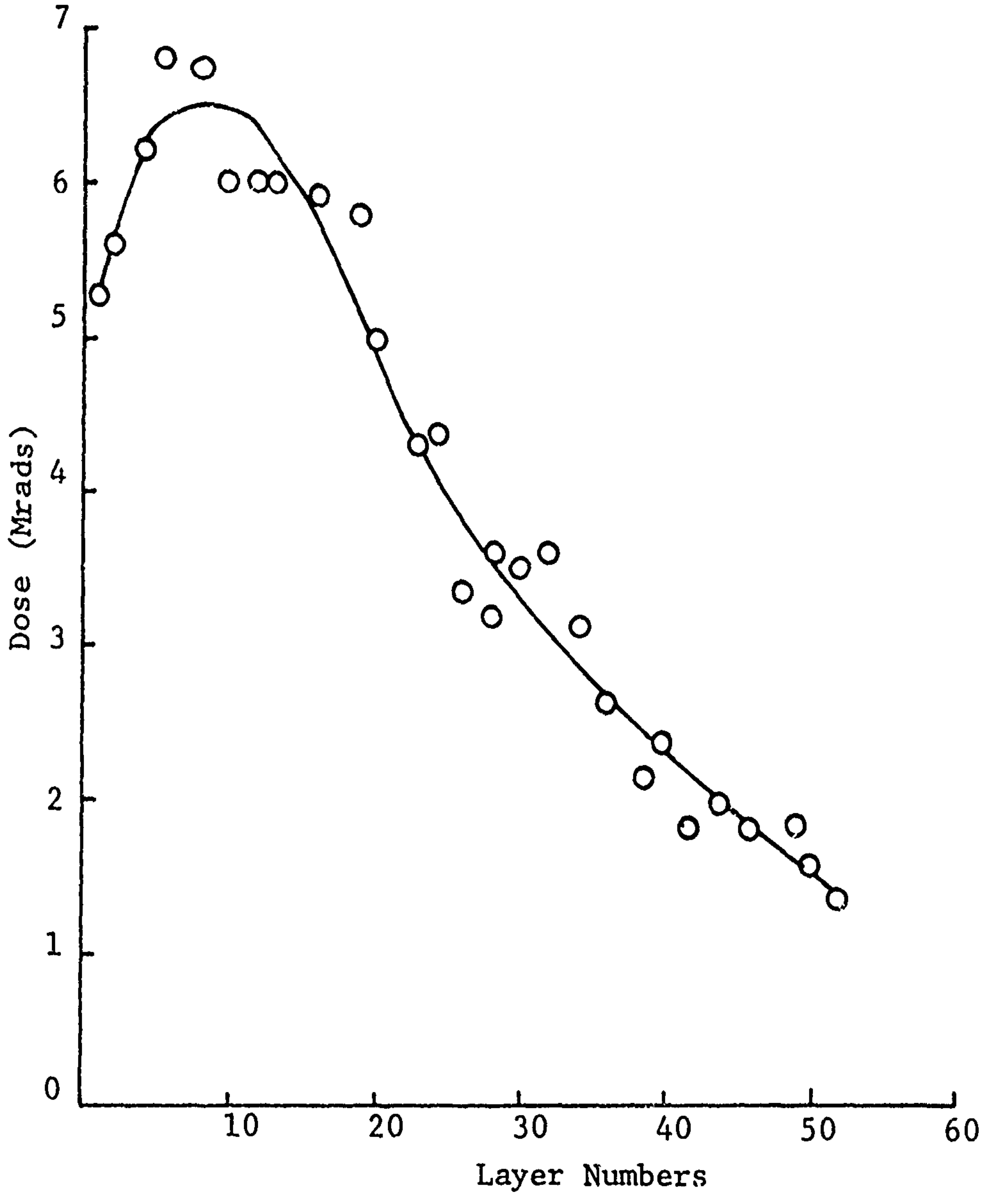


Figure 3-23. Dose Layer Curve for Arrangement of 3 Mil Film Spaced 0.8 Inch Apart Passing an Electron Beam.

TABLE 3-11

Comparison of Production Rates and Irradiation Time at the Irradiation Facilities of RDI and Columbia Research

Thick-ness	Actual velocity (v) (ft/min)	Thickness Factor	Width Factor	Estimated Production ft/min.	Estimated Production ft/hr.	Estimated Production ft/day	*7 Hour Day No. Days
Radiation Dynamic Incorporated							
1	10.22	1	2	20.44	1,226.4	8,584.8	11.6
2	9.35	2	2	37.40	2,244.0	15,708.0	6.4
3	7.95	3	2	47.70	2,862.0	20,034.0	5.0
Columbia Research							
1	16.76	1	2	33.52	2,011.2	14,078.4	7.10
2	15.19	2	2	60.76	3,645.6	25,519.2	3.92
3	15.95	3	2	95.70	5,742.0	40,194.0	2.49

*This assumes 7 hours of actual irradiation

Atmosphere	Modulus of Elasticity Machine Direction (psi)	Transverse Direction (psi)	Average (psi)
Air	102	65	84
N_2	328	213	271

This data indicates that in air the extent of crosslinking is less for the same amount of irradiation. The decrease in crosslinking for irradiations conducted in air is, in all likelihood, due to an increase in scission caused by oxidative degradation.

Based on these findings all irradiations were performed in a nitrogen environment and the festooning unit was designed to provide with a mechanism to permit nitrogen sparging.

2.3.6 Production Crosslinking

Analysis of the runs from crosslinking at RDI using the prototype unit yielded sufficient data to indicate the features required for construction of a production crosslinking unit. This data could also be used to establish the initial irradiation procedure.

The crosslinking unit was built in three sections, utilizing, where possible, standard equipment. The three basic units are a standard driven pay-out or let-off stand modified with a dancer arm for tension control, a festooning section in which the film traverses in front of the irradiation beam, and a take-up unit. Since this unit might also be used in winding the bundles of crosslinked film with the interlayers, the take-up stand was designed with two wind-up shafts which were driven by a single motor. The two shafts could be driven at the same speed or allowed to free-roll. The take-up unit also had a dancer arm for tension control. This dancer was placed on the legs of the festooning unit as shown in Figure 3-24.

The take-up unit was mounted on two "V" shaped rails and was fitted with wheels which would permit movement perpendicular to the direction of travel of the film. An electric eye was mounted on the stationary festooning unit and functioned as an edge guide. The eye controlled a motor drive which moved the take-up unit in the V grooves and kept the film positioned on-center. This unit is seen in Figure 3-25.

Calculations and data indicated that if the film was festooned in front of the beam twenty times and the beam current was 8 ma, 90 Megarads could be imparted to the film when the film was driven at about 7.5 feet/minute (Figure 3-9).

The radiation facility at RDI placed certain space restrictions on the design of the crosslinking unit. The distance available for the crosslinking machine was 8 feet, 7 inches. This allowed for a 14 inch diameter bundle on the wind-up stand and assumed a 2 inch clearance between the bundle and the wall. It also allowed 7½ inches between the window of the radiation horn and the window in the festooning unit.

The radiation horn center is 44 inches above ground and to make use of the space under the horn the pay-out unit was designed to a height of 24 inches. The festooning unit dimensions had to be cut from those used in the prototype. The critical change was a reduction in the distance between rollers. In the prototype, the top and bottom rollers were spaced 52 inches apart, the new festoon unit was decreased in height to 24 inches, and the length was set at 34 inches. Two 26 inch legs, 6 inches wide, were welded on to the frame of the festooning unit. The unwind stand was 38 inches in length and its front height was under 26 inches which allowed part of it to be positioned under the festooning unit. A schematic of the crosslinking machine is given in Figure 3-24.

The three components were mounted on 4½ inch steel beams which were tied together by 46 inch long strips on which the pay-out stand was mounted (Figure 3-25). Four wheels were placed on the bottom of the

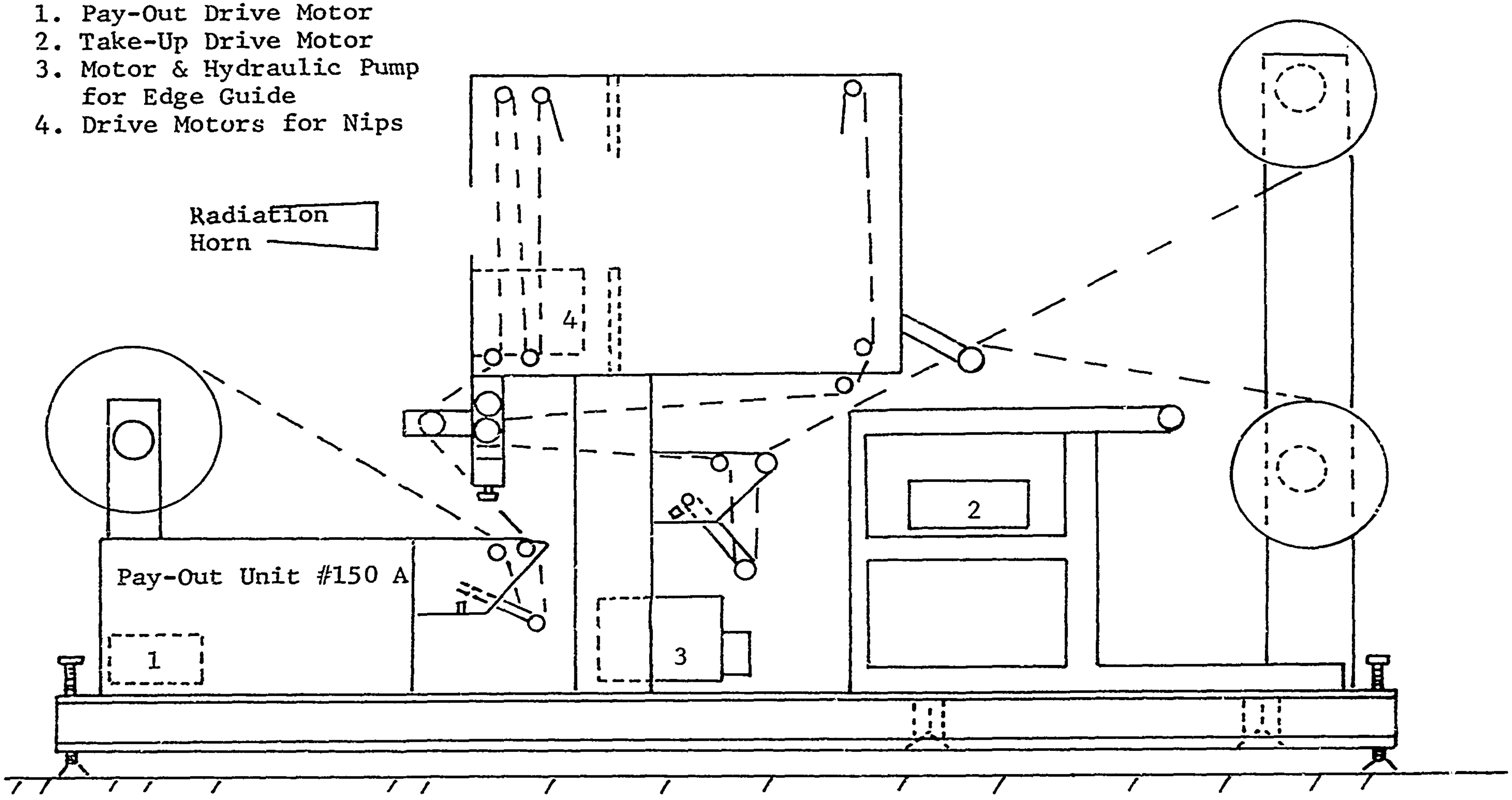


Figure 3-24. Schematic of Crosslinking Unit.

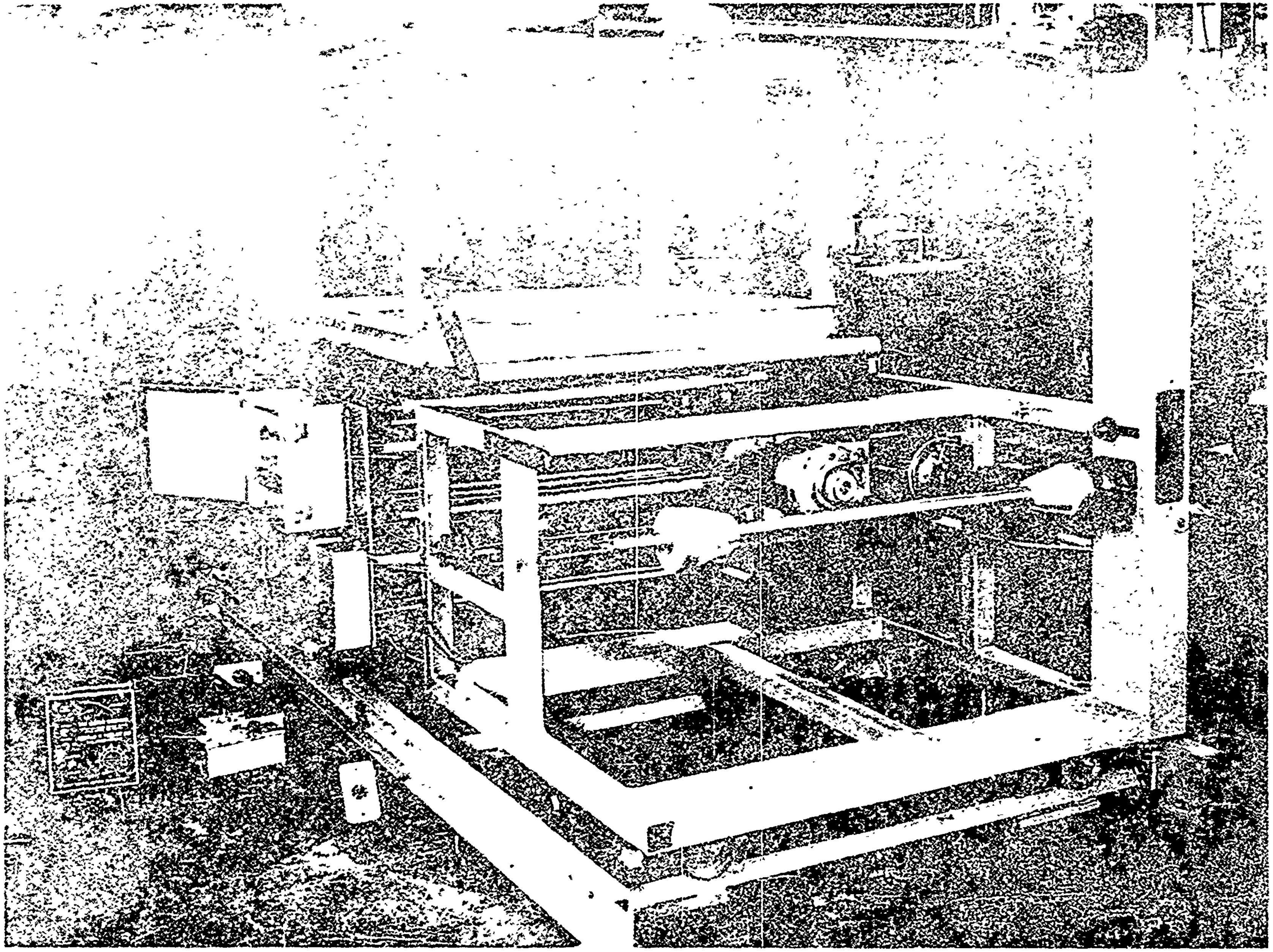


Figure 3-25. Crosslinking and Film Winding Equipment - Rear View.

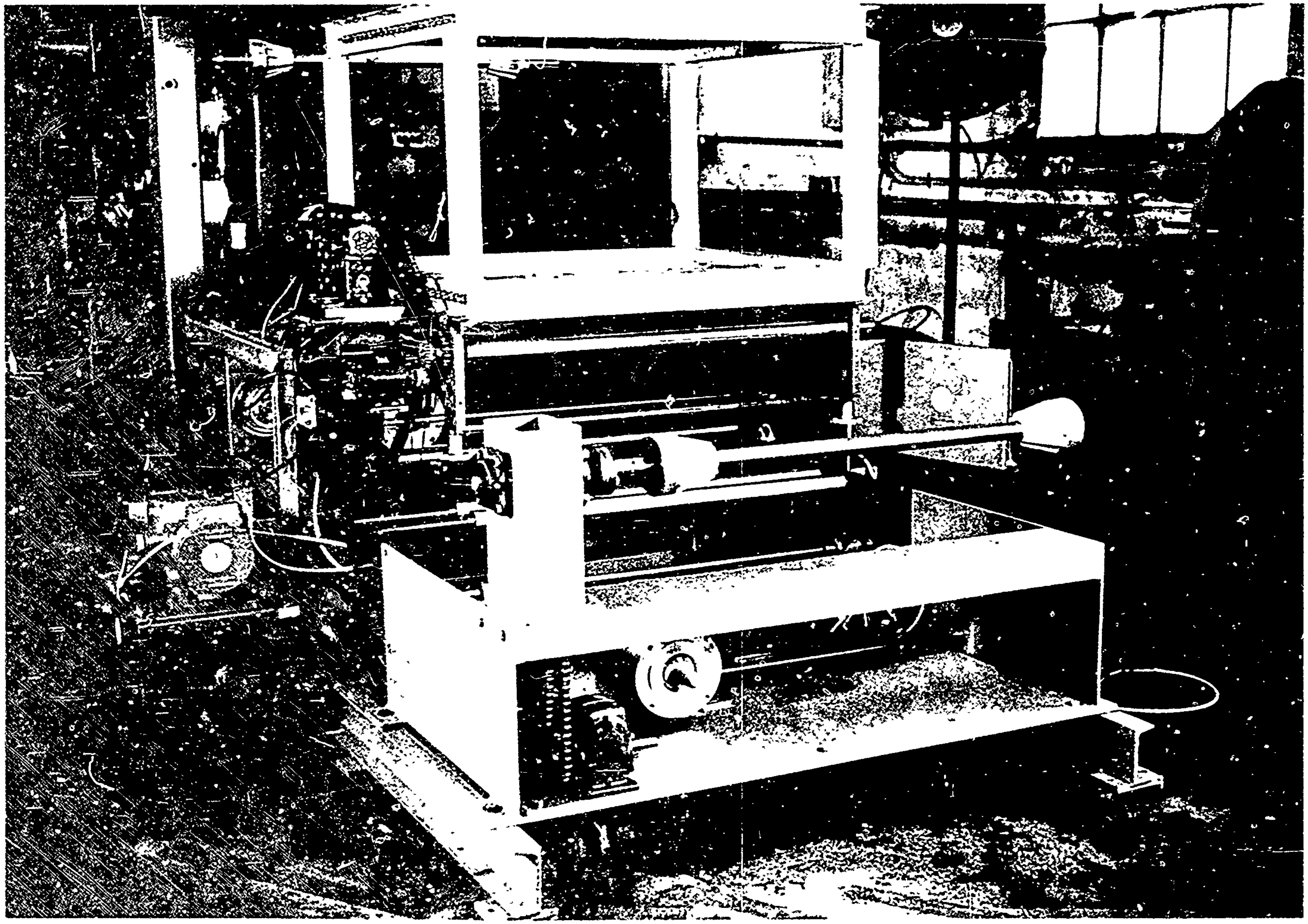


Figure 3-26. Crosslinking and Film Winding Equipment - Front View.

take-up unit and this was mounted on inverted V channels which were welded inside the 4½ inch steel frame. The wheels were grooved to fit the V channels and positioned to allow the take-up unit to move perpendicular to the direction of film travel. The festooning unit on 26 inch legs, was welded to the steel frame between the pay-out and take-up units. Figure 3-24 indicates the position of the three units.

Figure 3-24 also indicates the position of the dancer controls for the pay-out and take-up unit. Film from the pay-out roll is passed around the dancer on this unit then over a free rolling roller and into the festooning unit through a slit in the bottom of the box. It is then passed over 19 rollers (originally there were 20 rollers, one set was removed to allow a second window to be placed in the unit for heat control) and exits from the bottom of the unit at a point farthest from the electron beam. From here it goes through a set of motor driven rollers which pulls the film through the festooning unit as the pay-out unit unwinds film. The film then passes around the second dancer and is taken over an idler roller mounted on the exterior of the festooning unit. Here the film, if it is as two single lay flat sheets, could be separated and wound on the two take-up shafts. Since we were irradiating tubing, only the top wind up shafts was used to wind the film.

Four positioning screws were mounted through the 4½ inch steel frame on each corner. Provisions were also made to easily mount and remove wheels set under the frame. The wheels were used to roll the unit into position in front of the radiation horn. They were then removed and the positioning screws were used to line the center of the window in the festooning unit with the centerline of the titanium window in the accelerator horn. The window on the festooning unit was positioned 7½ inches from accelerator window to allow for a shutter which had to be kept over the radiation window. This shutter was opened only when the film was being irradiated.

There were four separate drive motors on this machine, the pay-out drive, the wind-up drive, a motor to drive the nips which pulled the films through the festooning unit as the pay-out unit fed the film in, and a drive motor coupled to a hydraulic piston which was controlled by the electric-eye and used to keep the film travel positioned on center. Figure 3-24 shows the location of these units. The motor and hydraulic pump for edge guide is seen on the left in Figure 3-26. This is mounted under the festooning unit during operation. The control panels are seen in Figure 3-27 which also shows the festooning unit closed and appropriate piping for water cooling the jacketed unit. Figure 3-28 is a picture of the speed control module which was used to set film speed and tension from outside the vault.

Evaluation of two mil film with the prototype unit, which had 10 rollers on top and 10 on bottom, indicated a linear speed of 9.35 feet/minute was required to impart 90 Mrads to the film. Speed control of the film is essential to obtain uniformly crosslinked film. A ± 3% deviation in speed is the maximum permissible on 90 Mrads film. This would give a permissible range of 87.3 - 92.7 Mrads or a ± 5 Mrad spread. The absolute variation in speed control, therefore, can not exceed ± ¼ foot per minute when the film is irradiated at 9.35 feet/minute.

The construction of the production unit was contracted to Progressive Machine Company Inc. of Patterson, New Jersey. Upon completion, the crosslinking unit was tested on site at the manufacturer's plant prior to acceptance. The following tests were performed:

The machine was run at speed from 0 - 200 ft/min. Checks were made on the tension of the film in the festooning unit and on rolls on the take-up unit. It was found that the machine kept the film under light tension and rolled the film on the take-up loosely. Stretching was found to be less than .25% at 10 ft/min. Speed control was found to be constant to better than ± 0.5 ft/min., the limit of accuracy of the tachometer used. A more sensitive tachometer, which is accurate to ± 0.2 ft/min. was obtained and installed.

The web guide unit functioned satisfactorily, keeping the film uniformly centered in the festooning

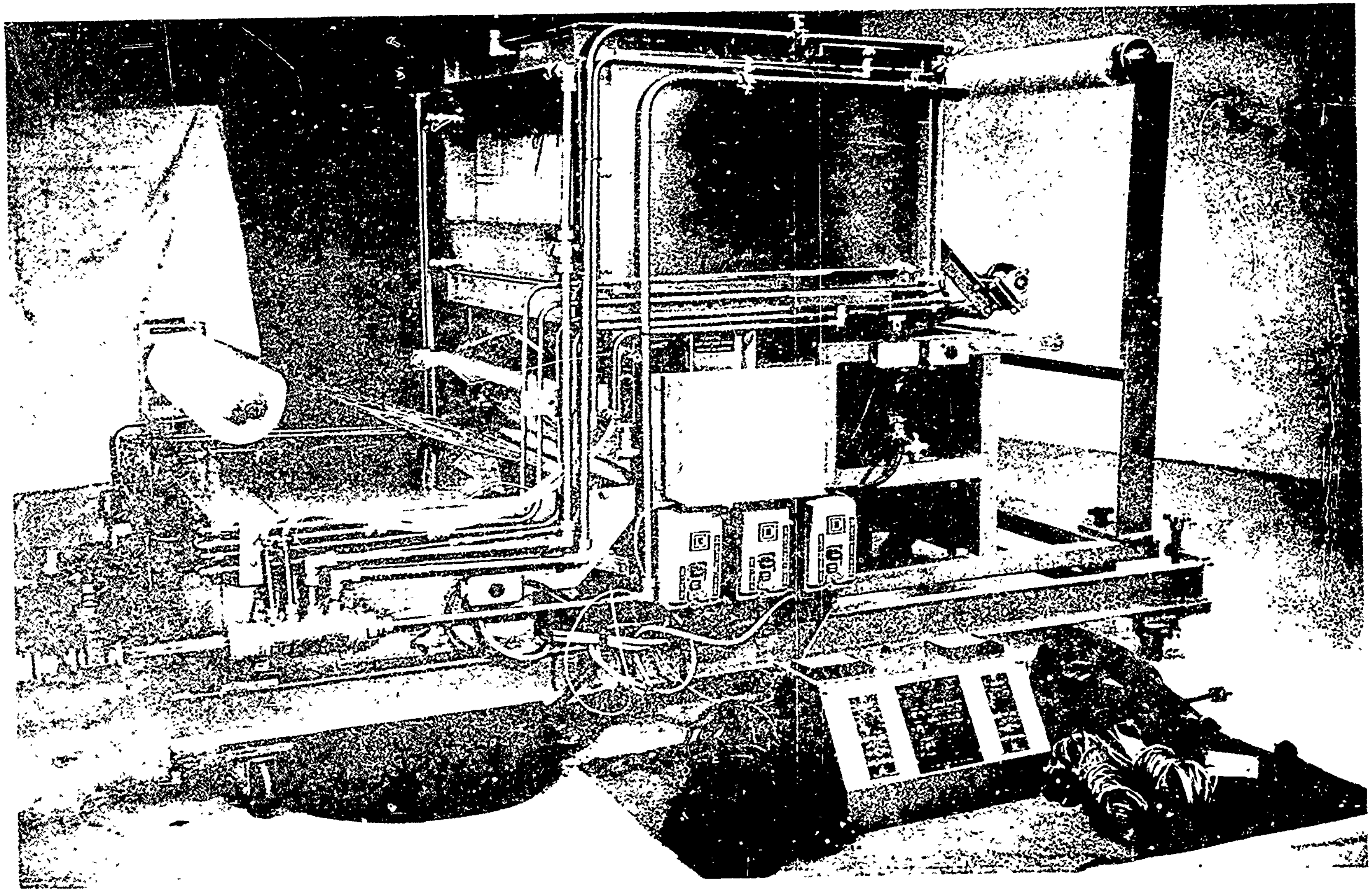


Figure 3-27. Modified Crosslinking Unit.

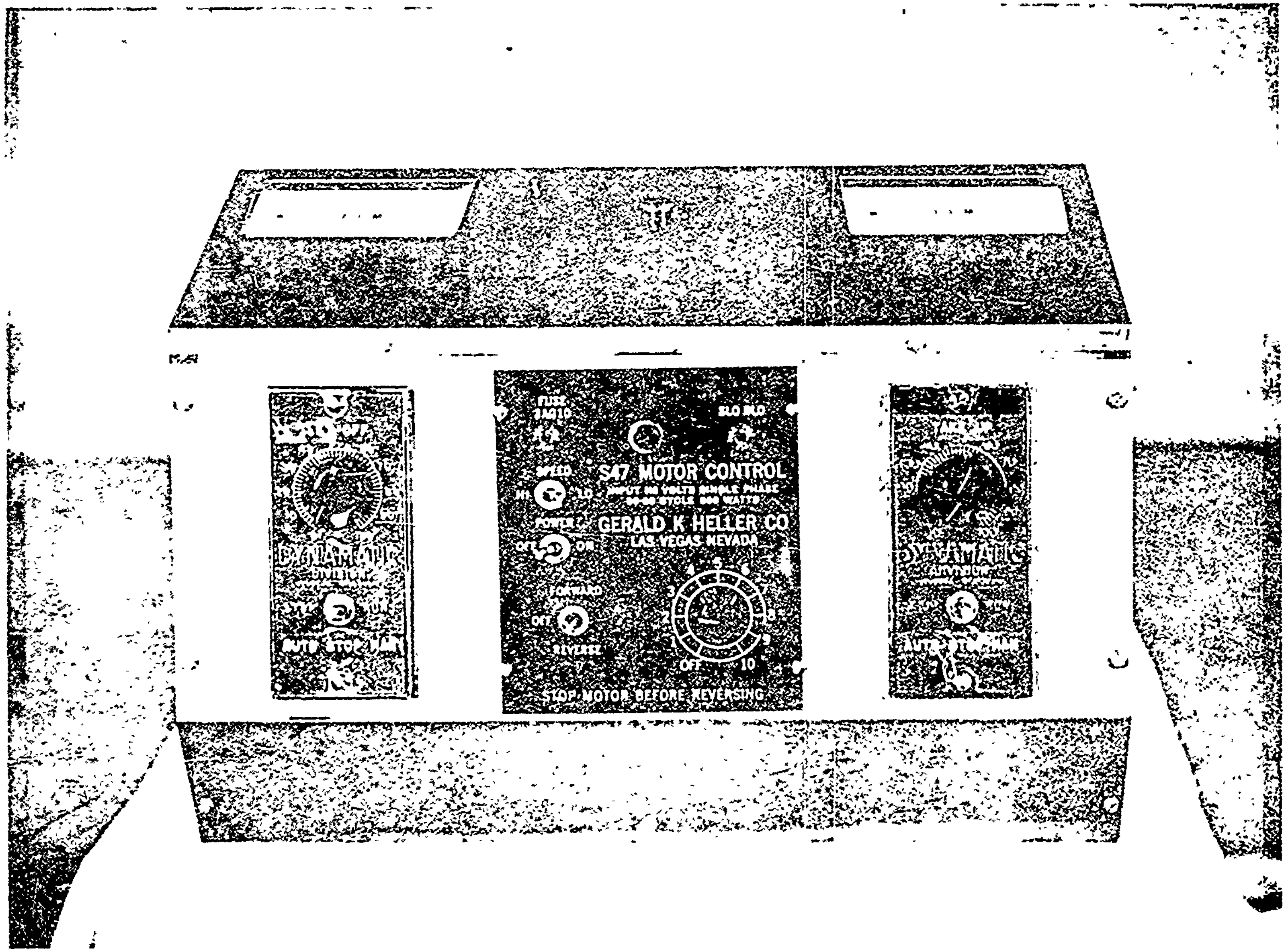


Figure 3-28. Speed Control Module.

rig and permitting winding of the film uniformly up to speeds of 70 ft/min. It was additionally found that the web guide can align 5,000 ft. rolls of film and cheesecloth.

The final completed and tested unit was delivered in early July of 1971. At RAI, the control and drive parts of the machine were shielded against excessive irradiation with lead sheeting. Additionally, the machine was put through "dry runs" to develop operating procedures for the actual irradiation. Quality control procedures, based on hot creep compliance tests, were also evaluated as a rapid method of evaluating the total dose a film receives per pass during irradiation. This was to be used on site to establish actual crosslinking as a check on dosimetry but the method proved to be too sensitive to thermal control for on site use.

Some modifications which were made at this time included:

- relocation of the hydraulic equipment which controls the edge guide system from the outboard side to underneath the festooning unit where it is protected from radiation and is out of the way of the operator;
- an additional roller was added to the base of the festooning unit, to avoid having the film rub against the structure of the festooning unit;
- an adjustable "bow" roller was added in front of the take-up spindle to remove wrinkles from the film before winding.

The first crosslinking run was made with the production crosslinking rig and it was found that further modifications were necessary before the film could be continuously crosslinked under production conditions. The main problem encountered was heat build-up on the festooning rollers and on the frame. The heat build-up was probably due to the radiation beam being more diffused than anticipated, i.e., spreading out in height more than the expected one inch per inch distance from the scan horn. This spread caused the last fifteen rollers to heat up to about 100°C. This, in turn, caused some of the rollers to seize, resulting in excessive tension built up on the film. The heat build-up additionally caused the film to block at wrinkles as it passed through the festooning unit. rendering it of no use for further processing. The problem of heat build-up was established by the direct measurement of the temperature on the back rollers and noting that there was little heat build-up when the radiation beam was diminished from 8 ma to 3 ma with the same film velocity and voltage. In addition, a velocity drop was observed within minutes after the beam was turned on due to the rollers seizing.

In general, the other units ran well under the irradiation conditions. A constant film velocity was possible when the unwind, take-up and dancer arm units were not overheated. The edge guide kept the film within the field of the beam at all times and kept the film neatly wound on the take-up roll.

The unit was modified after this run. Water-cooled jackets were placed in front of the rollers in the festooning unit to absorb the radiation and keep the rollers cool. In addition, bearings which rolled more freely were installed. The festooning frame also was water-cooled to insure a cool (room temperature) environment for irradiation. It is necessary to keep the irradiation temperature between 40-110°F since the temperature effect on crosslinking is small in this range.

The design of the cooling system permitted complete enclosure of the festooning unit. Two slits through which the film entered and exited the unit, were set in the bottom plate. In addition, another slit at the front end of the festooning unit permitted the film to be irradiated as it passed by the window. The water-cooled plates enclosed the festooning unit, thereby creating a box, which is readily filled with nitrogen gas. The nitrogen is fed in from the top of the unit and bleeds out at the slits. The film was in a nitrogen atmosphere during the irradiation process. The stainless steel plates and roller shields were water-cooled to dissipate heat rapidly. Nitrogen gas was fed into a "U" shaped tube at the top of the festooning module. Holes were drilled in this tube to permit the nitrogen gas to sparge the entire box.

Preliminary testing of the cooling plates in-house was satisfactory. The speed control shown in Figures 3-28 was also operated satisfactorily. A plot of the meter setting vs the actual measured film speed yielded a straight line with a slope of 0.91 which was used as a correction factor for determing actual line speed. This plot is shown in Figure 3-29. This value does not cause an error in the dose received by the film since the dose received is an experimentally determined value. The correction is necessary in determining the actual production rate and cost factors. A preliminary production run was attempted on film qualified under tasks two and eight using the parameter settings determined previously. These were: beam energy 1.3-1.4 MeV (in these runs 1.3 MeV was used), beam current 8.0 ma, scan width 24 inches and film speed setting 8.25 feet/minute. The front plate on the festooning unit was constructed with an 8 inch window. Under these conditions, with low nitrogen sparging rates and water cooling, excessive heating still occurred. This was evidenced initially by a decrease in line speed and then by complete stoppage of the film throughput after a short interval of continuous operation.

To compensate for the heat, a number of alternatives were possible. These included a decrease in beam current, doubling the film speed and irradiating twice, decreasing the window opening to prevent the radiation from striking the rollers and increasing the nitrogen flow. The first two alternatives resulted in a decrease in production rate. It was, therefore, decided to reduce the window opening, which decreased the total energy entering the festooning unit by 15%, and increase the liquid nitrogen flow through the heat exchanger. Using these modifications, the crosslinking unit was operated successfully on a continuous basis. The amount of liquid nitrogen required to do this, however, was significant and would increase the crosslinking cost of the film by approximately five cents per square foot.

Using the standard dosimeters, two runs were made to establish dose. Tables 3-12 and 3-13 give the results of these runs. After establishing parameters necessary to obtain a crosslinking dose of 90-95 Mrads, a continuous crosslinking run was undertaken. To sustain this operation, the nitrogen feed was set at an extremely high rate (50 lbs/in^2). This was liquid nitrogen pressure prior to entrance into the heat exchanger. The run was continued for approximately two hours and thirty-two hundred (3,200) feet of cross linked film was obtained. This film was checked and 2,500 feet was found to be acceptable for subsequent grafting. The remainder of the film had blocked due to a failure in the cycling of the cooling water on one of the side plates.

Based on an analysis of this run, it was established that the following modifications in the crosslinking unit were still necessary:

- Decrease the "window" at the front of the unit to 4½ inches in height.
- Individually cool the rollers with nitrogen gas to effect more efficient use of the gas.
- Raise the level of the top rollers 12 inches to remove them from the direct radiation of the beam and/or place a second "window" in the festooning unit. This approach would shield the back rollers from the diverging beam.

After a detailed analysis it was decided to install the second window, remove the cooling plates which were placed between rollers, decrease the front window to 4½ inches and to water-cool this window. An attempt to decrease the window to 4½ inches during a trial run by placing a strip of ¼ inch 24 ST aluminum on the 8 inch window resulted in melting the aluminum. This indicates the severity of heating which is possible. The individual rollers were also cooled by passing nitrogen into them from a common manifold. The second window was placed after the 7th roller and had a 7 inch opening. It was water cooled. Thermocouples were also placed through the top panel of the unit and one

TABLE 3-12

Dose Data with Thickness for 33 Layers of* 1 Mil Film in Festooning Unit

Film Layer No.	Mrad/Pass	Cumulative Dose (Mrads)
16	2.2	2.2
15	3.8	6.0
14	3.8	9.8
13	4.2	14.0
12	4.8	18.8
11	4.8	23.6
10	5.2	28.8
9	5.5	34.3
8	5.8	40.1
7	5.4	45.5
6	5.8	51.3
5	6.4	57.7
4	7.0	64.7
3	6.8	71.5
2	6.4	77.9
1	3.5	81.4

Energy	1.3 MeV	Window	4½ inches
Current	8.0 ma	Scan	24 "
Speed	7.5 feet/minute		

* This data was taken using standard dosimeters and standard calibration curve.

TABLE 3-13

Dose Data with Thickness for 33 Layers of* 1 Mil Film in Festooning Unit

Film Layer No.	Mrads/Pass	Cumulative Dose (Mrads)
16	2.2	-
15	3.8	6.0
14	4.7	10.7
13	4.9	15.6
12	5.4	21.0
11	5.9	26.9
10	6.9	33.8
9	6.4	40.2
8	7.1	47.3
7	6.9	54.2
6	7.3	61.5
5	7.3	68.8
4	7.4	76.2
3	7.6	83.8
2	7.8	91.6
1	3.6	95.2

Energy	1.3 MeV	Window	4½ inches
Current	8.8 ma	Scan	24 "
Speed	7.5 feet/minute		

* This data was taken using standard dosimeters and standard calibration curve.

was inserted in the 4th roller. These were used to monitor the temperature during the radiation run.

Dosimetry measurements were made to determine the effects of film speed through the beam and the effect of current and voltage on the resultant radiation dose received by the film. This was done prior to starting the production run. The data for these preliminary runs and the actual production runs are given in Table 3-14. Dosimetry was taken with new and old dosimeter.

TABLE 3-14
Trial and Production Crosslinking Runs

				Dose in Mrads[a]	
Run No.	Voltage (MeV)	Line Speed	Current Milliamps	New Dosimeters	Old Dosimeters
3	0.8	7.75	8.8	60	52
4	1.0	7.75	8.8	90	83
5	1.2	7.75	8.8	97	86
7	1.3	7.75	8.8	94	85
8	1.3	7.75	8.0	90	75
9	1.3	7.75	7.5	88	71
10	1.3	9.00	8.8	81	72
11	1.3	6.00	8.8	119	120
12	1.0	7.75	9.25	89	87[b]
13[b]	1.0	7.75	9.30		
14	1.0	7.75	9.30	92	82
15	1.0	7.75	9.3	94	82
28	1.0	7.75	9.3	92	87
18-27[c]	1.0	7.75	9.3		

a) The new and old dosimeters are blue dyed cellophane. The new dosimeters were standardized by the Bureau of Standards. The old dosimeters are blue dyed cellophane also but are over five years old. After establishing the correlation between new and old dosimeters, only the new dosimeters were used.

b) Production of 5,000 square feet - M_c values were checked and found acceptable.

c) Production runs.

Figure 3-30, which is a plot of the film speed vs dose at constant voltage and current, indicates that the new dosimeter give an almost linear decrease in dose as the speed is increased. The old dosimeters do not give the linear decrease expected. Figure 3-31 is a plot of the voltage in MeV vs the dose using both old and new dosimeters. This figure indicates a relatively linear increase in dose with an increase in voltage. The dose increase is probably due to backscatter. It is also noted that at a voltage of 0.8 MeV, there is a drastic drop in dose. It appears that below about 1.0 MeV, full penetration of the forty layers of film is not achieved. The small slope of these curves indicate a relatively small increase in the dose in going from 1.0 to 1.3 MeV. There is a significant decrease in heat input, however, since P in watts = IE and a decrease in E from 1.3-1.0 MeV is almost equivalent to a heat decrease of 30 percent.

Figure 3-32 indicates the effect of current on dose. The deviation here between the new and old dosimeters is significant. Again, the new dosimeters indicate an excellent linear increase in dose with current, as would be expected. The dose at the 1.0 MeV, 7.75 ft/min. and 9.3 milliamps level, which was used in production runs, was checked four times. The old dosimeters gave a dose range of 82-87 Mrads while the dose with the new dosimeters varied between 89-94 Mrads. Using the conditions specified in runs 18 thru 27 of Table 3-14, 85,000 square feet of film was crosslinked. Minor problems were encountered during these runs. The ozone generated during the continuous operation caused the electrical cable coating to crack; also many of the brass connectors on the cooling lines were cracked due to stress corrosion. The moisture coupled with the high ozone content obviously is a severe corroding environment. These problems are readily solved by use of ozone resistant cable and stainless cooling lines.

Samples of all production runs were taken for quality control testing. These materials were checked for M_c and gel values and the infrared was taken to determine if any oxidation of the film occurred during irradiation. All materials were acceptable. Details of this testing is given under Task 8.

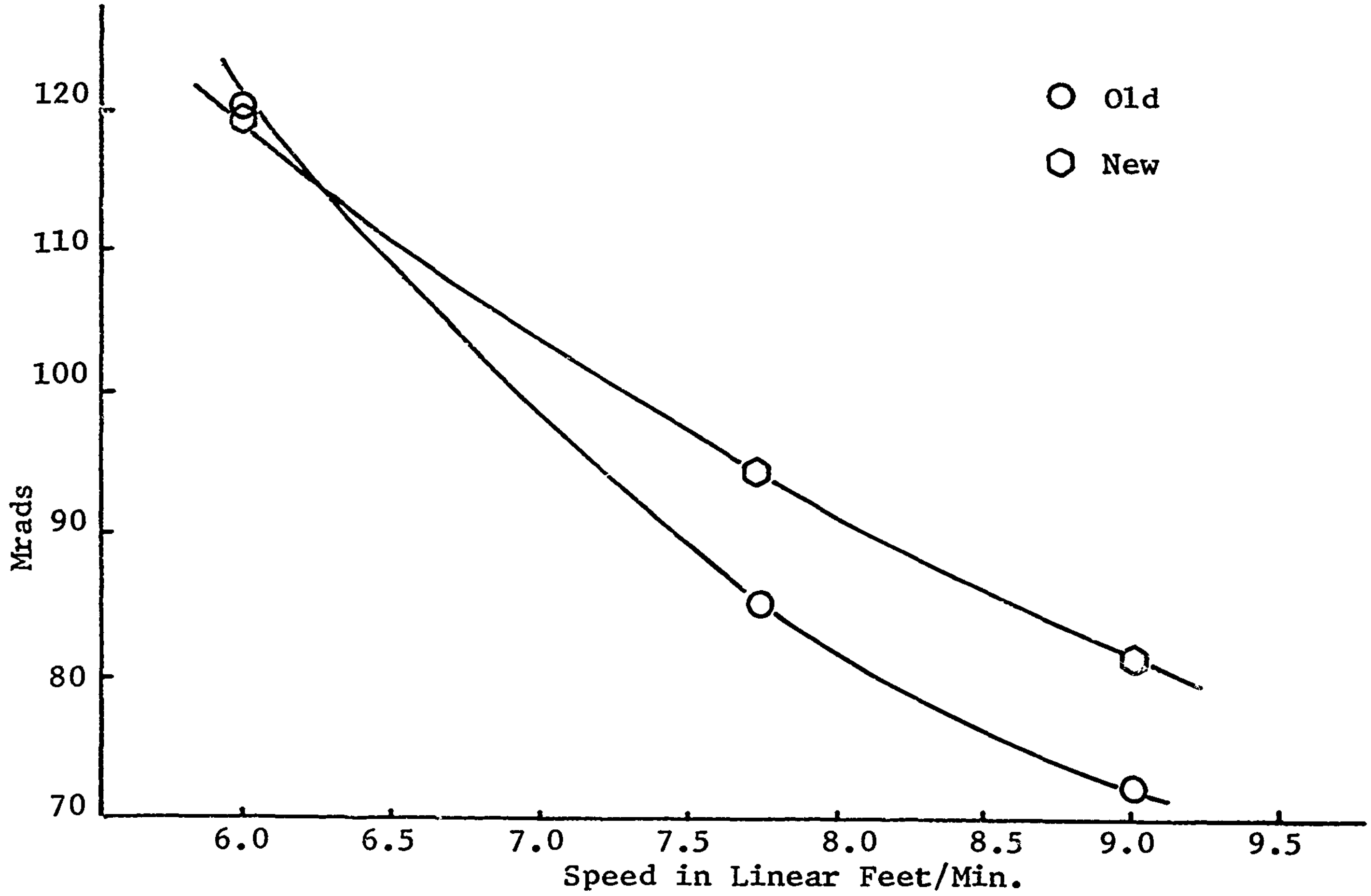


Figure 3-30. Relation Between Film Speed and Radiation Dose at Constant Accelerator Voltage and Current.

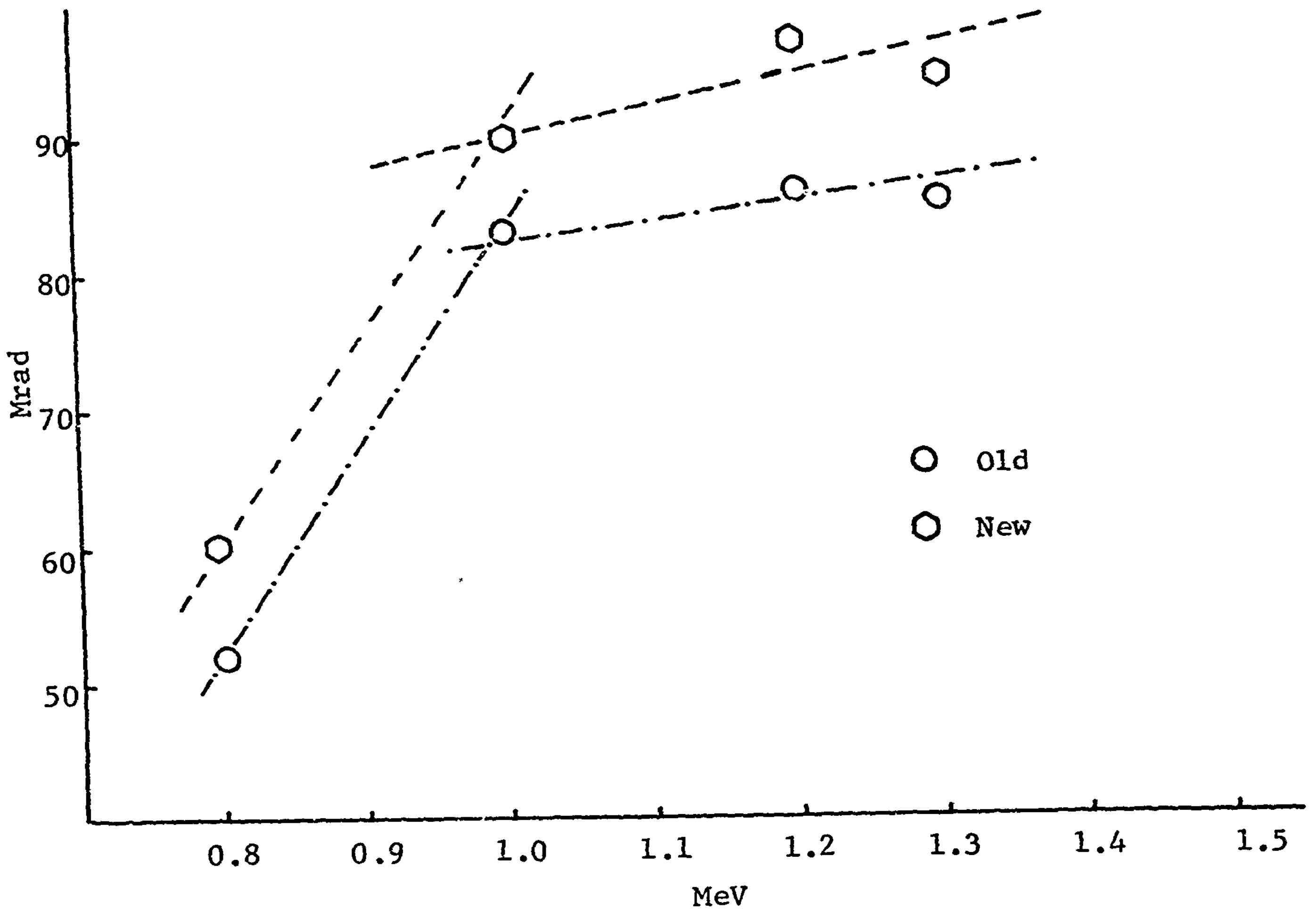


Figure 3-31 Relation Between Accelerator Voltage and Radiation Dose at Constant Current and Film Speed

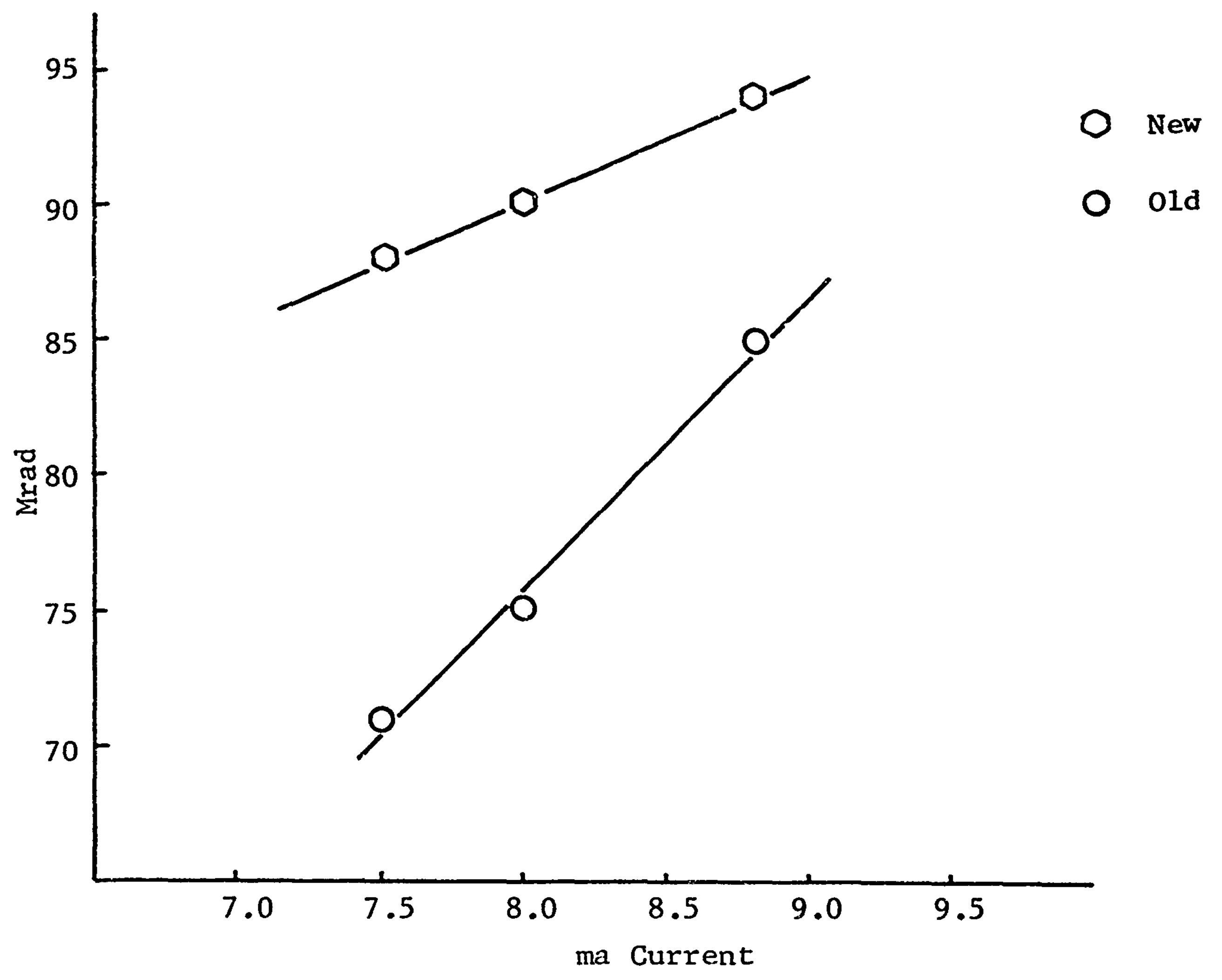


Figure 3-32 Relation Between Accelerator Current and Radiation Dose at Constant Voltage and Film Speed

Minor modifications of the crosslinking will be made for future production runs to eliminate some of the downtime experienced during this successful production run. Better insulation of our liquid nitrogen lines would also help to decrease the liquid nitrogen cost. It was shown during this production run that nitrogen cooling costs were less than \$0.01/ft^2. The radiation cost for crosslinking, based on a cost of \$50/hour for radiation time and a line speed of 7.75 linear feet/minute and an assumed 25 percent down-time, is less than \$0.05/ft^2. This would include labor and transportation costs.

Although the unit as is can be used to give excellent crosslinked film of acceptable uniformity and with an estimated cost of about \$0.05/ft^2, improvement of the unit is possible. Subsequent to completion of the contract, the crosslinking unit was again modified. A change was made in the method of cooling the individual rollers of the festooning unit. These rollers were redesigned to take a special sealing bearing which is very free wheeling and yet will contain water under pressure. This will decrease the film cost by about \$0.01/ft^2 and should give better cooling. A run using this unit will be made about May of 1972.

Film crosslinked under the contract with this unit was in the form of a 25 inch lay flat tube. After crosslinking, this film had to be rewound; then slit ½ inch on each end and on center to give twelve inch wide film. It was impossible to make a ½ inch cut on each end since even with the edge guide some edge travel occurred. Therefore one inch was cut from each end resulting in films of about 11½ inch width. This then had to be rewound into single sheet rolls. The labor for this was not acceptable.

Therefore, a 25 inch lay flat tube, slit by the extruder one half inch on each end and on center was obtained. This gave two sections of 12 inch double sheeting on a single wind. This film can now be separated into four single rolls by the take-up unit during the crosslinking and saves considerable labor. In addition, slitting in-house with poorly wound rolls results in film with slight "nicks" on each end. These cuts caused problems during washing since they tend to tear when the film is wet and under tension. All these problems will be eliminated with the new film.

2.4. TASK NUMBER FOUR: PREPARATION OF FILM FOR GRAFTING

The film used in grafting from Task 3 is crosslinked to a dose of 90 Mrads. The precrosslinked film is slit to 12 inches and is wound with an interlayer qualified under Task 8. This task deals with the choice of an interlayer, the winding equipment and the actual winding of film and interlayer into a double helix roll. The roll then is placed in the film reactor and swelled in a grafting solution for a set time as determined in Task 6.

The interlayer originally used was cheesecloth. It was later replaced by a new paper mesh interlayer, Lenonet, manufactured by the Bemis Bag Company. The Lenonet interlayer has much larger openings and thickness than the cheesecloth. The rational here is to permit a greater supply of monomer to contact the film during the grafting reaction. A picture of the two interlayers is shown in Figure 4-1 and 4-2. The superiority of the Lenonet interlayer was established. Two 150 feet samples were prepared, one using cheesecloth and the other Lenonet. They were grafted under identical conditions.

Base Film	-	Bakelite DFD-0602 crosslinked to 90 Mrads	
Grafting Solution	-	Benzene	78.3%
		Methacrylic Acid	19.0%
		Carbon Tetrachloride	2.7%
Dose Rate	-	9300 rads/hour	
Total Dose	-	1.31 Mrads	

The result from the 150 foot grafted samples, using cheesecloth and Lenonet as the only variable, indicated improved uniformity of the electrical resistance and a lower, final resistance of the membrane prepared with the Lenonet. The data for these samples are given in Table 4-1.

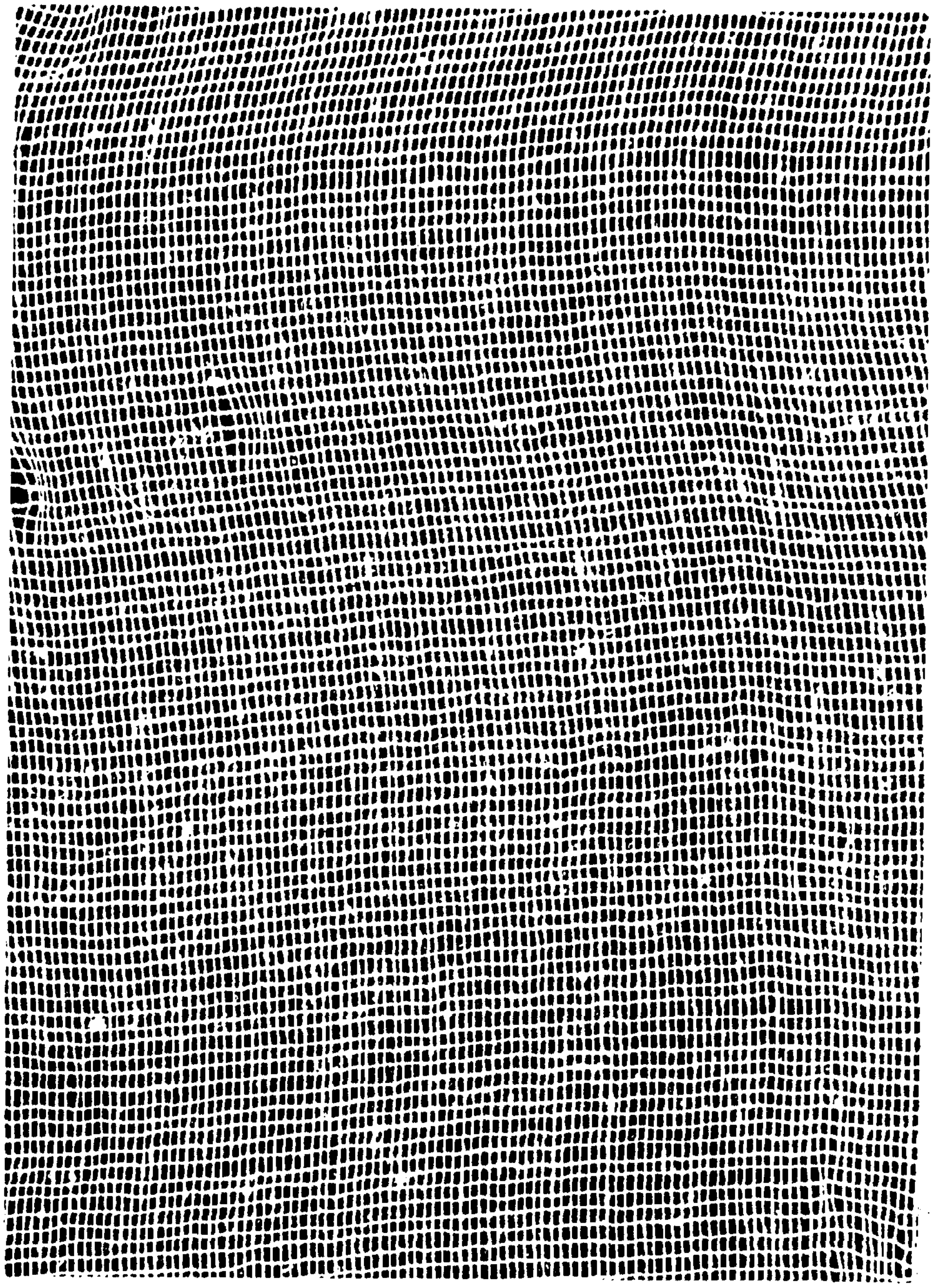


Figure 4-1. Interlayer Material - Cheesecloth Shown Full-Scale.

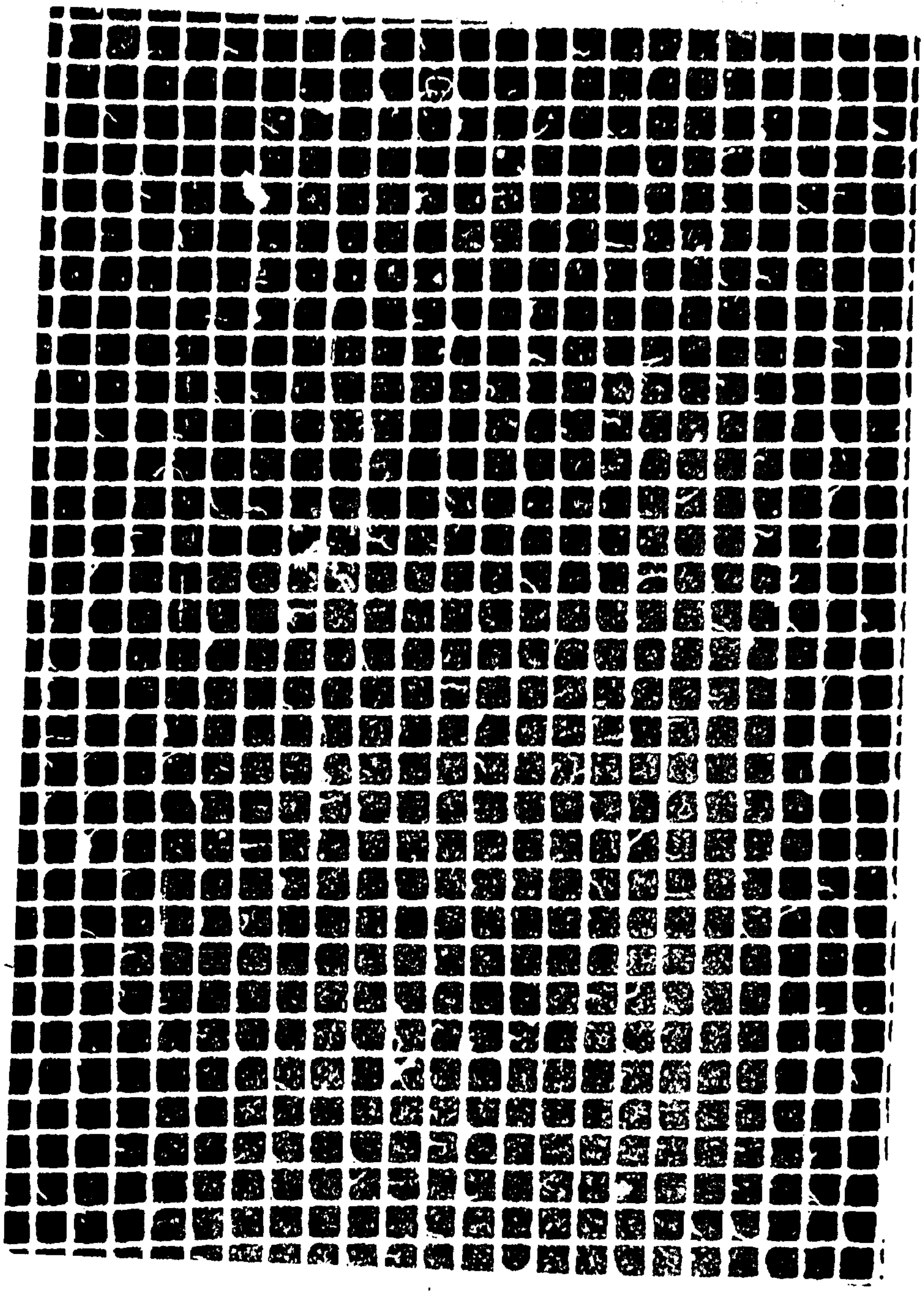


Figure 4-2. Interlayer Material - [illegible]
Shown Full-Scale.

TABLE 4-1

Comparison of Electrical Resistance on Film Grafted Using Cheesecloth vs Lenonet Interlayer

Distance Across the Film (inches)	Lenonet Interlayer Ac - 40% KOH (milliohm-in²)	Lenonet Interlayer DC - 45% KOH (milliohm-in²)	Cheesecloth AC - 40% KOH (milliohm-in²)
1.5	45	41	53
3.0	53	43	61
4.5	51	45	64
6.0	49	40	70
7.5	50	41	73
9.0	49	41	64
10.5	50	35	58
12.0	47	36	55
13.5	40	38	53
15.0	35	39	47

The results from these runs indicate the excellent graft uniformity possible even under static grafting conditions if the spacing between the grafting films is sufficiently wide to permit a reservoir of grafting solution to be maintained on the film surface. It is also to be noted that on using the wide mesh interlayer, the removal of air from the rolled bundle was much easier.

Based on this preliminary run, 1,000 feet of cross-linked film was wound on a 3 inch core. Normally, the film is 13 inches wide. In this case, two 12 inch wide films were wound simultaneously, side by side with a 2 inch spacing to give a 26 inch span of film. This was attempted to determine if the production rate could be increased by grafting a wider film. When these type of runs were conducted with cheesecloth as the interlayer, the grafting was very non-uniform. The grafting conditions were essentially identical to the 150 foot runs. The grafting results with the Lenonet interlayer were very satisfactory.

Initial testing showed the double-width film to be uniformly grafted. The electrical resistance across the 26 inch width taken in 40% KOH at 23°C ranged from 35-45 milliohm-in^2. These results indicated that grafting of a roll of 2,500 linear feet of film, 24 inches wide could be accomplished. In this way, 5,000 square feet of membrane might be made from a film bundle containing 2,500 linear feet of film, 24 inches wide. Consequently, the labor for handling and winding 5,000 feet of film should be significantly reduced by working with wider starting material.

Subsequent runs were made with Lenonet as the standard interlayer. Lenonet has a gauge of 30 mils but is of a very wide weave so that successive layers of film give a total thickness less than the sum of the individual layers due to statistical overlapping of the weave. Still, the diameter of the roll using Lenonet is much larger than the roll using 5 mil cheesecloth. The diameter of the film reactor was increased since the original design was based on the cheesecloth interlayer.

The winding unit to prepare the rolls for grafting consists of feed and take-up subunits. There are three feeding mechanisms, two for the precrosslinked film and one for the interlayer. On the axis of the interlayer feed-roll, there is a brake pressure system, the brake pressure of which is adjustable with compressed air. The tension on the other two film feed-rolls were adjusted by changing weights. Figure 4-3 is a picture of the winding unit with films and interlayer during winding. Both the films and the interlayer were wound on the take-up unit as a double helix roll at a constant rate. As the radius of the take-up roll increases, the torque increases so that the tension on the feed rolls must decrease accordingly. Table 4-2 gives the actual data relating brake pressure with roll diameter.

Prior to grafting three bundles were wound using Lenonet as the interlayer. These were made under various conditions to determine the number of square feet of film that could be placed on a single roll. Results are given in Table 4-3. It is obvious that for a given radius a tighter roll will contain more film. Under the conditions given in Table 4-3, roll three was wound tighter than roll two which in turn was tighter than roll one.

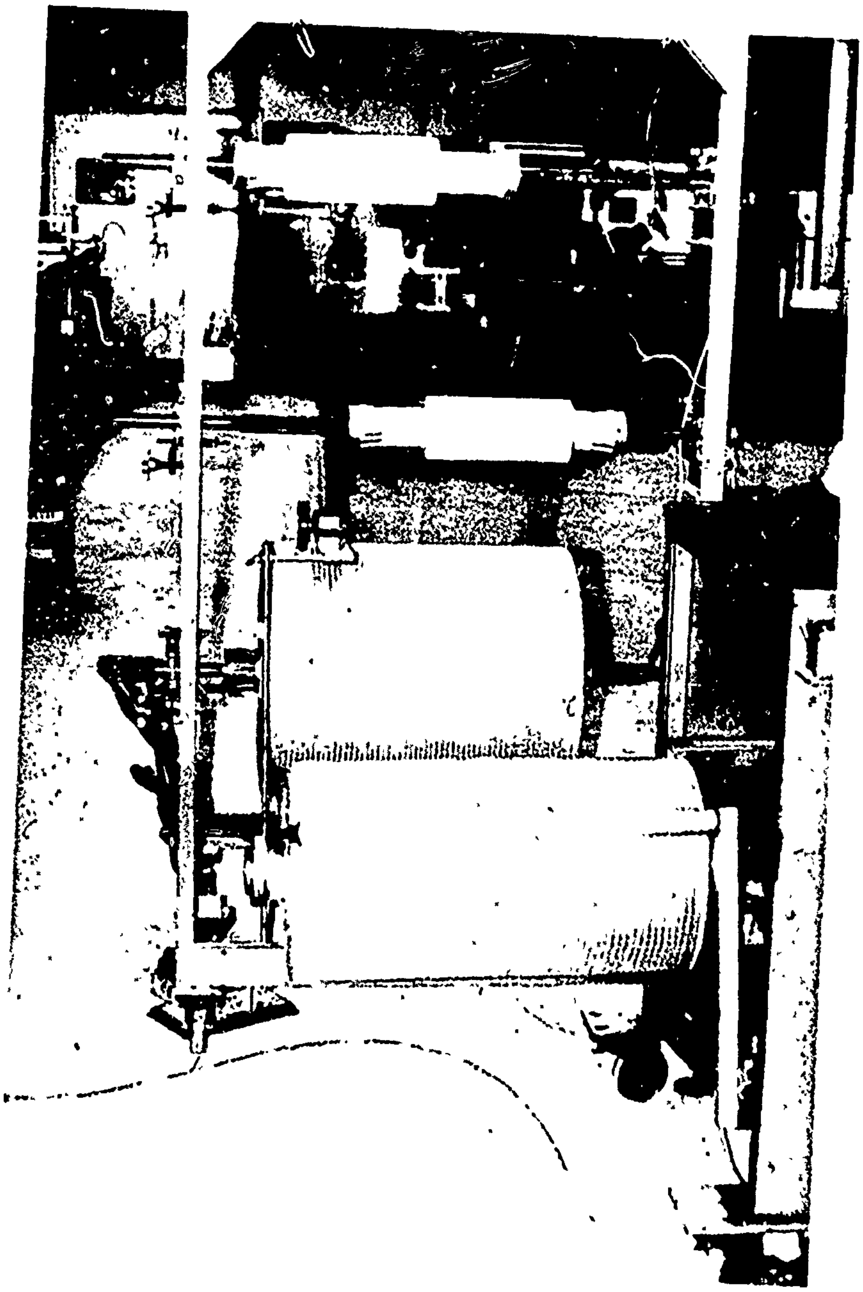


Figure 4-3. Winding Crosslinked Film.

Figure 4-4 indicates that if the roll diameter were 14.5 inches, roll one would have 3,600 square feet, roll two 4,600 square feet and roll three would exceed 5,000 square feet. Since the inside diameter of the reactor is 31.5 inches, a 14.5 inch radius roll is about the maximum size that can be placed in the reactor vessel since the core on which the roll is wound has a 1.75 inch radius.

Data on rolls wound for grafting runs 8-12 are listed in Table 4-4. The rolls were used in the determination of grafting parameters established under task 6.

TABLE 4-2

Preparation for Grafting Run #7

Take-Up Roll Radius (inches)	Position of Test Pieces for Graft Uniformity	Linear Foot in Take-Up Roll (Feet)	Brake Pressure On Feed-Roll (Lbs.)
1	-	32	88
1½	-	57	88
2	-	85	86
2½	-	119	82
3	1.2nd	158	78
3½	-	197	74
4	-	237	70
4½	-	278	66
5	-	326	62
5½	-	385	58
6	3.4th	442	54
6½	-	500	50
7	-	559	48
7½	-	636	46
8	-	708	44
8½	-	775	42
9	5.6th	823	40
9½	-	885	38
10	-	953	36
10½	-	1,032	34
11	-	1,120	32
11½	-	1,198	30
12	7.8th	1,296	28
12½	-	1,388	26
13	-	1,485	24
13 1/3	-	1,650	-

TABLE 4-3

Winding of Film and Interlayer into a Roll for Grafting

Take-up Roll Radius[a] (inches)	Linear Feet in a Roll		
	No. 1[b]	No. 2[c]	No. 3[d]
1	25	34	37
1.5	40	59	66
2.0	61	82	98
2.5	90	110	130
3.0	123	-	169
3.5	153	183	213
4.0	180	219	252
4.5	217	257	304
5.0	260	315	365
5.5	301	377	432
6.0	343	424	-
6.5	385	482	-
7.0	440	570	-
7.5	505	642	-
8.0	570	710	-
8.5	637	-	-
9.0	709	794	-
9.5	778	-	-
10.0	-	931	-
12.0	1108	-	-
12.5	-	1650	-

[a] The radius of the core on which the film was wound was 1.75 inches and must be added to the take-up roll radius to obtain the actual radium of the finished roll.

[b] The pressure of the brake on the axis of the feed roll was 60 lbs. Initial diameter of the feed roll (interlayer) was 27.5 inches. Speed setting was constant.

[c] Brake pressure on the axis of the feed roll was 56 lbs. The initial diameter of the interlayer roll was 27.5 inches. Speed setting was constant.

[d] Pressure of brake on the axis of the feed roll was 60 lbs. Initial diameter of interlayer roll was 13.5 inches. Speed setting was constant.

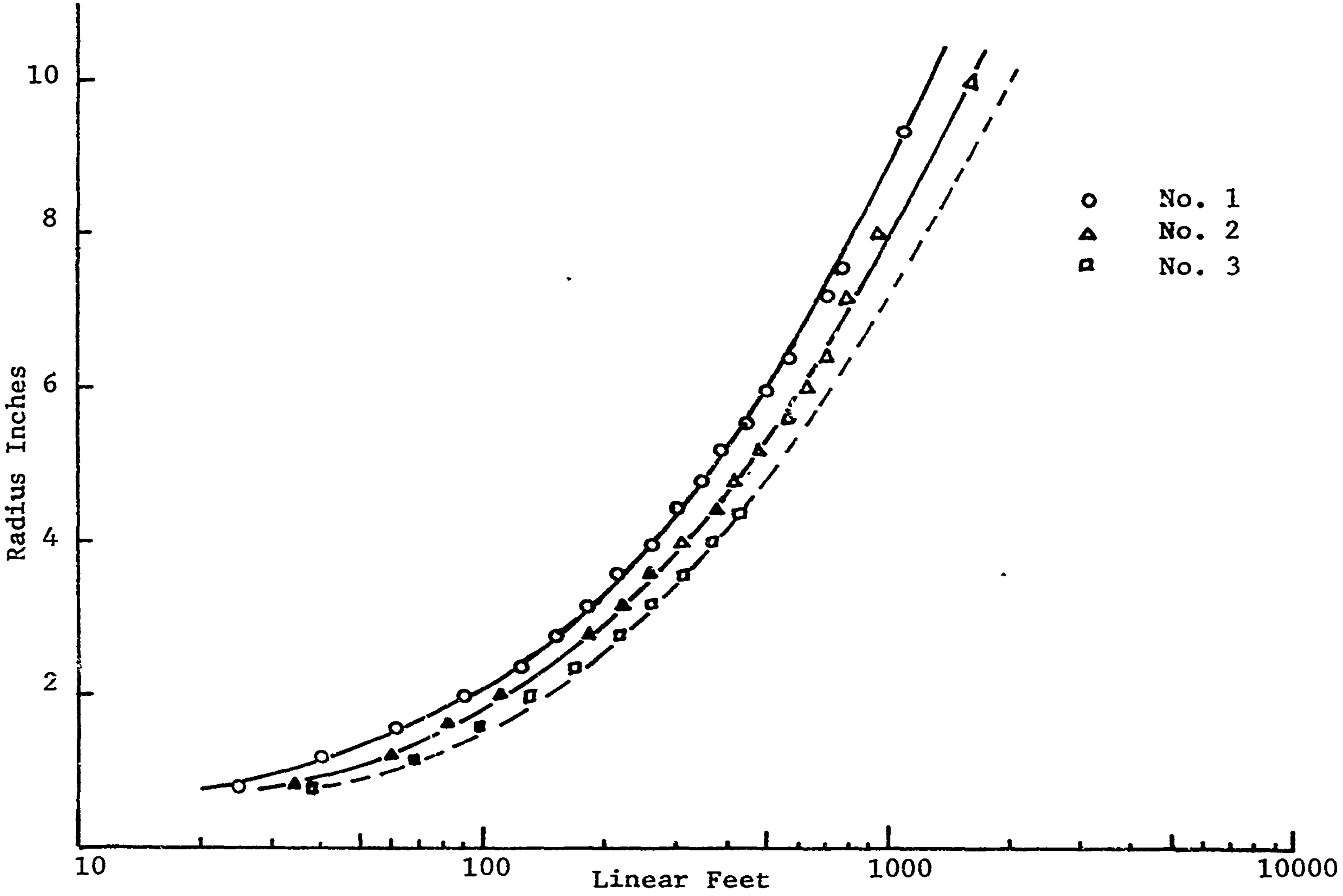


Figure 4-4. Relation Between Core Radius and Footage of Film in the Core.

TABLE 4-4

Winding Data on Runs #8-12

Take-Up Roll Radius (inches)	Position of Test Pieces for Graft Uniformity	Linear Foot in Take-Up Roll (Feet)	Brake Pressure on Feed-roll (Lbs.)
#8 0	-	13½	36
1	1.2nd	43	32
1½	-	68	28
2	-	102	24
2½	-	130	20
3	-	169	16
3½	-	201	-
4	-	245	14
4½	-	282	-
5	-	324	-
5½	3.4th	373	-
6	-	436	-
6½	-	498	-
7	-	558	-
7½	-	634	-
	Change New Roll of Lenonet Interlayer		
8	-	732	38
8½	-	807	34
9	5.6th	886	30
9½	-	989	26
10	-	1052	22
10½	-	1119	20
11	-	1253	18
12	7.8th	1403	10
13 2/3	-	1650	-
#9 0	1.2nd	0	70
1	-	34	-
1½	-	62	68
2	-	96	66
2½	-	132	64
3	-	170	62
3½	-	211	60
4	-	263	57

TABLE 4-4 (Cont'd)

Take-Up Roll Radius (inches)	Position of Test Pieces for Graft Uniformity	Linear Foot in Take-Up Roll (Feet)	Brake Pressure on Feed-roll (Lbs.)
4½	-	311	54
5	-	369	50
5½	3.4th	425	46
6	-	489	42
6½	-	550	38
7	-	614	32
7½	-	683	26
8	-	760	20
8½	-	832	15
9	-	892	10
9½	-	949	-
10	-	1018	-
10½	5.6th	1105	-
11	-	1177	-
11½	-	1250	-
12	-	1341	-
12½	-	1436	-
13	-	1529	-
13½	-	1611	-
13 5/8	7.8th	1650	-
#10 0	1.2nd	15½	38
1	-	30	38
1½	-	59	38
2	-	91	38
2½	-	124	38
3	-	169	36
3½	-	211	34
4	-	256	32
4½	3.4th	312	30
5	-	359	26
5½	-	418	22
6	-	474	20
6½	-	538	18
7	-	593	16
7½	-	667	15
8	-	748	15
8½	-	811	15
9	5.6th	885	15

TABLE 4-4 (Cont'd)

Take-Up Roll Radius (inches)	Position of Test Pieces for Graft Uniformity	Linear Foot in Take-Up Roll (Feet)	Brake Pressure on Feed-roll (Lbs)
9½	-	959	15
10	-	1040	15
10½	-	1128	15
11	-	1250	-
	Change Lenonet Roll		
11½	-	1359	38
12	-	1475	36
12½	-	1552	34
13	-	1619	32
13½	7.8th	1670	-
#11 0	1.2nd	24	60
1	-	31	60
1½	-	60	60
2	-	90	60
2½	-	125	60
3	-	173	58
3½	-	219	56
4	-	259	54
4½	3.4th	330	52
5	-	382	50
5½	-	451	48
6	-	514	46
6½	-	590	44
7	-	669	42
7½	-	752	40
8	-	838	36
8½	-	914	32
9	5.6th	1004	28
9½	-	1076	24
10	-	1147	20
10½	-	1226	16
11	-	1302	16
11½	-	1382	16
12	-	1464	16
12½	-	1549	16
13	-	1635	16
13½	7.8th	1655	16

TABLE 4-4 (Cont'd)

Take-Up Roll Radius (inches)	Position of Test Pieces for Graft Uniformity	Linear Foot in Take-Up Roll (Feet)	Brake Pressure on Feed-roll (Lbs.)
#12 0	1.2nd	0	36
1	-	29	36
1½	-	58	36
2	-	92	36
2½	-	128	36
3	-	175	34
3½	-	216	32
4	-	262	30
4½	3.4th	318	28
5	-	382	26
5½	-	441	24
6	-	498	22
6½	-	570	20
7	-	638	18
7½	-	711	16
8	-	795	14
8½	-	865	12
9	5.6th	951	10
9½	-	1023	8
10	-	1104	8
	Change New Roll of Lenonet		
10½	-	1195	22
11	-	1262	22
11½	-	1369	22
13½	7.8th	1640	-

2.5 DESIGN OF FILM REACTOR

2.5.1 Introduction

As part of the deliverable items of the research and development contract preceeding this manufacturing processing contract, five thousand feet of Permion P-2291 were prepared. This material was made in stainless steel reactors containing 500 foot rolls of crosslinked film interwound with cheesecloth. The rolls were approximately 10 inches in diameter. The grafting solution consisted of 26.6% methacrylic acid 70% benzene and 3.4% carbontetrachloride.

The rolls of film were equilibrated in the grafting solution overnight and subsequently the containers were irradiated at 10,000 rads/hour for seven days. The irradiation was not conducted on site since at that time the R A I facility housed only a small source used for research purposes. No control over irradiation temperature was possible off site nor could continuous monitoring be made to determine the decrease in acid concentration with time. Under these "manufacturing" conditions relatively uniform grafted separators having an average resistance of approximately 51 milliohms/in^2 in 40% KOH were obtained.

To scale up the manufacture of Permion 2291 to 1,000,000 square feet per year a number of approaches were possible. The most obvious would be to use the same procedure i.e. irradiation of containers of 500 foot capacity. This approach was soon rejected since it would require processing 40 containers/week. The radiation time for grafting was 7 days which therefore meant the vault area would have to be capable of housing 40 containers at one time. Calculations indicated that to irradiate this number of containers simultaneously would require a vault with inside dimensions of 20 feet by 20 feet and about 50,000 curies of cobalt 60. The cost of such a facility would be extremely expensive and normal depreciation costs would add considerably to the membrane price.

To bring capital costs within a reasonable range it was necessary to increase the reactor size over ten fold; i.e. process 6,000 foot rolls. Initial estimates indicated that if we prepared bundles with a five mil cheesecloth interlayer the reactor diameter had to be approximately 27 inches. Further two layers of 12 inch film had to be placed next to each other in winding the bundles. This gave a height requirement of at least 26 inches. The reactor height was set at 36 inches to allow for entrance of nitrogen into the bottom of the tank and to allow the bundle to be kept at least four inches off the bottom plus permit for head space.

Early in this manufacturing program, prior to initiation of construction of the reactor, it was found that large bundles of film interwound with cheesecloth would be very difficult to wind uniformly. In addition, irradiation of bundles with 1,000 feet of film, using cheesecloth as an interlayer presented problems in manufacturing uniformly grafted film. It was apparent that monomer solution in such rolls was stagnant and further, heat dissipation was a severe problem. This resulted in over-grafting within the bundle and blocking of the homopolymer formed on the film and the cheesecloth. Such bundles were very difficult to unwind and film embrittled and cracked.

To overcome this problem a new interlayer material had to be obtained. It was reasoned that if the spacing between layers of film were increased, more monomer would be present at each unit area of film and better diffusion of solution through the bundle would result. This approach should also decrease the heat transfer problems. To further aid in reduction of heat transfer the reactor had to be designed to permit rotating of the bundle at one-to-two revolutions per minute (rpm) and monomer had to be circulated through a constant temperature control unit which must be outside the radiation vault.

At this time a paper mesh made by Bemis Bag Company called Lenonet was obtained. Using this mesh a 1,000 foot bundle was wound and irradiated in a stainless reactor using conditions previously used in the 500 foot reactor. Controls were run using the cheesecloth interlayer. As shown in the previous section, excellent results were obtained with the new mesh on grafting across a film width of 26 inches. (This was actually two 12 inch films with two inch spacing.)

Based on these results and the poor graft uniformity obtained using cheesecloth, it was decided to design the reaction vessel to take the large mesh interlayer. The first roll prepared using the new interlayer contained 3300 square feet of film and was 13-1/3 inches in diameter. The mesh width was 28 inches. Although this was less film per roll than originally planned it was felt that the excellent results obtained in uniformity and low resistance warranted the change.

2.5.2 Initial Reactor and Auxilliary Equipment Design

The basic requirements, deemed necessary for grafting film uniformly, originally designed in the system includes the following:

1. The reactor vessel was to be stainless steel with an internal diameter of 32 inches and 36 inches in height.
2. The reactor was made portable to permit loading outside the vault and permit transfer into the vault for irradiation. Subsequent to irradiation the vessel had to be unloaded outside the radiation vault in a hooded area.
3. The radiation reactor was fitted with a thrust bearing on which could be loaded the bundle of crosslinked film. This is turn could be rotated in the solution.
4. Nitrogen sparging was to be maintained throughout the reaction and a means for nitrogen sparging at the bottom of the vessel was to be provided.
5. Monomer was to be pumped out of the reactor from the top and after traversing the system was to be pumped into the bottom.
6. A cover and gasket were also necessary. The cover would contain a safety blow out patch, a sampling valve and would house an explosion proof motor and gear box for rotating the bundle.

7. The monomer was to exit from the tank pass through a filtering system and then pumped through a heat exchanger to maintain a predetermined solution temperature.

8. Four temperature probes were to be mounted on the reaction vessel on one side and one probe was to be mounted through the bottom of the vessel. All probes were to be read and recorded outside the vault.

9. Flow meters were to provide for N_2 and liquid flow control.

10. Initially, oxygen analysis in line was not part of the system, however, it was found during the grafting study that the oxygen content in the solution was a critical governing parameter and if controlled could decrease the radiation time necessary to effect grafting.

Figure 5-1 is a flow diagram of the initial reactor system. The filtering system shown here was eliminated when it was found that the homopolymer formed was colloidal in nature and tended to easily clog the filter. After a number of runs the system was modified.

2.5.3. Final Reactor Design System

Based on the experiences gained after a number of runs a much simplified and improved reactor design system was evolved. Data from the initial runs indicated (1) a hot zone existed during reaction at the bottom-center of the reactor. All probes on the reactor wall indicated a uniform temperature could be maintained. Therefore the solution was circulated from the bottom center through the heat exchanger and then back into the reactor from the top (2) the filtering system was eliminated (3) a foot valve was placed on the exit line from the reactor. This made initial priming very simple. (4) It was demonstrated that if oxygen were removed prior to irradiation the reaction time was reduced from 7 to about 2 days. Provisions were therefore made for pulling a vacuum on the reactor and letting back with nitrogen. (5) An oxygen

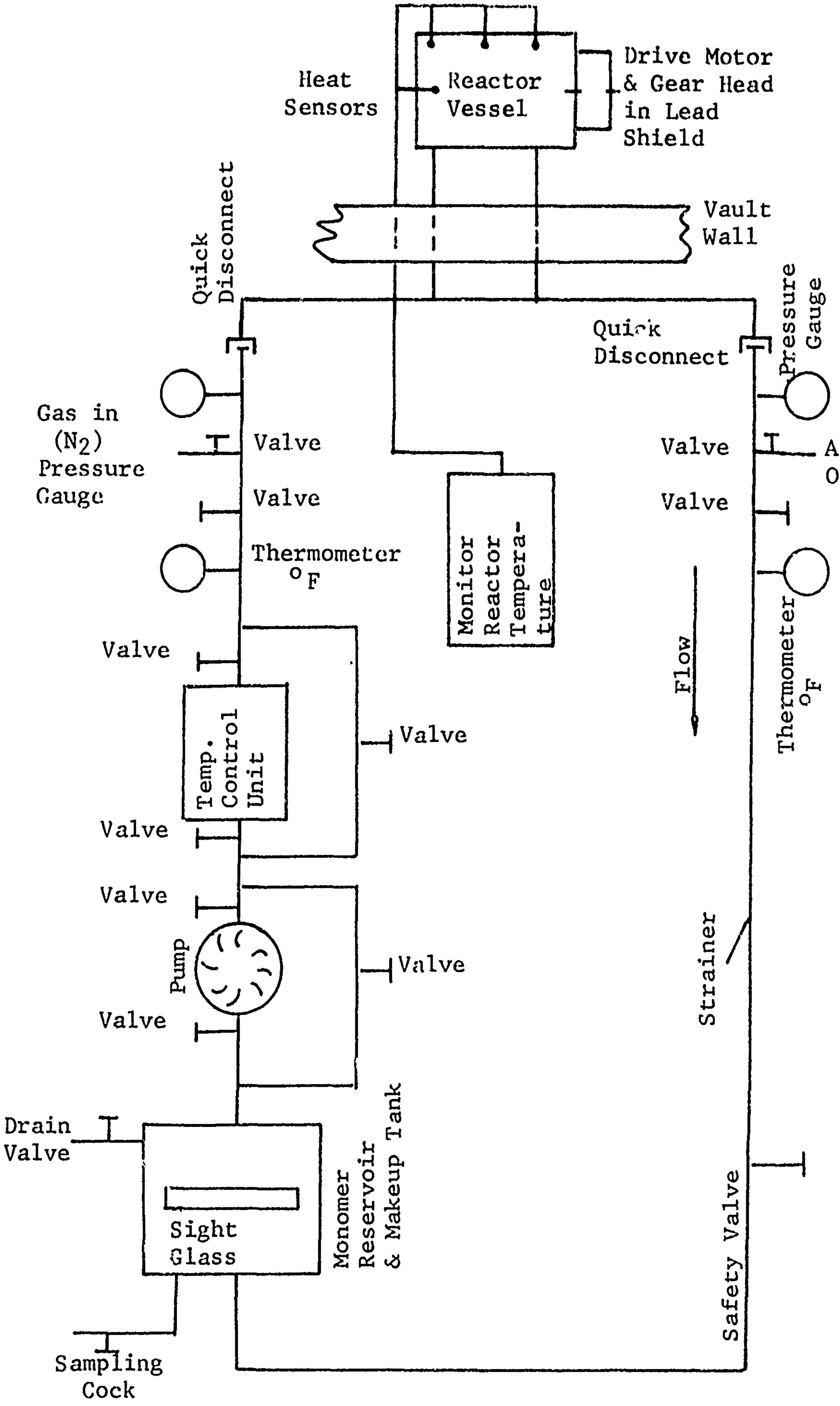


Figure 5-1. Radiation Grafting Reactor - Initial Design.

analyzer was added to the system. (6) Controls for heating and cooling which controlled the selonoid were refined to give a small dwell time. (7) a 7 amp breaker was added to the pump circuit to prevent overloading the pump as the solution viscosity increased. (8) The pump was enclosed and operated under nitrogen. The schematic showing these changes is illustrated in Figure 5-2. A schematic of the tank is given in Figure 5-3. Figure 5-4 is a picture of the tank in place in the vault and Figure 5-5 is a picture of the exterior east wall showing the exit and entrance lines from the radiation vault and the schematic system shown in Figure 5-1. This system has been used very satisfactorily for the last ten runs. It is easily maintained but must be broken down after each run and thoroughly cleaned. Because of the nature of the reaction and the homopolymer formed, the system cannot be satisfactorily cleaned in place.

One of the runs made early in the contract, run number three, gave a uniform high graft with no homopolymer formation. It is believed this was due to leakage of just the correct amount of air into the circulating monomer which prevented homopolymer formation but did not stop grafting. Time did not permit experimentation to find this optimum oxygen level. Work in this area will continue in-house to determine if we can in fact graft and prevent homopolymer formation. This could materially decrease the cost of the film since it would decrease the wash time, clean-up time and general labor requirements.

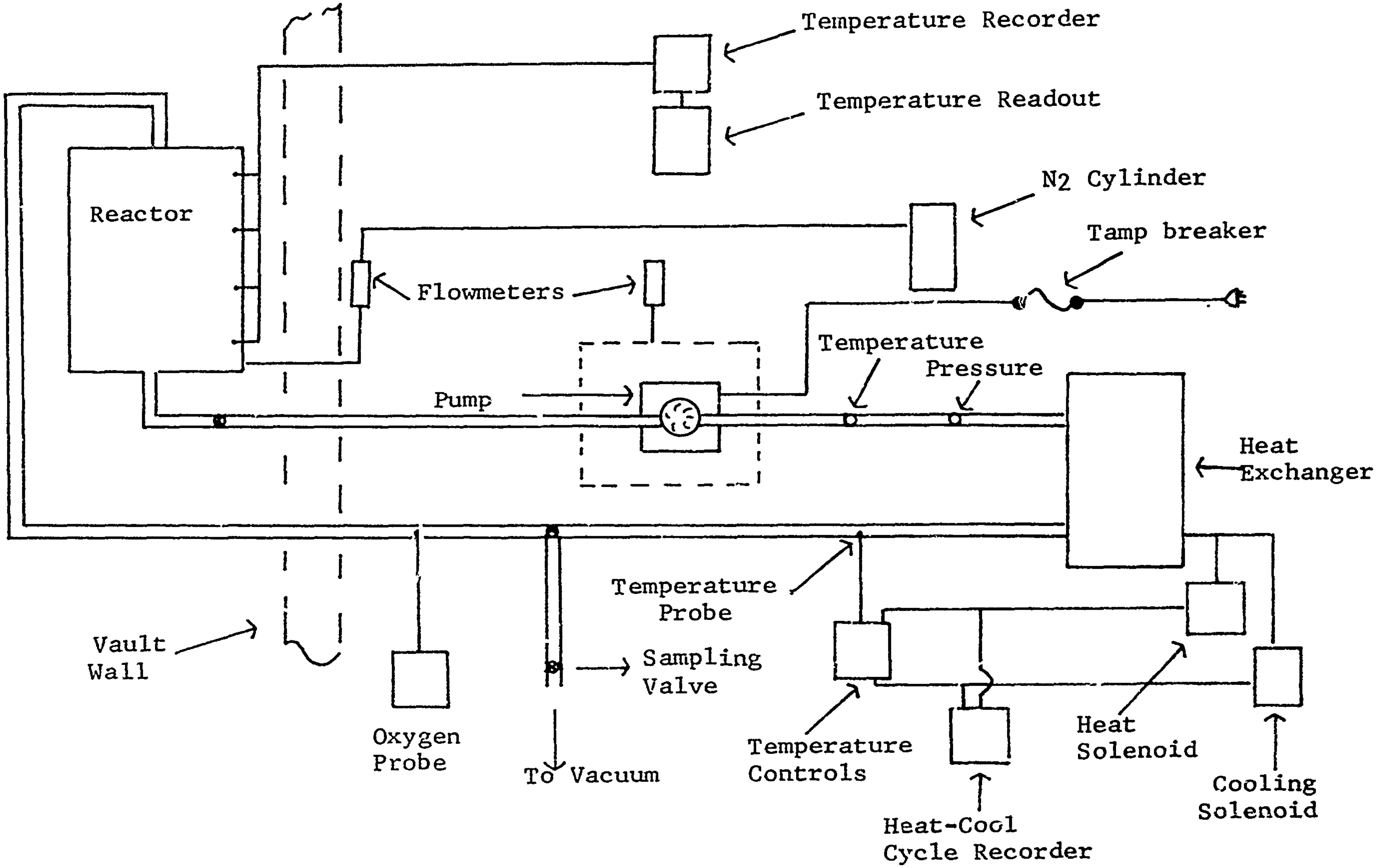


Figure 5-2. Schematic of Final Reactor System.

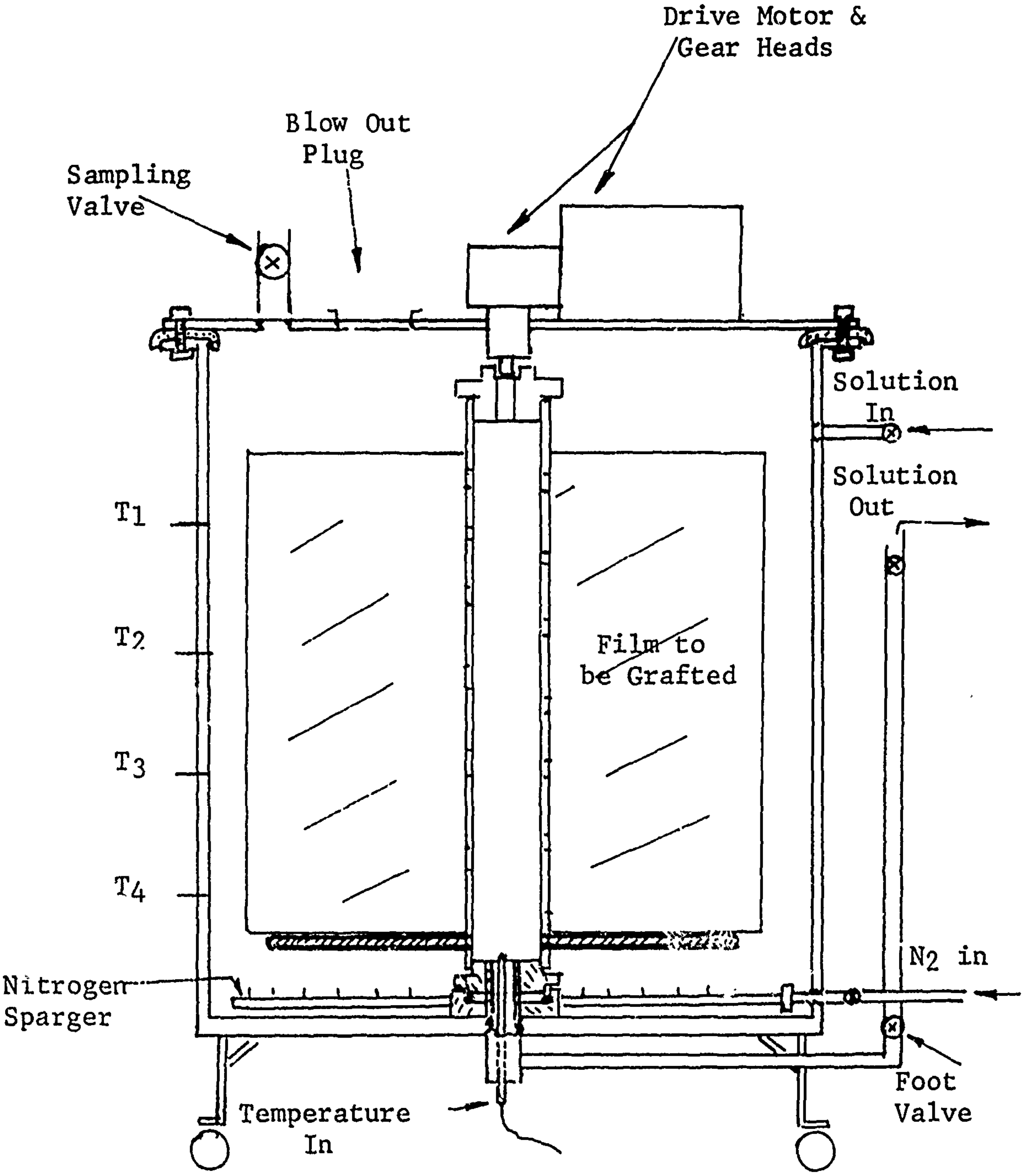


Figure 5-3. Schematic of Film Reactor

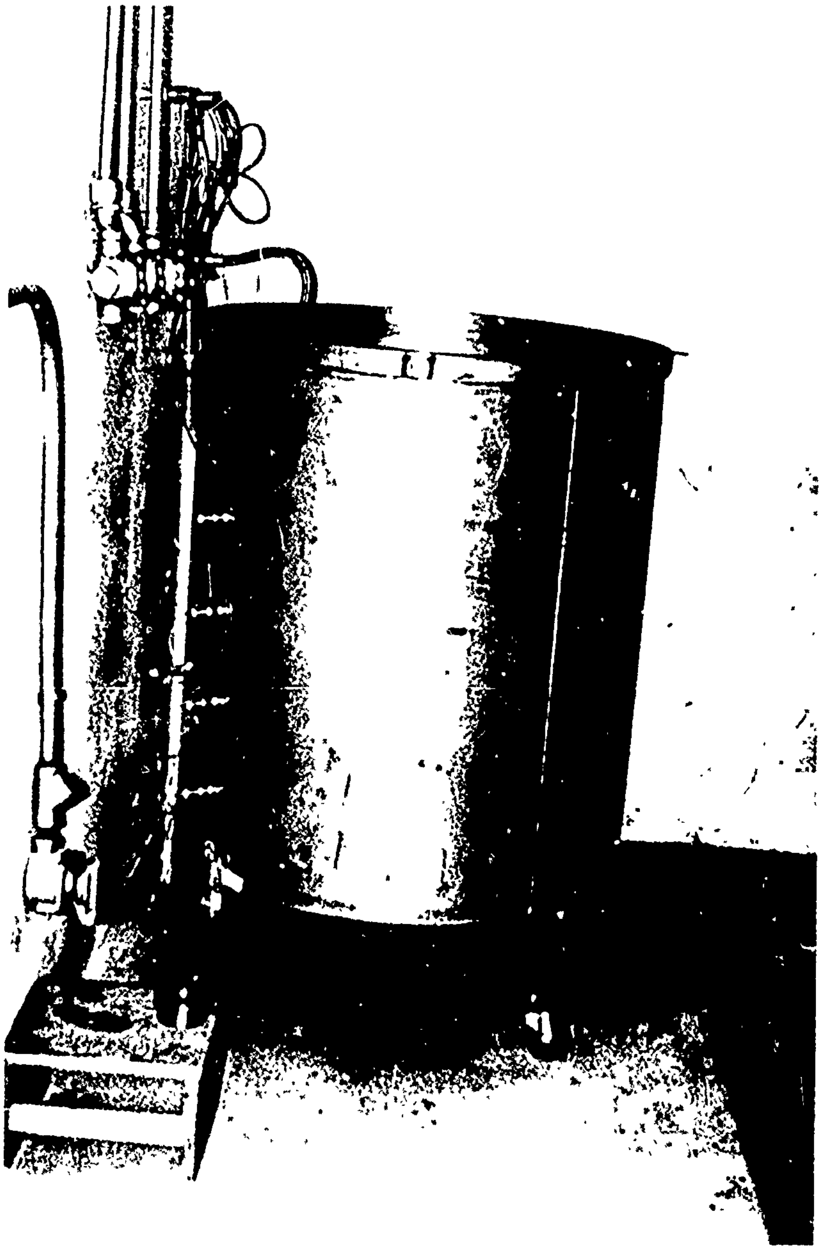


Figure 5-4. Film Reactor in Vault.

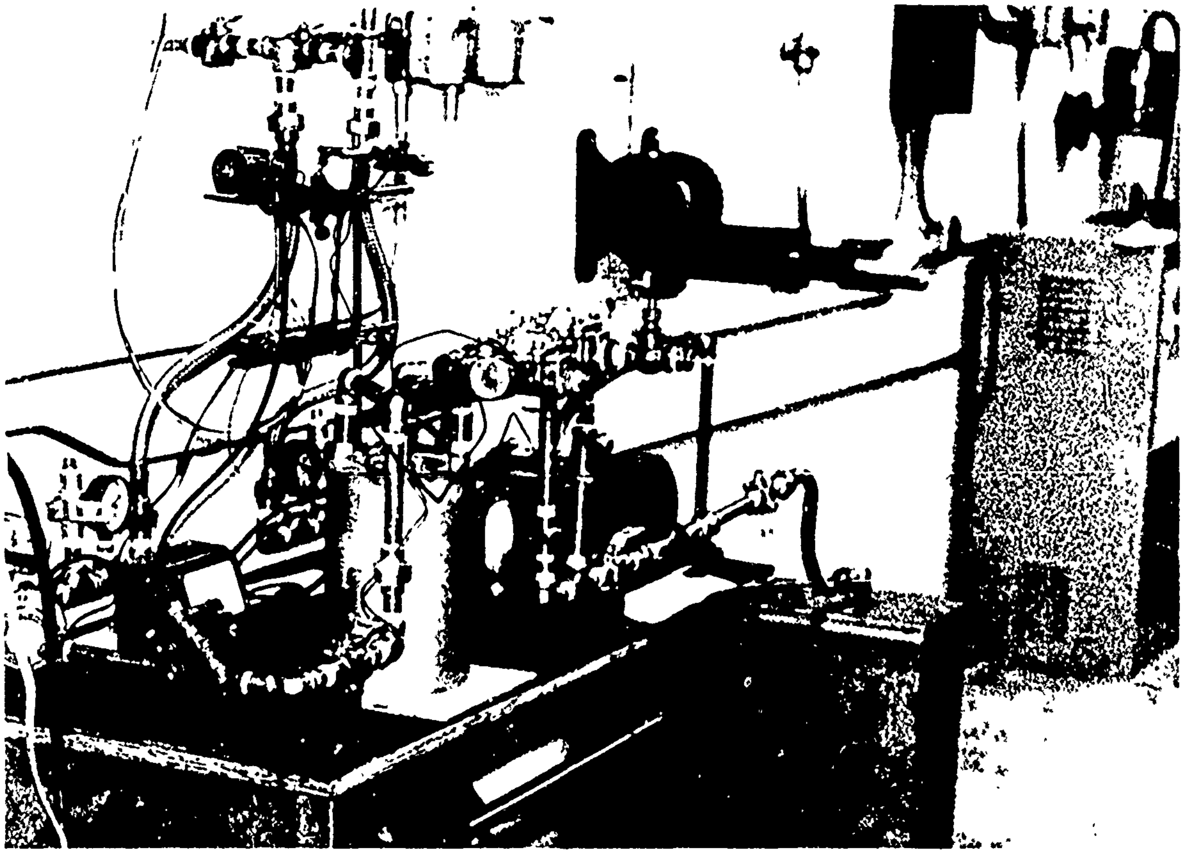


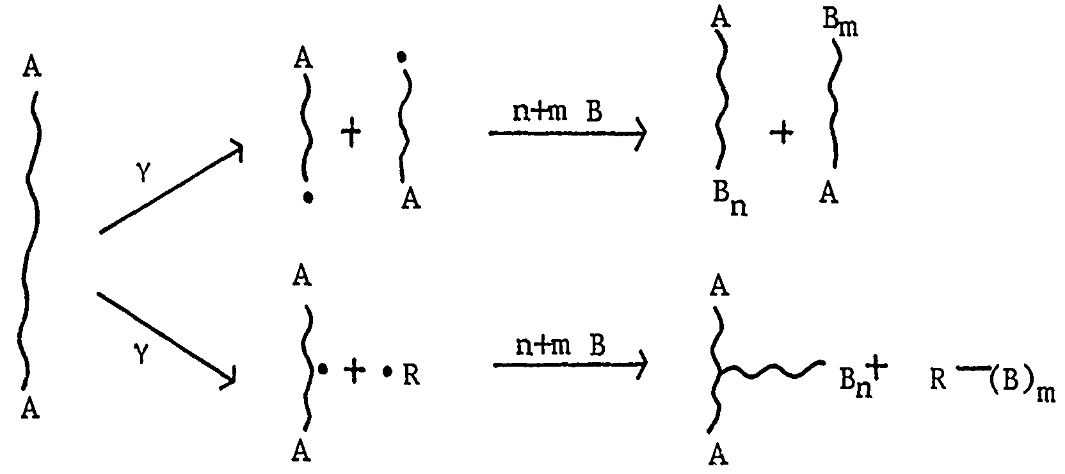
Figure 5-5. Monomer Circulating System

2.6 TASK NUMBER SIX: GRAFTING STUDIES

2.6.1 Introduction

The grafting process is the single most important step in the manufacture of separators. Polyethylene ungrafted does not exhibit ion transport properties. To impart ion transport properties, the film must be modified; this is done by grafting. Grafting as practiced here means the introduction of polymeric side chains to the backbone of the base polymer which is accomplished by means of high energy gamma radiation.

There are numerous techniques for grafting recorded in the literature (6-8). The method employed in this program is that of direct grafting. It involves irradiation of polymeric film in a solution of monomer. Schematically this is shown below:



where $A\sim\sim\sim A$ is the polymer, $A\sim\sim\bullet$, $A\sim\overset{\bullet}{\sim}\sim A$ are polymeric free radicals, R• is a low molecular weight radical or hydrogen atom, and B is the monomer to be grafted. If the polymer is of the degradation type, then under radiation, a block copolymer is formed, this is shown as $A\sim\sim\sim B$. If the polymer is of the crosslinking type, irradiation gives a graft copolymer, $A\sim\underset{B}{\sim}\sim A$ and homopolymer R-$(B)_m$.

Since polyethylene crosslinks on exposure to radiation, the formation of both graft copolymer and homopolymer is to be expected. Another source of homopolymer formation is due to the direct radiolysis of the monomer. The scheme shown above is over-simplified. It must be realized that there are many parameters that affect the grafting reaction, such as the G_R values of the polymer, monomer, solvent and the interlayer (G_R is the free radical yield per 100 eV of energy absorbed in the irradiation medium) the gel, the energy transfer process, the dose, the dose rate, air, additives, the rates of monomer diffusion, the temperature of the system, and the interdependence of all these parameters as the grafting proceeds. The interplay of these parameters make grafting very complicated. Of importance in this manufacturing development is the fact that the grafted membranes should have specific desired end properties, such as, graft uniformity, low electrical resistance, zinc dendrite resistance and extended cycle life. These properties are fully discussed in Task 8.

2.6.2. Grafting Procedures

The manufacturing technique for grafting prior to the award of this contract was as follows: five hundred feet of precrosslinked film was rolled loosely with cheesecloth as the interlayer. It was not possible to know how tight or how loose the roll was. There was no data relating tension during the winding of the roll.

The grafting solution was made using 26.4 percent glacial methacrylic acid, 70.0 percent benzene and 3.6 percent carbontetrachloride. The solution was thoroughly mixed and five gallons was added to a stainless steel reactor. The roll was prepared on a stainless steel three-inch diameter hollow core and was placed in the reactor. The roll of film and interlayer were positioned on the core so that the roll was kept approximately ten to twelve inches from the bottom of the reactor and the center of the polyethylene was at the center of the vertical height of the can.

The reactors were thirty inches in height. After positioning the roll in the reactor a cover was bolted on the vessel. There is a port in the cover approximately one inch in diameter to allow for pressure relief which might develop during the initial phase of the reaction. The film was allowed to swell in the monomer solution for twenty-four hours and then placed in the radiation vault. The reactors were placed on rotators and revolved at about 25 revolutions per minute during radiation. The roll of film in the reactor was stationary relative to the reactor can.

The dose rate and total dose as determined on small samples was 10,000 rads/hr. and 1.51 megarads respectively. The dosimetry of the vault in which the radiations were conducted was determined by personnel at the Industrial Reactor Laboratories of Princeton, New Jersey using standard techniques. The temperature of the radiation vault was about 75°F. At the dose rate specified (10,500 rads/hour) the reactors were exposed to the Co^{60} gamma rays for 144 hours giving a total dose of 1.51 megarads.

These were the standard conditions in the manufacture of Permion 2291 as developed under the research subcontract with the Delco-Remy Division of General Motors Corporation (1). Since the irradiations were performed by an outside company, it was not possible to follow the grafting reaction. There was essentially no thermal control and no record of the grafting temperature was possible. The reactor was exposed to the atmosphere and this appears to be the primary reason why grafting had to be carried out over six to seven days.

In the new procedure, grafting as developed under the present contract, a standard run of 3,300-3,500 feet of precrosslinked film was wound into a roll with a new paper mesh interlayer. The tension in the roll was controlled by the winding unit by adjusting the braking pressure and the hanging weights on the axis of feed rolls. The grafting solution was changed to 17.6% methacrylic acid, 80.2% benezene and 2.2% carbon tetrachloride. This new solution concentration was established as a result of the series of grafts shown in Table 6-1. The solution was thoroughly mixed. After positioning the roll in the film reactor, air was evacuated by pulling a vacuum and letting back with nitrogen. This was done 14 times prior to passing the sparged grafting solution into the nitrogen filled reactor. This solution was then pulled into the reactor by vacuum from the bottom to displace nitrogen gas pockets. The reactor is 36 inches in height with an inside diameter of 32 inches. There are positions for four thermistors on the reactor wall and one in the bottom of the reactor to follow the grafting temperature throughout the reaction. In addition, there were inlets and outlets to circulate the graft solution. The solution was pumped through a heat exchanger to maintain temperature control. The film bundle was rotated at two revolution per minute by an explosion proof motor mounted on the reactor cover. A safety rupture disc was also located in the cover to guard against possible pressure build-up during the reaction. The dose rate ranged from 9,000 to 10,000 rads/hour and the total radiation time was two days depending on the extent of reaction as followed by the temperature and monomer concentration. In summary, the new procedure uses a different interlayer, and has incorporated features which permit development of manufacturing parameters for scaling up the grafting process with the design equipment. The induction period, air effect, nitrogen sparging, temperature heat monitoring, and new grafting solution composition were evaluated to optimize the manufacturing process. In general, the induction period ranges from a few hours to a few days. This is discussed in a later section. A new technique was also used to study the uniformity of graft. Test pieces of film were inserted into the roll and their percent graft was determined directly. The electrical resistance and the cycle life were then related to the percent graft of the membrane.

2.6.3 Results and Discussion

Twenty grafting runs were made under this task. Preliminary studies involving small samples to establish the best interlayer were reported under task four. Initially the grafting reaction was followed only by the temperature profile. Subsequently this was supplemented by titration of the monomer and following the exotherm-endotherm recordings. An oxygen probe was employed in following the initiation of the grafting reaction in the last few runs. During the course of the grafting reaction the viscosity and the precipitation in the graft solution increases so much that the pump can not circulate the solution beyond a certain point and had to be disconnected. At this point the titration step, the exotherm-endotherm reading and the oxygen measurements which were made on circulating solution can not be made. The temperature readings, however, were still valid as they represented the true temperature locally throughout the reactor. Table 6-1 is a summary of the results of the grafting runs.

Production material was taken from runs 12-20. The resistance, cycle life and other quality control test used in passing on these materials is given in a subsequent section. The variation noted in total dose is due to the uneven residual oxygen content in the system prior to the onset of the grafting reaction. An oxygen probe was added to the grafting system to determine the actual grafting time and to establish the true oxygen concentration in the system. Run number 20 was made with this unit in the line. The results are given in Table 6-8. A description of the runs listed in Table 6-1 follow.

TABLE 6-1 GRAFTING STUDIES

Code#	Run#	T°F	Film (Ft^2)	Monomer Solution	Dose Rate	t(hrs)	Total Dose	Remarks
231-28	1	75	2,300	60/26.4/3.6	10,202 r/h	168	1.71	No graft. Air pumped to solution.
231-43	2	75	2,300	70/26.4/3.6	10,100	80	0.81	No pumping. After 73 hrs, temp. rose rapidly. Low graft.
231-46	3	85	3,300	70/26.4/3.6	9,998	165	1.65	Grafting good. Uniform resistance.
231-53	4	100	3,600	70/26.4/3.6	9,998	168	1.68	Grafted, but not uniform.
231-58	5	100	4,100	70/26.4/3.6	9,898	164	1.62	Grafted, but not uniform.
231-62	6	100	3,300	70/26.4/3.6	9,898	144	1.43	No graft. Air entrained.
231-67	7	100	3,300	70/26.4/3.6	9,799	17.25	0.17	% graft, high, Uniform resistance.

TABLE 6-1 GRAFTING STUDIES (cont)

Code#	$T^{o}F$	Run#	Film (ft^2)	Monomer Solution	Dose Rate	t (hrs)	Total Dose	Remarks
231-71	85^{o}F	8	3,300	70/26.4/3.6	9,799	11.33	0.11	Graft not uniform.
231-74	85	9	3,300	83/15/2	9,700	6.33	0.06	Low graft. Not uniform.
231-78	85	10	3,300	88.7/10/1.3	9,602	21	0.20	Low graft. Not uniform.
231-81	85	11	3,300	88.7/10/1.3	9,602	48	0.46	Low graft. Quite uniform.
231-83	85	12	3,300	80.2/17.6/2.2	9,506	45	0.43	Good graft.
231-86	85	13	3,300	80.2/17.6/2.2	9,506	16.5	0.16	Good graft.
231-88	85	14	3,300	80.2/17.6/2.2	9,411	48	0.45	Good graft.
231-90	85	15	3,300	80.2/17.6/2.2	9,411	130	1.22	No grafting. Air trapped.
231-93	85	16	3,300	80.2/17.6/2.2	9,411	42	0.39	High graft.
231-95	85	17	3,300	80.2/17.6/2.2	9,316	44	0.41	Graft low, but uniform.
231-97	85	18	3,300	80.2/17.6/2.2	9,316	135	1.26	Graft satisfactory.

TABLE 6-1 GRAFTING STUDIES (cont)

Code#	Run#	T°F	Film (ft^2)	Monomer Solution	Dose Rate	t (hrs)	Total Dose	Remarks
231-03	19	85°F	3,300	80.2/17.6/2.2	9,222	20	0.18	Outside not uniform. Otherwise, O.K.
231-103	20	85	3,300	80.2/17.6/2.2	9,222	25	0.23	Graft O.K. Uniformity, good.

* The monomer solution is given in weight % solution for benzene/ methacrylic acid/ carbon tetrachloride.

Run No. 1 failed to graft after irradiation for seven days. It was evident from visual inspection that no homopolymer formed in the reactor. The film had an extremely high electrical resistance and the thermal profile given below indicates no temperature rise.

THERMAL PROFILE FOR RUN #1

Radiation Time In Hours	Temperature in °C 1st Probe	
0	27.0	
6	28.0	
12	28.7	
18	28.9	
24	22.2	Cooling started and then stopped
28	25.8	
34	28.1	
40	28.5	
46	29.0	
52	29.5	
58	30.1	
64	30.5	
70	29.0	
76	29.0	
82	28.0	
88	29.0	
94	28.8	
100	28.7	
106	29.5	
112	29.0	
118	29.0	
124	31.0	
130	29.9	
136	29.9	
142	29.2	
148	29.5	
166	29.5	
168	29.5	Reaction terminated

The fluctuations in temperature at the 24th hour was due to changes in hot water supply and some shut-down of pump and temperature controller. No large temperature rise (5-10°C) observed. After a careful check of the reactor, it was noted that air was being pumped through the grafting solution in the make-up tank. Further checking disclosed that air was entering the system from the suction end of the pump which pulled the grafting solution from the radiation vault.

It was quite obvious that the oxygen being added to the system was effectively inhibiting the grafting reaction.

Run No. 2 was a continuation of No. 1. The graft solution from Run No. 1 was discarded and a fresh solution was added. Since the pump pulled air in the make-up tank, it was disconnected. The reaction was run without circulation of the monomer solution. This was done to establish the importance of oxygen exclusion. Nitrogen was bubbled into the bottom of the reactor while the bundle was rotating at 2 revolutions per minute. After irradiation for 90 hours, the temperature in the film reactor rose rapidly, indicating the grafting reaction had started. The thermal profile for this run follows:

THERMAL PROFILE FOR RUN #2

Radiation Time In Hours	Temperature in ^{o}C		
	1st Probe	4th Probe	
0	21	21	
15.5	22.2	22.2	
39.5	22.5	22.5	
63.5	22.5	22.5	
79	22.5	22.5	
85	25.5	25.8	
86	26.2	30.4	
87	27.0	30.9	
89	29.9	33.9	
89.5	30.5	35.0	
90	31.6	38.9	Source down
90.5	31.2	44.2	

For 79 hours of irradiation, there was no temperature rise, implying no polymerization taking place. Then the temperature slowly climbed up, and at the 90th hour, the rise was very rapid. At this point, the source was lowered down. From the above chart, it was concluded that the induction period was about 80 hours under the condition of this run. Testing indicated that the film was only lightly grafted, the electrical resistance was almost 2ohm/in^2. The run was terminated too soon. Two points were established (1) even under sparging conditions the amount of oxygen caused a lengthy induction period and (2) grafting under static conditions would give poor thermal uniformity.

Run No. 3 was conducted at 85°F using precuations against air entrainment. Nitrogen was bubbled through the tank from the bottom of the reactor. The pump was connected to provide circulation of the graft solution and thermal control. The film bundle used in this run was wound at 52 lbs. tension to a full bundle of 3,300 ft^2. Monomer was circulated through the heat exchanger to maintain a constant temperature. After irradiating 165 hours, the film was highly grafted. Testing indicated that the electrical resistance was quite uniform all around 30 milliohm-in^2. Other characteristics of the grafted membrane made in this Run showed properties similar to the standard P2291. The temperature profile is shown below.

THERMAL PROFILE FOR RUN #3

Radiation Time In Hours	Temperature in °C 1st Probe
1	30.0
5	32.2
11	39.0
23	36.0
59	37.5
71	31.2
81	30.5
95	29.5
121	32.2
145	31.4
165	25.9 Reaction Terminated.

The grafting reaction appears to have started after 5 hours and reached a peak temperature of 39°C. From the 11th thru the 59th hours the temperature was maintained by the exothermic nature of the reaction and then the temperature slowly declined as the reaction subsided. The reaction was well controlled and the solution was circulated during the full run.

Run No. 4 was performed at a higher temperature, 100°F. It was reasoned that an increase in temperature should bring an increase in grafting rate. The amount of film used was 3600 square feet and this was irradiated for 7 days. Test results indicated that the grafting was not uniform, and the graft level was low. There was little increase in temperature as shown below, from 38°C to a peak of 41°C.

THERMAL PROFILE FOR RUN #4

Radiation Time In Hours	Temperature in °C 1st Probe
0	37.0
13	36.0
16	37.0
49	41.0
79	41.0
101	38.5
117	38.5
141	39.0
162	34.0
168	34.0 Reaction Terminated

Run No. 5 was a repeat of Run No. 4. The reaction temperature was 100°F. The roll used here contained 4,100 square feet of crosslinked film. After irradiation for 164 hours, the graft was again found to be low and non-uniform. It was suspected that the film was wound too tightly on the bundle. However, it was also suspected that sufficient air may have been entrapped in the film bundle, or that air was still being pumped into the solution. An examination of the thermal data revealed that there was no temperature increase throughout the reaction. This suggest very strongly the presence of an inhibitor.

THERMAL PROFILE FOR RUN #5

Radiation Time In Hours	Temperature in °C 1st Probe
0	25.0
7	33.5
19	37.0
31	37.0
43	37.0
55	37.5
67	37.5
79	37.5
91	38.0
103	38.0
115	37.5
127	37.5
139	38.0
151	38.0
163	38.0
164	37.0 Reaction Terminated

In order to avoid diffusion problems, it was decided to wind only 3300 square feet on each roll. Run #6 was made with a bundle containing only 3300 square feet. The temperature was kept at 100°F as in Run #5. A recorder was also installed to record the heat and cooling cycle in the heat exchanger to facilitate the study of the exotherm and for endotherm of the reaction. After irradiation for 7 days, both visual inspection and electrical resistance measurement indicated no graft. There was no temperature increase and no call for cooling by the heat exchanger temperature probe.

THERMAL PROFILE FOR RUN #6

Radiation Time In Hours	Temperature in °C 1st Probe		Heat-Dwell-Cool Reading
0	45.0		Heat
3	41.0		Heat
16.5	45.0		Heat-Dwell
27.0	38.5*		Heat-Dwell
42	37.0		Heat-Dwell
54	37.0		Heat-Dwell
66	37.0		Heat-Dwell
89	37.0		Heat-Dwell
113	37.0		Heat-Dwell
138	37.0		Heat-Dwell
144	37.0	Reaction stopped	Heat-Dwell

*The temperature Controlling Probe was reversed from the outlet to the inlet position.

A recheck on the system showed that air was still being pumped into the grafting solution and this resulted in the inhibition effect noted. Based on the poor results obtained to this time, the grafting was altered for Run #7. The film bundle was positioned in the reactor and subjected to a vacuum nitrogen let back cycle 14 times. Monomer solution was let in from the bottom of the reactor to displace gas pockets and the mixture was allowed to swell overnight with nitrogen bubbling through the reactor. In addition, the pump was housed into a box which was maintained under a positive nitrogen pressure. A new technique was also introduced to follow the percent graft and graft uniformity. Test pieces were set in various parts of the film roll. Under these conditions, the reaction was completed in about 17 hours.

From the temperature profile and the heat-cool information it was noted that there was no reaction for the first 2 hours. Then the temperature of the system slowly rose from 28°C to 40°C when it was terminated. The recording also showed that the exchanger was maintained on dwell and no heat was added to the system after the reaction had started, indicating an exothermic reaction. The pertinent data on Run #7 was given in Table 6-2. For the first time, the exact percent graft of the film relative to the film footage was available, and a graft distribution curve could be constructed based on the data from Table 6-2. The graft distribution curve is shown in Figure 6-1. The electrical resistance of the membrane was very uniform, having a resistance in 40%KOH from 10 to 21 milliohm/in^2 throughout the entire roll. This indicated a uniform resistance, however, the material was not uniformly grafted. Figure 6-1 indicates that the percent graft varied from about 80% to 130%. The explanation for this characteristic is due to the fact that the resistance of a grafted membrane exhibits very little change above a certain percent graft and in fact a plot of resistance versus percent graft illustrates this effect. Figure 8-18 which is given under Task 8 indicates that above 80% the resistance is asymptotic with the graft level. Further below 25% graft the resistance increases sharply with a slight change in graft level and is in fact asymptotic with the resistance.

TABLE 6-2 TEMPERATURE AND HEAT PROFILE OF RUN #7

Irradiation Time (Hours)	Temperature in ^{o}C 1st Probe	Exotherm-Endotherm Recording
20:45 PM	28.2	Heat
4:10	28.5	Heat
6:10	31.5	Heat
8:10	33.5	Heat
10:10	37.0	Dwell mostly, very little heat
12:10 AM	37.5	Dwell mostly, very little heat
2:10	38.0	Dwell mostly, very little heat
4:10	38.5	Dwell mostly, very little heat
6:10	39.0	Dwell mostly, very little heat
8:00 Terminated	Terminated	Dwell mostly, very little heat

TEST STRIP RESULTS FOR RUN #7

Radius into Roll	3" (316 ft)	6" (882 ft)	9" (1646 ft)	12" (2592 ft)
Position in Roll	Top	Top	Top	Top
Percent Graft	102.2%	125.7%	126.3%	84.6%
Resistance*	21	11	14	11
Position in Roll	Bottom	Bottom	Bottom	Bottom
Percent Graft	117.3%	135.3%	117.9%	80.1%
Resistance	15	14	10	15

* Resistance given in milliohms/in^2 at 23^{o}C in 40% KOH.

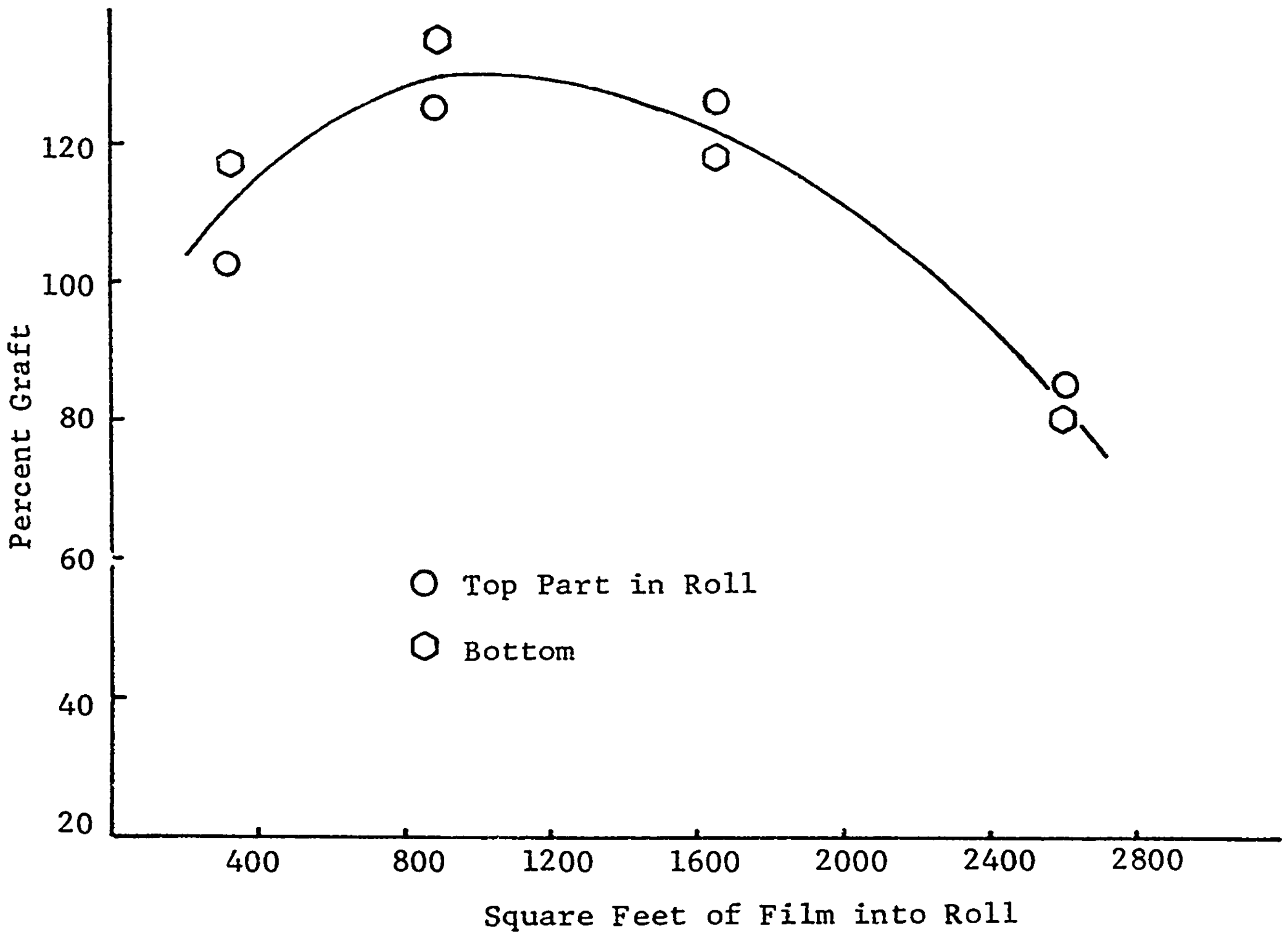


Figure 6-1 Graft Distribution Curve for Run #7

The conditions for Run No. 8 were the same as in Run #7 except that the initial temperature was set at 85°F instead of 100°F. It was reasoned that a decrease in temperature would decrease the grafting rate so that the percent graft would be less than that of Run #7. After about 12 hours of irradiation, the reaction was stopped. The thermal data showed that the temperature of the system started to rise after three hours of radiation from 30°C and was 42°C after 12 hours. Data from the heat recording also agreed with the above finding. After three hours of irradiation, less heat was added and the heat exchanger remained in the dwell mode. After 9 hours of radiation, no heating was required, only dwell, implying an exotherm had occurred. The results are shown in Table 6-3.

Results showed that percent graft was lower and non-uniform. The percent graft ranged from 1-93% throughout the roll, with electrical resistance going from 5.3ohm/in^2 to 11 milliohm/in^2. Only the section from 5½" (746 ft) to 9" (1772 ft) was satisfactory. The run was probably stopped a few hours too early.

The effect of monomer concentration was studied in runs #9, 10, 11, and 12 at 85°F. The rate of grafting should be proportional to the monomer concentration as indicated in

$$R_p = k_p \left[\frac{R_i}{2k_t} \right]^{\frac{1}{2}} [M]$$

where R_p is the rate of graft polymerization, k_p and k_t are the constants of polymerization and termination, R_i is the rate of initiation and M the monomer concentration. This equation predicts that the rate of grafting is linearly related to the monomer concentration. Consequently, if we decrease the monomer concentration, a decrease in percent graft is expected provided the rate of initiation (or dose rate) is constant.

Run #9 was made with a methacrylic acid concentration of 15% instead of the usual 26.4%. All other parameters being held constant, as in Run #8. After irradiation for 6½ hours, the reaction was stopped. The thermal data revealed that the exotherm had started after two hours of irradiation. The temperature of the system started to rise slowly after two hours of irradiation indicating the reaction had started. Results are shown in Table 6-4.

TABLE 6-3 TEMPERATURE AND HEAT PROFILE OF RUN #8

Irradiation Time (Hours)	Temperature in °C 1st Probe	Exotherm-Endotherm Recording
0	26.0	Heat
2	29.5	Heat
4	31.0	Heat - little dwell
6	32.5	Very little heat - mostly dwell
8	34.0	Mostly dwell
10	40.0	Dwell only
12	42.0	Dwell only

TEST STRIP RESULTS FOR RUN #8

Radius into Roll	1" (86 ft)	5½" (746 ft)	9" (1772 ft)	12" (2806 ft)
Position in Roll	Top	Top	Top	Top
Percent Graft	5.2%	92.2%	83.5%	22.8%
Resistance*	(64 milliohm-in^2)	11	13	50
Position in Roll	Bottom	Bottom	Bottom	Bottom
Percent Graft	0.2%	92.6%	82.8%	38.6%
Resistance*	(5300 milliohm-in^2)	11	15	42

* Resistance given in milliohms/in^2 at 23°C in 40% KOH.

TABLE 6-4 TEMPERATURE AND HEAT PROFILE OF RUN #9

Irradiation Time (Hours)	Temperature in $^{\circ}$C 1st Probe	Exotherm-Endotherm Recording
0	30.1	Heat and dwell
1	30.1	Heat and dwell
2	30.8	Less Heat - more dwell
3	31.2	Mostly dwell
5	31.4	Mostly dwell
6	31.6	Dwell only
6½	32.0	Dwell only

TEST STRIP RESULTS FOR RUN #9

Radius into Roll		5½" (850 ft)	10½" (2210 ft)	13 5/8" (3300 ft)
Position in Roll	Top	Top	Top	Top
Percent Graft	1.3%	7.6%	24.3%	9.2%
Resistance	11,700	8,000	39	5500
Position in Roll	Bottom	Bottom	Bottom	Bottom
Percent Graft	1.1%	13.7%	27.6%	11.7%
Resistance*	5,300	490	72	4900

* Resistance given in milliohms/in^2 at 23°C in 40% KOH.

Although the percent graft for this run was less than Run #8, the graft uniformity was poor, from 1% to 28% throughout the roll. The electrical resistance was also non-uniform. Again, a longer grafting time was needed to improve the uniformity.

Run No. 10 was a run with 10% methacrylic acid. The reaction started after a 4 hour induction period which was now quite reproducible if the procedure to purge air from the system were followed. There was no temperature rise noticeable during this run partly because the monomer concentration was low, and partly because the circulation of solution through the heat exchanger was operating ideally. The beginning of the reaction was evident from the exotherm recording. After 21 hours of radiation, the reaction had to be stopped because of a pump failure. Pertinent data are shown in Table 6-5.

The percent graft of Run No. 10 was low, being between 17 and 24%. The uniformity of the graft as a function of position in the roll was excellent with the mean deviation being ± 3.5%. The electrical resistance was not acceptable, however, as would be expected based on the low level of graft. The relationship between percent graft and resistance is given in Figure 8-18.

Run No. 11 was comparable to Run No. 10 with the exception of reaction time. This was extended to 48 hours from the 21 hours scheduled for Run No. 10. It was anticipated that the increase in radiation time would increase the percent graft. Data on this run and the percent graft obtained are given in Table 6-6.

As in Run No. 10, the graft uniformity of Run No. 11 was very good varying from 26 to 32% although the percent graft was slightly higher for Run No. 11, due to the longer reaction time, the electrical resistance was still found to be unacceptable. It was therefore decided to increase the monomer concentration.

For Run No. 12 the monomer concentration was set at 17.6% while all other conditions were maintained constant. Table 6-7 gives the data from this run.

TABLE 6-5 TEMPERATURE AND HEAT PROFILE OF RUN #10

Irradiation Time (Hours)	Temperature in °C 1st Probe	Exotherm-Endotherm Recording
0	30.2	Heat-Dwell
2	30.6	Heat-Dwell
4	30.8	Less Heat - More Dwell
6	30.8	Dwell only
8	30.8	Dwell only
10	30.8	Dwell only
12	30.8	Dwell only
16	30.6	Dwell only
20	30.8	Dwell only
21	30.8 Terminated	Dwell only

TEST STRIP RESULTS FOR RUN #10

Radius into Roll	0" (31 ft)	4½" (624 ft)	9" (1770 ft)	31½" (3300 ft)
Position in Roll	Top	Top	Top	Top
Percent Graft	22.6%	17.0%	23.9%	23.7%
Resistance	105 milliohm-in^2	61	75	45
Position in Roll	Bottom	Bottom	Bottom	Bottom
Percent Graft	16.5%	23.4%	24.0%	18.1%
Resistance	280	41	71	175

TABLE 6-6 TEMPERATURE AND HEAT PROFILE OF RUN #11

Irradiation Time (Hours)	Temperature in °C 1st Probe	Exotherm-Endotherm Recording
1	30.0°	Heat-Dwell
2	30.8	Heat-Dwell
3	31.0	Less Heat - More Dwell
6	31.0	Mostly Dwell
10	30.0	Dwell only
16	[illegible]	Dwell only
22	31.0	Dwell only
28	30.2	Dwell only
34	30.2	Dwell only
40	30.2	Dwell only
48	30.2 Terminated	Dwell only

TEST STRIP RESULTS FOR RUN #11

Radius into Roll	0" (48 ft)	4½" (660 ft)	9" (2008 ft)	13½" (3300 ft)
Position in Roll	Top	Top	Top	Top
Percent Graft	27.0%	27.0%	26.0%	32.0%
Resistance	50 milliohm-in^2	46	86	44
Position in Roll	Bottom	Bottom	Bottom	Bottom
Percent Graft	26.0%	29.0%	27.0%	30.5%
Resistance *	122	37	47	67

*Resistance given in milliohms/in^2 at 23°C in 40% KOH.

It appears that the reaction started after one hour of irradiation and the temperature continued to rise. This probably caused an increase in the homopolymer formation which resulted in failure of the pump after 12 hours. The reaction exotherm peaked at 41°C after 14 hours and subsequently the temperature decreased. The irradiation was continued for 43 hours. The graft uniformity was not as good as the two previous runs but the electrical resistance was satisfactory, varying from 23 to 44 milliohms/in^2 throughout the entire roll. The percent graft varied from 35 to 66%. It appears from this run and previous runs that the percent graft decreases with decreasing monomer concentration, as was expected. It was also apparent that the graft uniformity was more uniform when a low monomer solution was used. This relationship between uniformity and monomer concentration is shown in Figure 6-2. It must be remembered that the thermal control of the system is more severe as the monomer content increases and that better thermal uniformity is probably the primary factor in maintaining better uniformity.

Figure 6-2 indicates Runs 10 and 11 gave the best graft uniformity but the percent graft and the resistance were low. Runs Nos.8 and 9 gave poor uniformity. Run No. 12 was the best compromise in terms of percent graft, electrical resistance and graft uniformity.

Runs Nos. 13 to 20 were then undertaken to establish the reproducibility of the process and to make initial production material. The conditions for these production runs were fixed. Each roll contained 3,300 square feet of 90 Mrad crosslinked film wound into a bundle using the Lenonet paper mesh interlayer. The bundle size was 27 inches in diameter. The composition by weight of the grafting solution was:

Benzene	80.2%
Methacrylic Acid	17.6%
Carbon tetrachloride	2.2%

Previous results indicated the importance of removing air from the system, therefore, the reactor when in position in the vault was evacuated and let back with nitrogen 14 times. After the final evacuation, pre-sparged (nitrogen)

TABLE 6-7 TEMPERATURE AND HEAT PROFILE OF RUN #12

Irradiation Time (Hours)	Temperature in ^{o}C 1st Probe	Exotherm-Endotherm Recording
0	30.5	Heat only
1	30.5	Less Heat - More Dwell
3	31.0	Heat
6	33.0	Mostly Dwell
12	39.5	Pump broke down
14	41.0	
18	36.5	
24	38.0	
30	37.0	
36	35.5	
40	35.0	
45	35.0 Terminated	

TEST STRIP RESULTS FOR RUN #12

Radius into Roll	0" (0 ft)	4½" (636 ft)	9" (1902 ft)	13½" (3280 ft)
Position in Roll	Top	Top	Top	Top
Percent Graft	66.3%	46.2%	44.6%	35.3%
Resistance	23 milliohm-in^2	28	28	37
Position in Roll	Bottom	Bottom	Bottom	Bottom
Percent Graft	55%	47.4%	44.4%	38.5%
Resistance	25	27	29	44

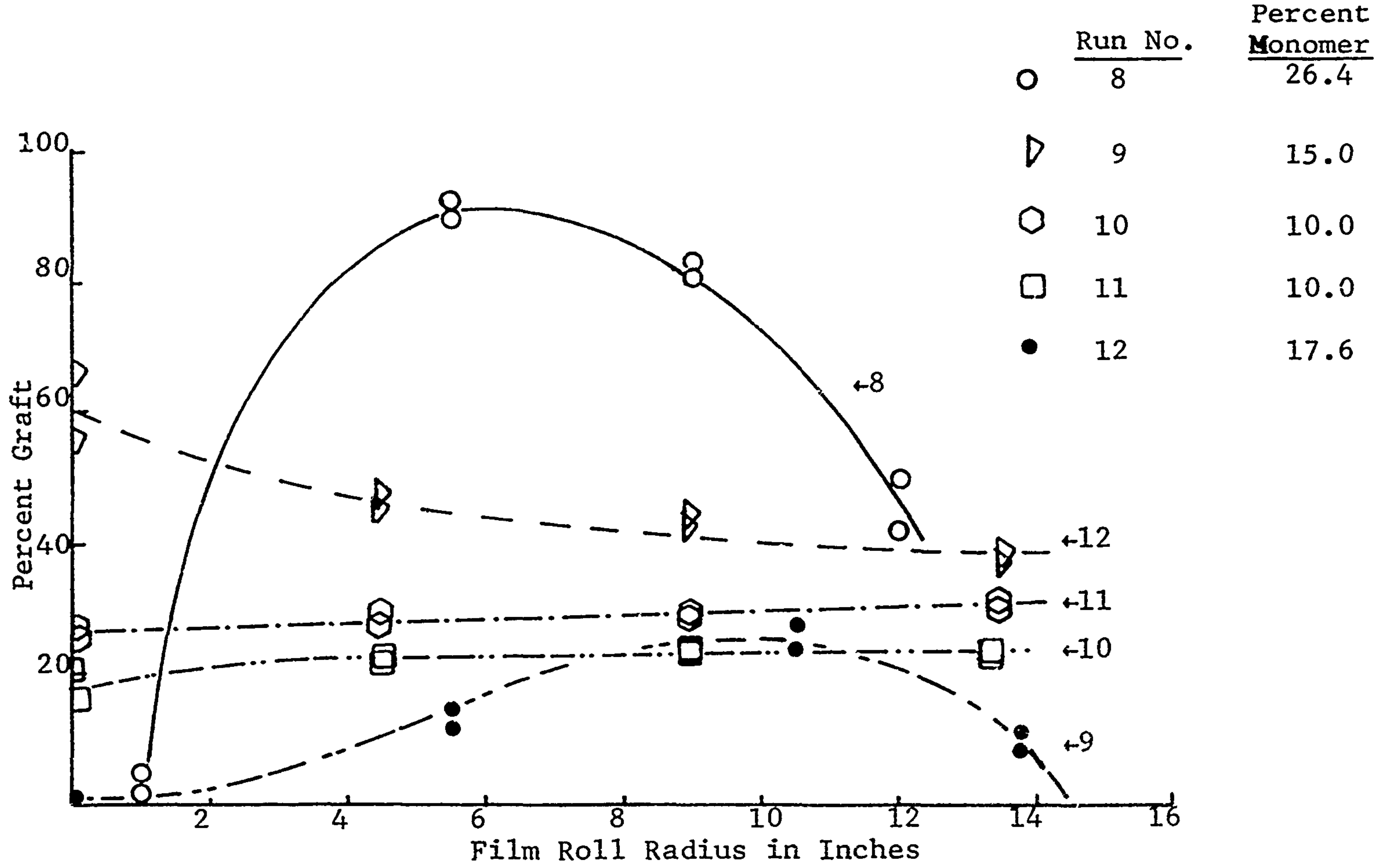


Figure 6-2. Effect of Monomer Concentration on Percent Graft and Graft Distribution.

monomer solution was let into the reactor from the bottom. The system was then heated to 85^{o}F with continuous nitrogen sparging. An oxygen electrode was used only during Run No. 20 but is now part of the procedure in determination of the dissolved oxygen in solution. This oxygen level should be less than 1 ppm prior to irradiation. When thermal equilibrium is reached, and the oxygen level is below 1 ppm the reaction vessel is exposed to gamma radiation from the Cobalt-60 source. The radiation field intensity varies from 0.9 to 1.0 x 10^4 rads/hr and the total dose given depends on the thermal data and the change in methacrylic acid content as determined by a modified acid titration during the irradiation cycle.

Continuous monitoring of the system heat-cool cycle is an indispensable step in following the grafting reaction. When methacrylic acid polymerizes, 15.8 Kcal/mole are given off as heat of reaction. Depending on the rate of reaction this could result in a slow or rapidrise in temperature. Normally the course of the graft polymerization should result in a temperature rise to a maximum followed by a decline as the reaction nears completion. When the temperature rises due to the heat of polymerization, the exothermic nature of the reaction is followed by the call for "cool or dwell" in the heat exchanger unit. When the temperature falls the endothermic nature of the reaction is recorded by a call for "heat". These cool, dwell or heat cycles are readily observed during the grafting reaction.

In addition to the above, the reaction can be followed by monitoring the residual monomer concentration. This is done by a modified titration. In the beginning of the reaction, when no homopolymer is present, titration is straightforward. As the reaction proceeds methacrylic acid homopolymer forms resulting in an increase in viscosity of the grafting solution and precipitation of homopolymer. When this occurs the solution is no longer a clear liquid but rather a viscous slurry and both the monomer and homopolymer will be titrated by the alkali. Only the monomer concentration is of interest. To determine the monomer concentration, a sample must first be centrifuged and a known quantity of the clear supernate treated with a weighed amount of methanol to precipitate homopolymer in solution. This leaves the monomeric methacrylic acid in solution. The mixture is again centrifuged and a portion of the clear liquid is pipetted out and titrated. The monomer concentration is then calculated after correcting for dilution with methanol. By centrifuging out the homopolymer, the major source of error in titrating for residual acid is removed. The soluble low molecular weight homopolymer is also removed by use of methanol. The small contribution that the low molecular weight fraction makes to the total volume of supernate liquid still constitutes a small error. The results of numerous evaluations have been found to be reproducible.

The analysis for dissolved oxygen is very simple and straightforward. The oxygen probe in the Fieldlab Oxygen Analyzer is first calibrated against air containing 20.8% oxygen. The probe is then calibrated against air saturated benzene which is used as an internal standard since it is known to contain 55 ppm of dissolved oxygen. The scale reading obtained is then equal to 55 ppm of dissolved oxygen. To check the functioning of the probe, nitrogen is bubbled through the air saturated benzene. The oxygen content in solution gradually falls to almost zero, indicating oxygen is displaced by the nitrogen and the dissolved oxygen ultimately almost reaches zero. When the nitrogen flow is stopped, the solution takes up oxygen. This is readily followed and it appears that the oxygen uptake is linear with time. After standardization and checking the oxygen probe is placed in the grafting solution line just before the pump to monitor the oxygen in solution in the circulating liquid. Table 6-8 shows the data for benzene and the grafting solution. The uptake of oxygen in the grafting solution is linear with time. The oxygen uptake curve is given in Figure 6-3.

Typical data on the use of all four methods in following the grafting reaction are given in Table 6-9 for production Run No.20. A graph of the temperature of the system and the monomer acid concentration as a function of irradiation time is illustrated in Figure 6-4. The temperature rises from 28.5°C to a maximum of 33°C and then falls off with time. The monomer concentration decreases almost linearly from an initial 17.6% to a final value of 6.1%. The average rate for the disappearance of monomer which goes to both homopolymer and graft copolymer is calculated from the slope of the curve to be 0.46% hr.$^{-1}$. It must be noted

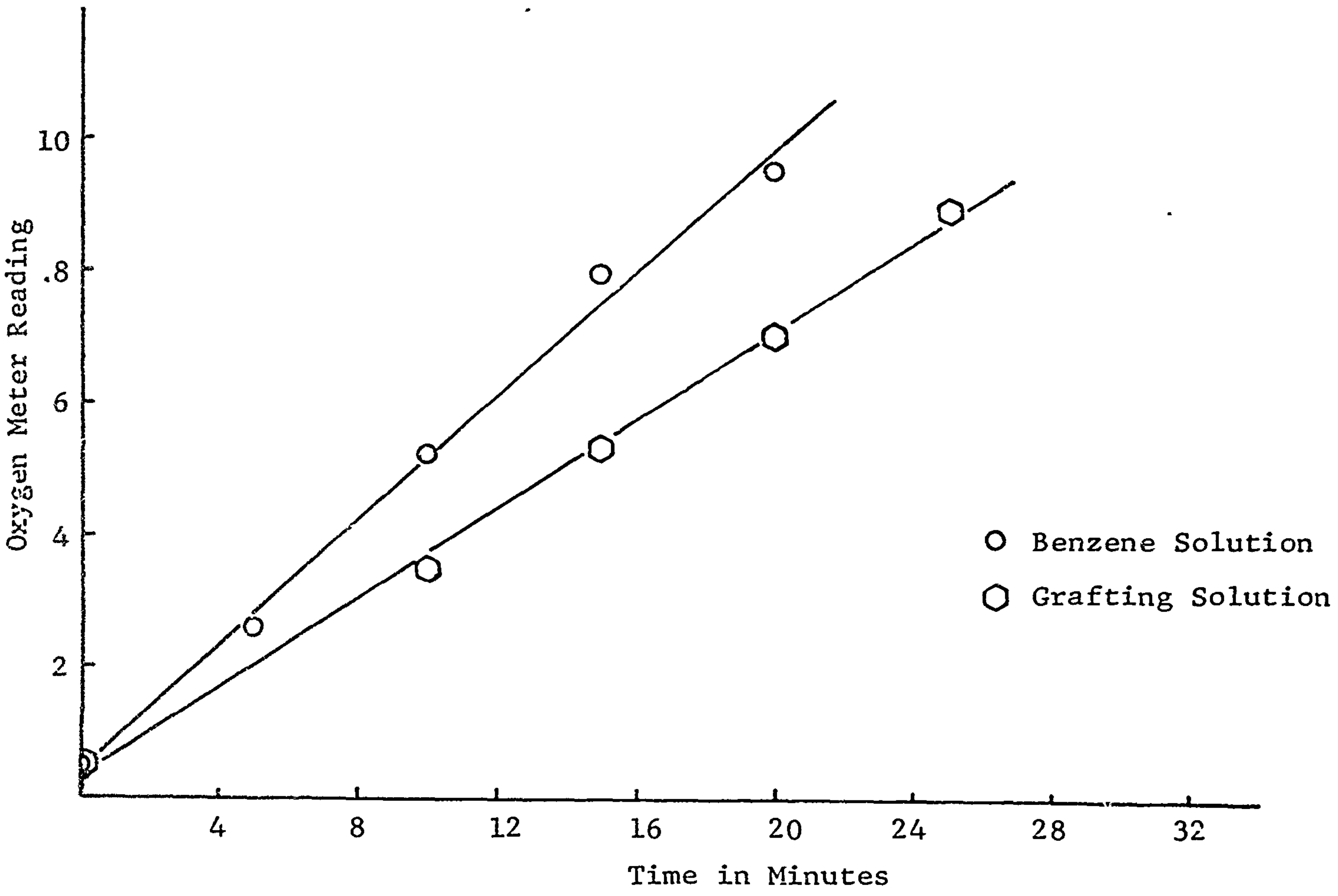


Figure 6-3 Oxygen-Uptake for Benzene and Grafting Solution

TABLE 6-8

Dissolved Oxygen Monitoring by Oxygen Analyzer

Condition	Probe Reading	Time
Calibration against air	21.0%	
In air saturated benzene	19-18%	
Nitrogen bubbling	0.4 to 0%	
No nitrogen bubbling	0.4%	3:50 P.M.
	2.6	3:55
	5.2	4:00
	8.0	4:05
	9.5	4:10
	18.5	8:30 A.M.
In air saturated grafting solution	20.3%	
Nitrogen bubbling	0.2 to 0%	
No nitrogen bubbling	0.5	4:25 P.M.
	3.5	4:35
	5.3	4:40
	7.0	4:45
	8.9	4:50
	19.5	9:00 A.M.

that only a small fraction of this monomer is necessary to give the required percent graft in the membrane. The exotherm recording and the dissolved oxygen analysis were discontinued when the pumping was stopped since there was no circulation of the grafting solution to the heat exchanger and the oxygen probe. Data prior to this did indicate the exotherm started after three hours of irradiation and the oxygen in the system was practically zero.

Under this task the conditions for manufacture of the grafted separator have been established. Various methods to follow the grafting reaction have been devised and a test for the graft distribution was developed. Time did not permit evaluation of grafting at higher temperatures and other intermediate monomer concentrations.

During this program it was established that the grafting reaction could be realized without the formation of homopolymer. This occurred in one run. Time did not permit exploitation of this finding. It is suspected that under optimal conditions dissolved oxygen in solution could retard the rate of homopolymerization without greatly hindering the grafting reaction. The results of this run was a clean roll which was easily handled and readily washed. It is highly desirable to investigate this beneficial behavior further. We feel that if this could be duplicated it would result in a reduction in the cost of manufacturing the separator, and increase the efficiency (in time and labor (savings) of production. With the oxygen probe now available, a controlled oxygen study is recommended.

TABLE 6-9

Studies of Run #20
During Grafting Process

Time	Temperature of 1st Probe	Endo-Exotherm Reading	Monomer in Solution	Oxygen Probe Reading
9:25 A.M.	28.5°C	Heat-Dwell	17.6%	0.2%
10:45	28.5	Heat-Dwell	-	0.1%
11:35	28.5	Heat-Dwell	-	~ 0
12:45 P.M.	29.0	Dwell	16.0%	-
1:55	29.0	Heat-Dwell-Cool	-	0.1%
2:45	29.0	Heat-Dwell-Cool	13.8%	0.1%
3:30	29.0	Heat-Dwell-Cool	-	~ 0
4:05	30.0	Heat-Dwell-Cool	13.8%	-
5:45	30.2	Discontinued	-	Discontinued
7:45	31.0		-	
9:45	32.5		-	
11:45	33.0		-	
1:45 A.M.	33.0		-	
3:45	32.5		-	
5:45	32.0		-	
7:45	31.2		-	
8:35	31.2		7.4%	
9:45	31.2		-	
11:45	30.8		-	
12:00	30.8	Reaction Terminated	6.1%	

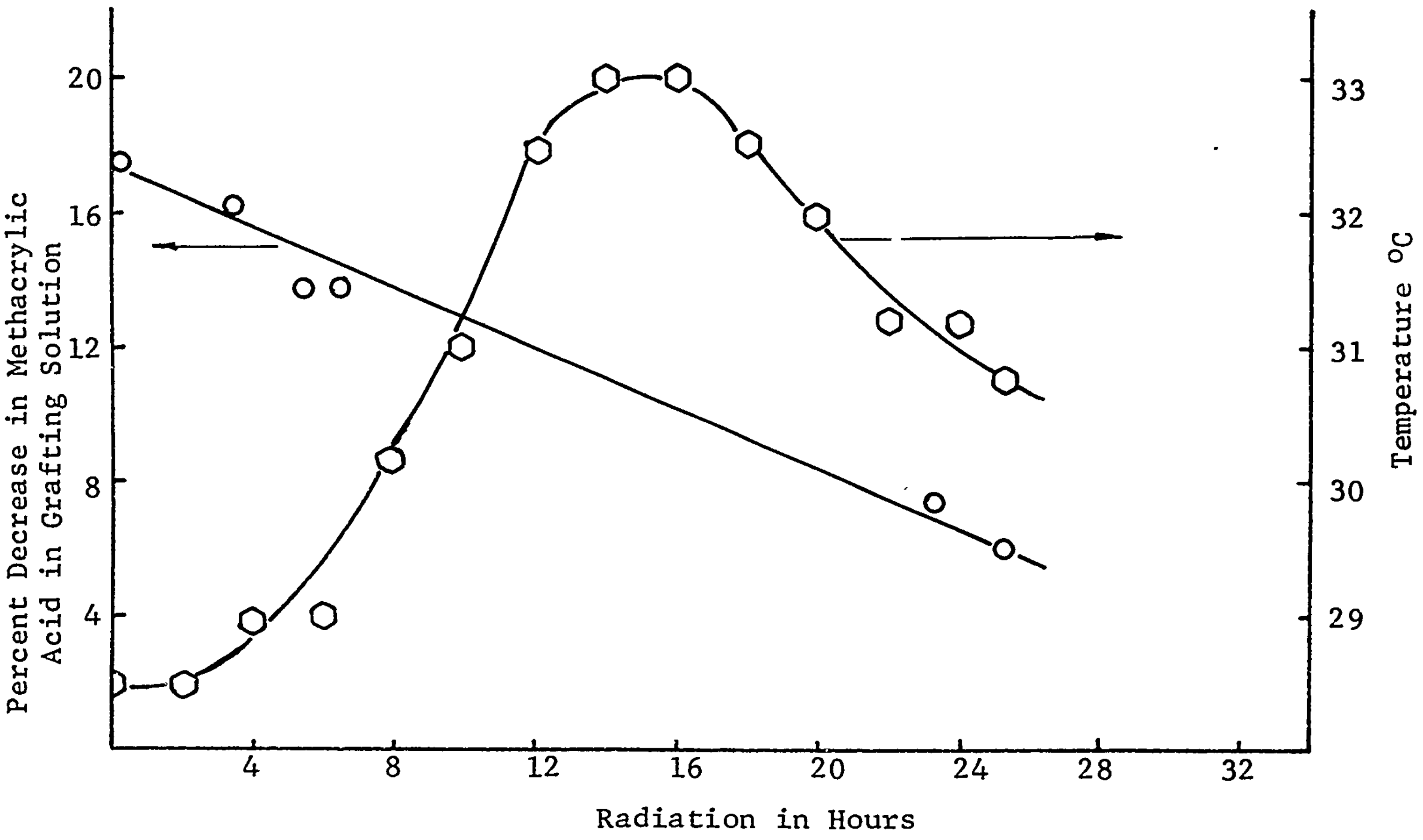


Figure 6-4 Relationship of Monomer Concentration, Temperature and Reaction Time for Run #20

2.7 TASK NUMBER SEVEN: GRAFTED FILM PROCESSING

2.71 Introduction

Membrane prepared by radiation grafting contains considerable homopolymer which is an undesirable reaction product that forms during the grafting step. The methacrylic acid homopolymer is a white water soluble powder which can be removed by washing with hot water. In addition to removing the homopolymer, the grafted membrane must be converted from the acid form to the salt form. This is done by passing the grafted washed film through a 5% potassium hydroxide solution maintained at 90-95°C. Subsequent to this conversion step the residual base is removed by washing in water. A single hot water wash at 90°C followed by a medium temperature wash 50-60°C is adequate to remove the residual base. The last wash water should be changed often enough to maintain the pH in the last wash tank below eight.

The conversion time for formation of the potassium salt from the acid was determined previously to be about two minutes. A single eight foot tank can be used to hold film for longer than this time interval if the line speed is approximately twelve feet or less and the film is festooned three times across the length of the tank. To effectively convert film to the base form, the homopolymer must be removed prior to the conversion step; therefore, two hot water wash tanks were designed to precede the conversion tank. Film entering the first tank, which is maintained above 90°C, is festooned three times through this bath, then is passed through a set of nip rollers to remove the softened homopolymer. The film then enters the second wash tank and is washed again with water maintained above 90°C. It is again passed through nip rollers before passing into the conversion tank.

Improvement in washing film was possible by first passing the grafted film between brushes to remove as much homopolymer as possible prior to entering the first wash tank. This improved feature was developed late in the program while preparing the 20,000 feet of membrane required as a deliverable item. Further improvement is possible by using rotating brushes. This will be set up, but was not part of the wash line during the washing of the 20,000 feet.

It was also found that the use of external heaters which were set under the tank did not supply sufficient heat to maintain wash temperatures for more than five hours during washing. Washing had to be stopped when the temperature dropped to 90°C. A steam boiler was therefore added to the wash line. With this unit live steam can be fed to the tanks to increase the wash temperature very quickly.

The use of the steam boiler also permits discharging the tanks after four hours and heating incoming water for the two first tanks to above 90°C over a lunch period. This should result in better washing and decrease the conversion time requirement in the potassium hydroxide conversion tank. Here again, this additional feature was added late in the program after the problem was noted.

The wash line therefore consists of five stainless steel tanks; the first and third tanks have three sets of rollers and the remaining three tanks contain only two rollers which permits the film to pass only once through the wash water. Tanks one and two are water wash tanks and wash the grafted film when it is in the acid form. Tank three contains 5% potassium hydroxide and converts the grafted membrane to the salt form. Tanks four and five are water wash tanks, and are necessary to scrub the converted membrane and remove residual base. Figure 7-1 is a schematic of the process line. Figure 7-2 is a drawing of the rollers which are set into tanks one and three. Nips rollers are mounted between tanks one and two, two and three, three and four, four and five, and at the end of tank five. Figure 7-3 details one nip showing a dancer which is associated with each nip.

2.7.2 Wash Line Controls

A. Speed Control: The swelling characteristic of the grafted membrane changes considerably when the film is converted from the acid to the base form. In the basic form the film expands considerably while it exhibits little swelling in the acid form. Further, the degree of swelling depends on the percent graft, the temperature of the water, and the concentration of the solution, i.e., percent potassium hydroxide. The film tends to swell more in water than in potassium hydroxide.

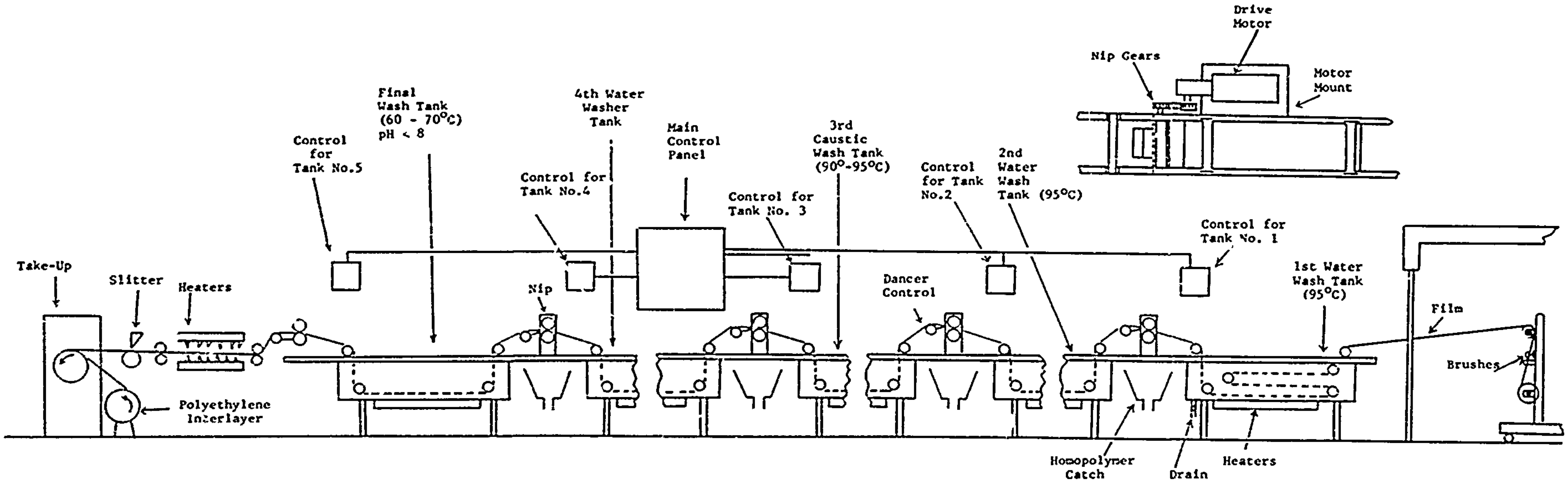


Figure 7-1. Schematic of Process Line.

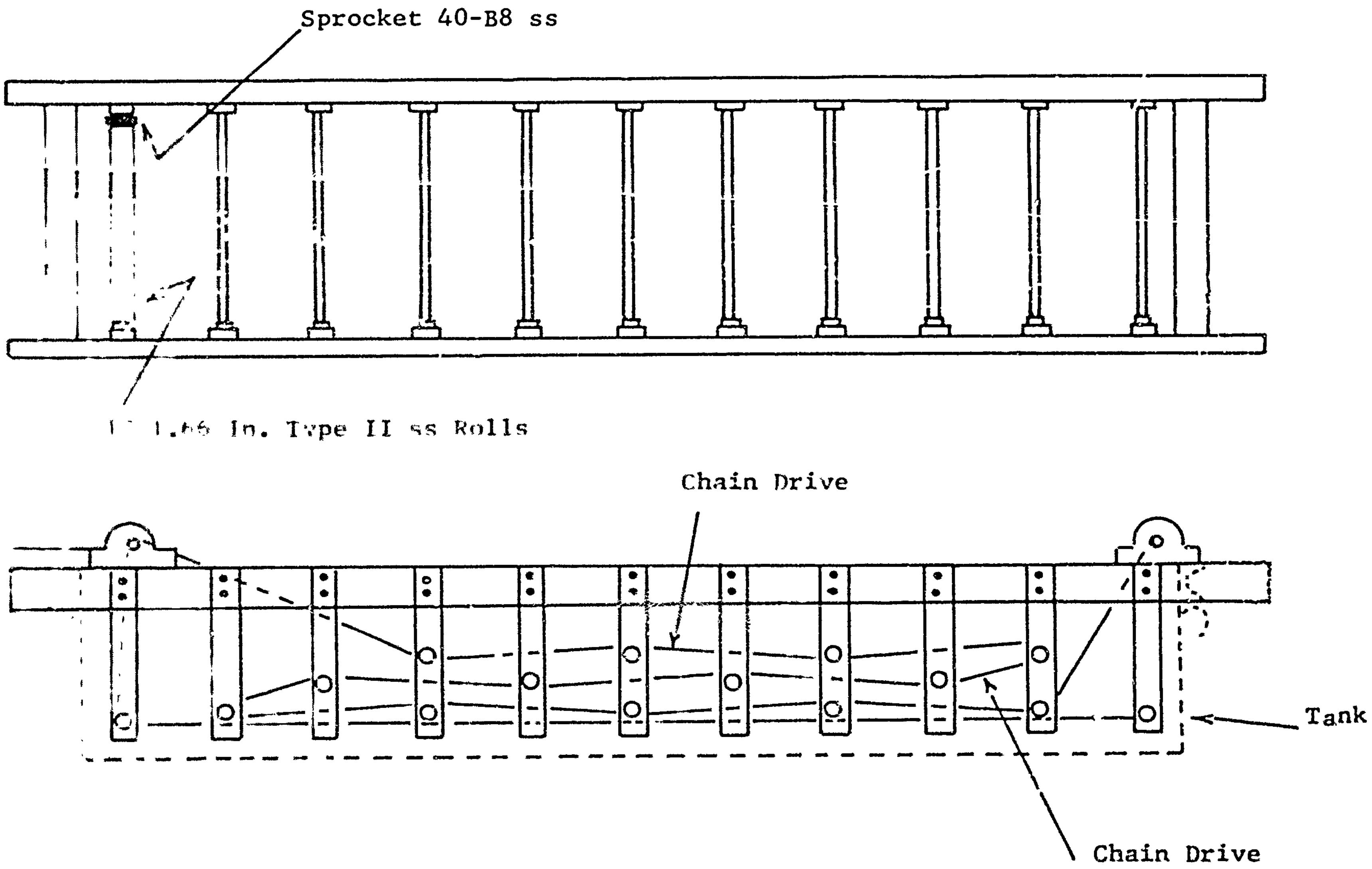


Figure 7-2. Festooning Fixture for Tank 1 and 3.

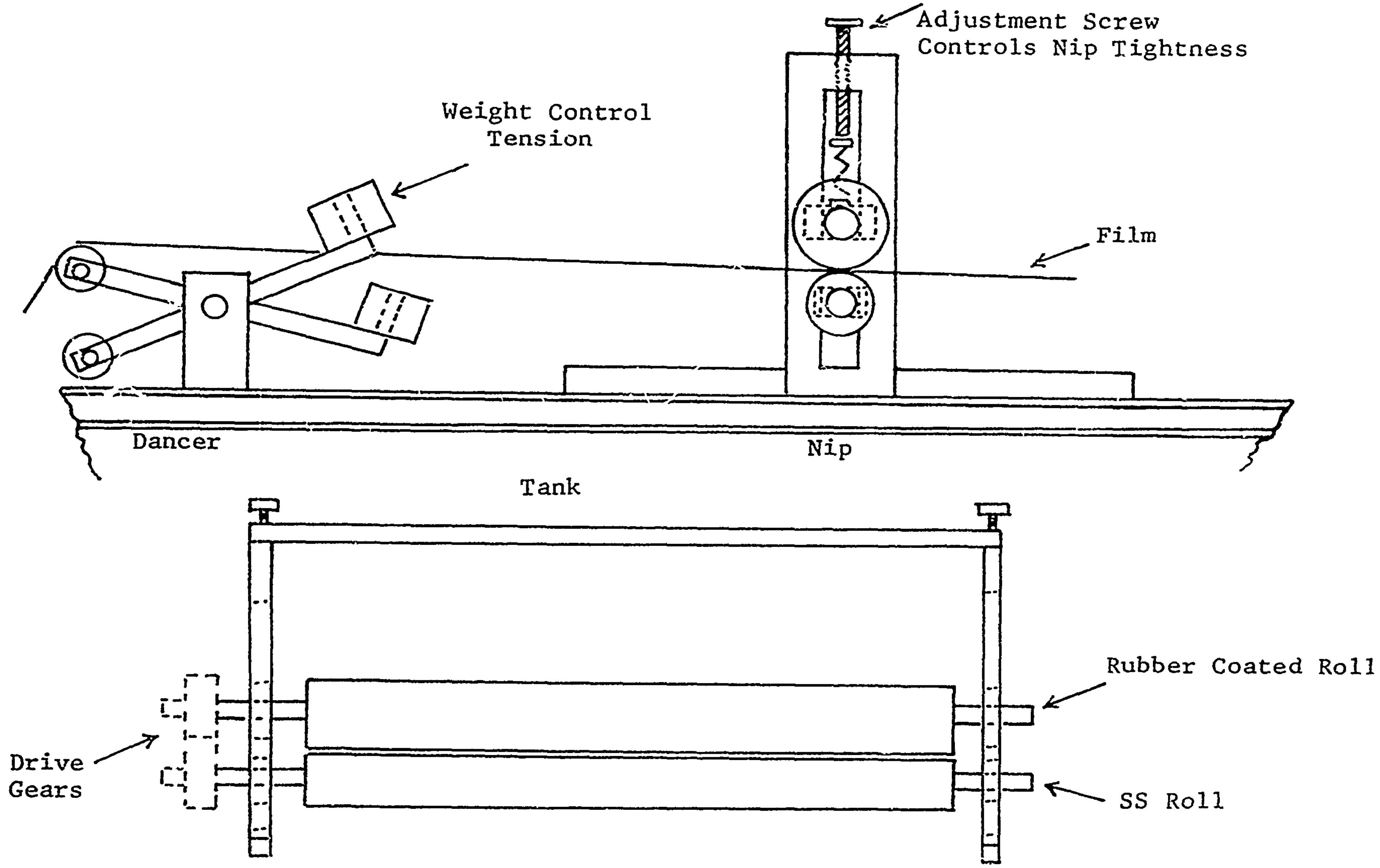


Figure 7-3. Schematic of Nip and Dancer.

This differential swelling characteristic complicates the washing since on going from tank two to tank three the film can swell as much as twenty percent. Under these conditions the relative speed of the film in tank three must be increased with respect to tank one and tank two. Additional expansion is realized on passing from tank three to tank four; therefore, a further increase in relative line speed in this tank is necessary to prevent the film from "piling up" in this tank. In tank five the film speed is slightly decreased.

To compensate for these changing conditions, the film rides over a dancer arm after leaving the nip mounted between each tank. The dancer arm is attached to a potentiometer which controls the motor speed of the tank preceeding the arm in the wash line. The electronic control system to perform this function was purchased from Wolock and Lott of Kenilworth, New Jersey, and was operated very satisfactorily after experience was gained in setting wash conditions. Basically, with this electronic system a single main line speed is set using a master control and then the line speed in each individual tank is changed relative to this preset line speed. The relative speed in each tank is controlled by a dancer on the nip roller, and can change from dead stop when the dancer is in the up position to a preset percentage above the line speed. Therefore, if the film is being wound up after drying (where maximum shrinkage occurs) at a line speed of ten feet per minute, it could be traveling twelve or thirteen feet per minute in the conversion tank.

Considerable attention has been given to simplicity of design utilizing where possible latest techniques in printed circuitry and the latest solid state components in order to develop a compact, reliable package that can be utilized with the greatest flexibility. This flexibility is accomplished with utilization of modulated circuitry so that a variety of optional accessories and function may be added to the basic controls with minimum cost. The design evolved offers control with a minimum of maintenance. The operation of this control system is as follows:

The integral horsepower eddy current drive has 90 teeth on the output rotor which are used to provide a speed feedback signal. As the teeth pass the magnetic pulse pickup, a signal is developed in the pickup whose frequency is proportional to speed. This frequency is converted to a DC voltage proportional to the frequency of the input to the Printed Circuit Board. This (+) feedback voltage is summed with the (-) reference signal from the speed potentiometer. The net results of this summation is the error signal which appears at the junction of R46 and R17 (367-62) as shown on the block diagram (Figure 7-4). This error signal, if summed negative, advances the firing angle of the clutch SCR resulting in increased voltage applied to the eddy current clutch, thereby increasing output speed to the preset reference. If the summation of the error signal is positive, indicating the output speed is faster than the referenced speed, the voltage will then be shut off to the clutch coil until the output speed is reduced down to the referenced speed. Should this overspeeding by inherent and control is desirable, an Electronic Transmission combining an eddy current clutch and brake with a dual channel servo control could be utilized.

The signal from the magnetic pulse pickup is amplified by Q7 and detected by the level detector (Schmitt Trigger) at Q8 and Q9 (Figure 7-5). The output of the level detector is used to trigger the one shot multivibrator (Q10, Q11) which produces pulses at a uniform height and width. The pulses are then averaged to provide filtered DC proportional to frequency.

B. Temperature Control: In washing film it has been noted that the wash temperature must be maintained above 90°C in each of the first four banks. Previous experience with three wash tanks of similar design was used to guide our selection of heating elements for each tank. Immersion heaters though more efficient always tended to interfere with the wash operation and corrosion inevitably caused contamination. It was therefore decided to mount external heaters on the bottom of each tank and to insulate the entire tank. Each tank was originally fitted with three 2000 watt strip heaters which are 72 inches long. Individual temperature control was set on each tank. The heaters were "Chromalox Heaters" manufactured by E. L. Wiegand Company. A fourth strip heat was added to tanks one and three when it was found that the temperature during washing would drop below 90°C

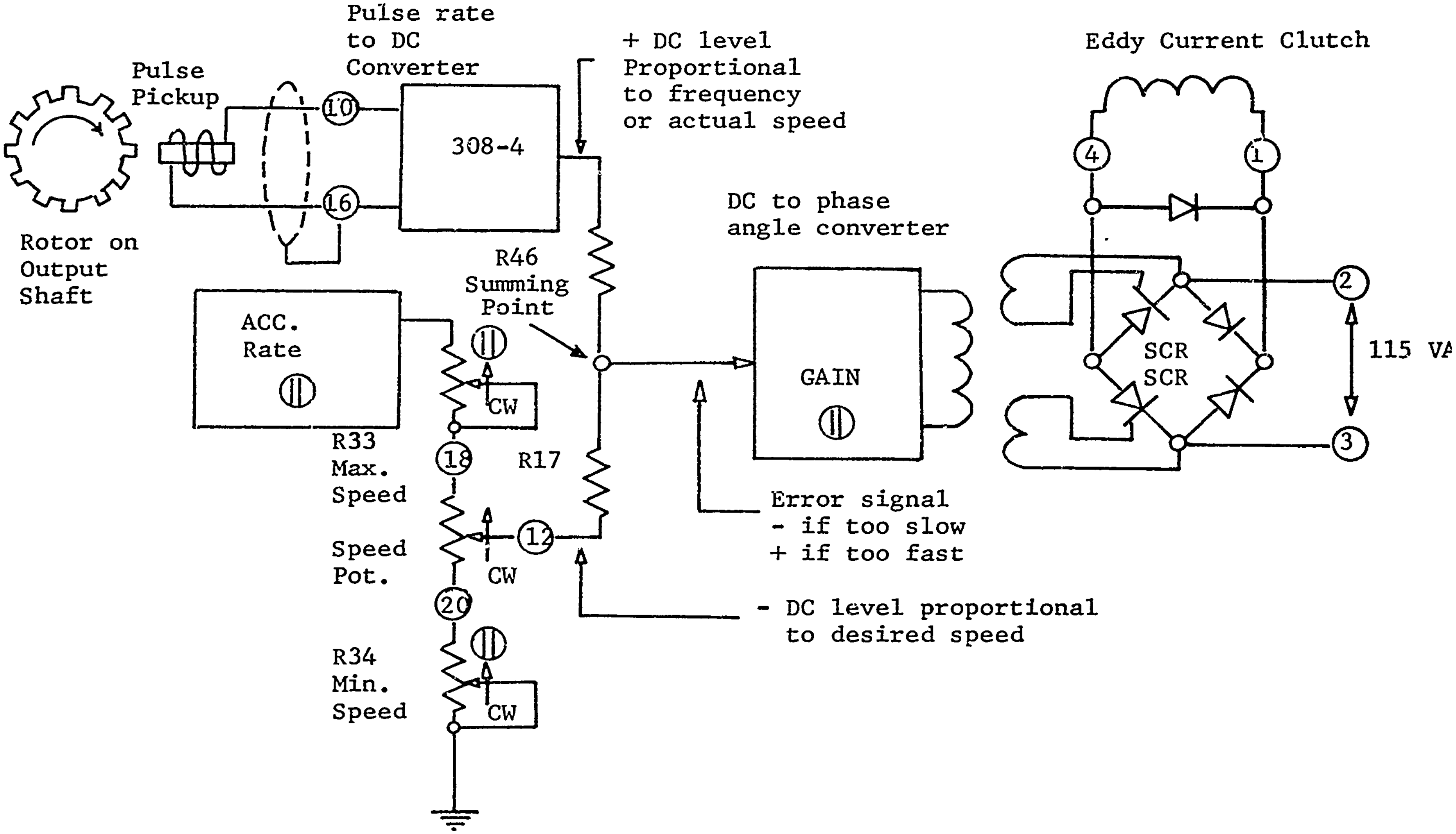


Figure 7-4. Block Diagram for 367-62.

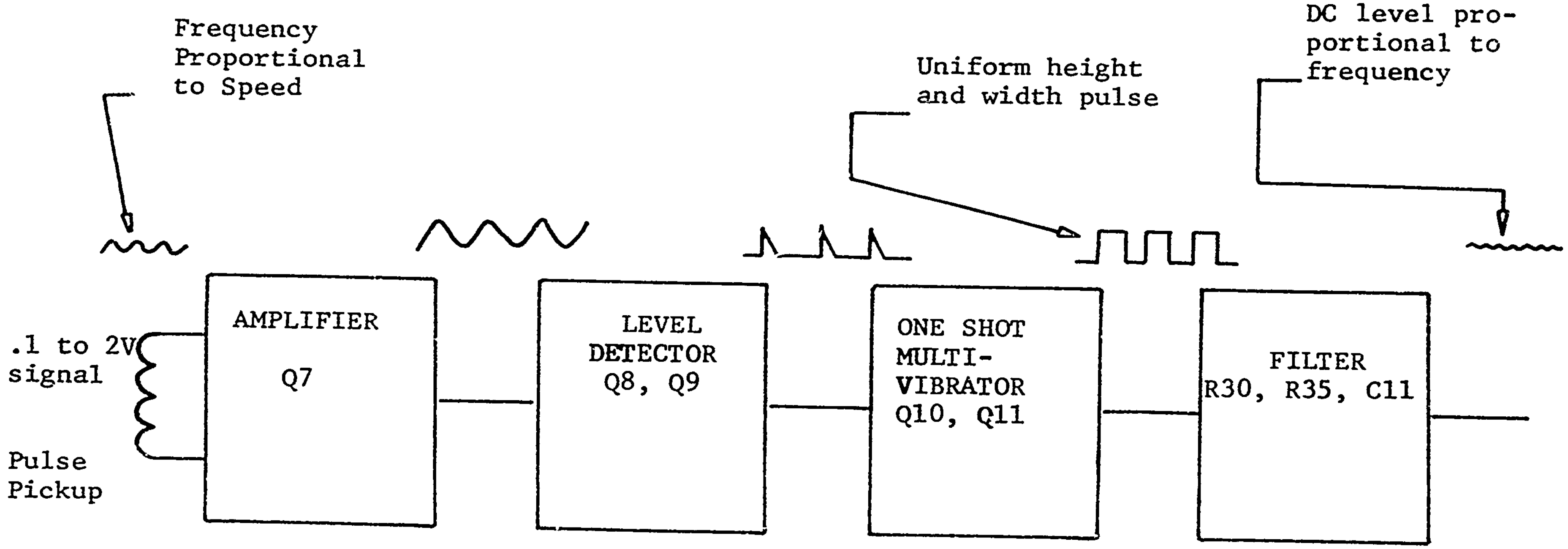


Figure 7-5. Block Diagram for 308-4 Pulse Amplifier.

after about five hours of washing. This did not solve the problem. Polyethylene sheeting 2 mils thick was kept in contact with the water level in each tank to prevent evaporative heat loss. This material improved the situation considerably but it was necessary to set up a steam boiler to effect a solution. As experience was gained in washing the film, more film could be washed in a single shift if the tanks were changed after washing about two thousand feet of film. This can be done within one half hour if we pass live steam into the hot (70°C) line water used to refill the tanks. The strip heaters are also used in heating the water during this time and are kept on continuously to maintain temperature.

C. Drying: Film exiting from the last wash tank is passed through a driven set of nip rollers. One of the rollers is rubber coated, the other is a stainless roller. This final nipping removes most of the free surface water. Problems can arise if the film entering this last nip is not flat. If the edge of the film curls in the wash tanks it can pass through the nip and retain water in the curled section. It is necessary to physically smooth the film prior to entering this last nip. Severe curling in the last wash tank can cause the film to rupture when it enters the nip rolled up.

When leaving the last nip the film is pulled by the take-up unit through the heating unit. This unit consists of two gas infrared catalytic heaters which are 18 inches by 30 inches. These catalytic heaters are preheated electrically and they burn gas using a catalyst system. They give an odorless, smokeless heat of high intensity and are flameless. They have been used for four years and have given excellent service with no maintenance problems. The heaters are mounted on a framed stand and placed along side each other, spaced 8 inches apart. The total heating area is 7.8 square feet. Fourteen rollers are set 9 inches above the heaters and film leaving the last nip is festooned around these rollers. It has been found that by festooning the film through the heating unit the edges of the film can be maintained relatively flat.

An auxiliary set of heaters is stationed about 10 inches above the film. It was not necessary to use these heaters when the drying line was operating below ten feet per minute. Problems in drying and washing of the 20,000 feet of film made during this program were realized. This is detailed in a following section.

D. Final Stages in Processing: When film comes from the dryer it sometimes has curled edges. To prepare film which is trimmed and ready for packaging requires slitting. There are two procedures which can be used to slit film. One involves in-line slitting of the film as it comes from the heater, while the second procedure, called "balony cutting", cuts the bulk roll. Each has its advantages.

Because of the poor edges of the film after drying, we could not easily use the first procedure since the film could not be guided evenly into the slitter. Further, after slitting in order to wind a uniform roll the film must be guided between the interlayer film.

In processing, the film coming from the dryer was overlapped on the interlayer film, i.e. the interlayer was 10½ inches and the membrane was 11 inches, and then rolled onto a single core. The bulk roll was then cut to give a neat package with clean edges having no folds. This procedure is wasteful in that we lose one half inch of film width. It appears that we can eliminate this problem if we start grafting clean-cut crosslinked film. As noted in a previous section, steps are being taken to affect this change.

As noted above, after slitting, the film is wound with a interlayer of high density polyethylene and cut to 10½ inches. This was done with the 20,000 feet made during the trial production run. Film made in the future will be 12 inches wide. This can be realized because of the improved crosslinking procedure wherein preslit film is used.

The cut rolls are then packaged in polyethylene bags, after test samples are evaluated, coded and packaged in cartons for shipment. Figure 7-6 shows the wash line.

2.7.3 Problems in Washing

As evident from the foregoing sections, there are problems inherent in the washing process which adversely affect production speed. Most of the problems are directly related to the condition of the film just prior to washing.

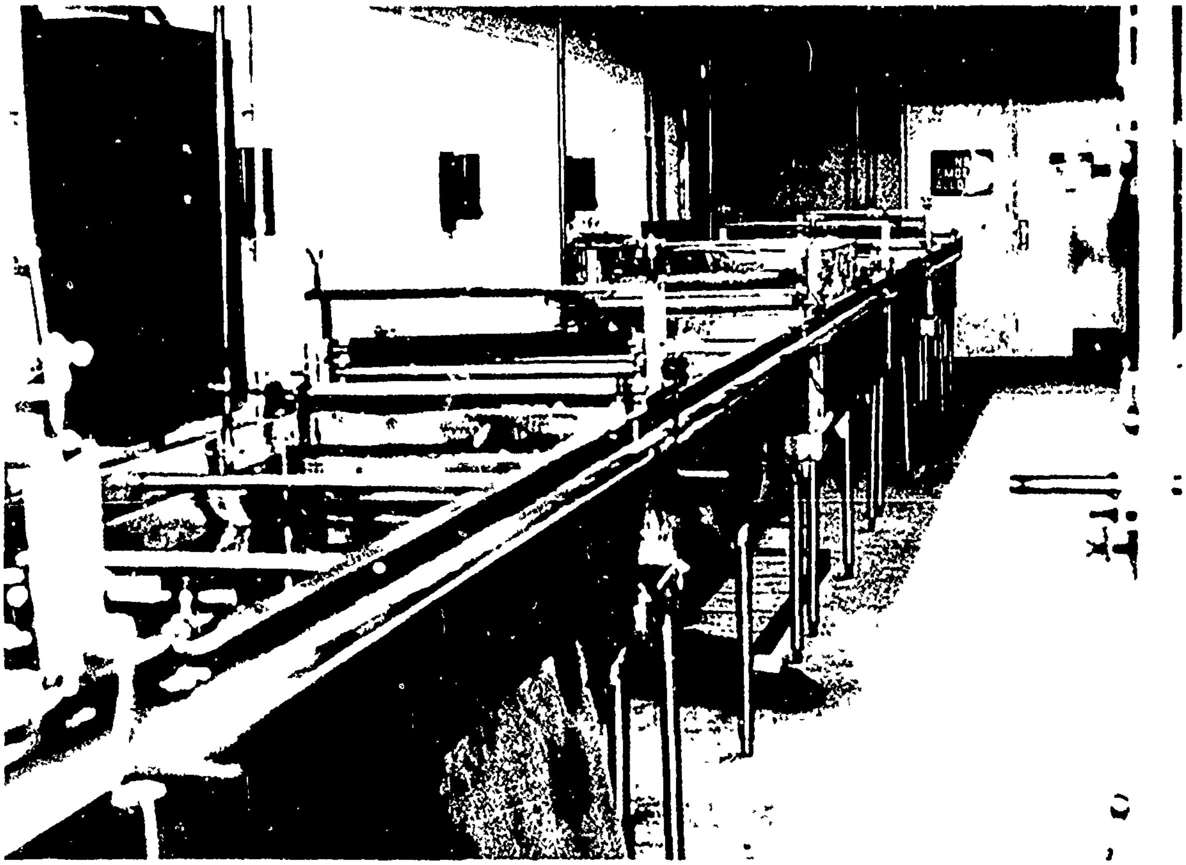


Figure 7-6. Washline.

The problem associated with tearing of the film in the wash tank was shown to be related to two basic conditions of the film. One, if the film prior to grafting has poor cut edges then when the film is being washed tears starting from the "nicks" rupture the film in the tank. A second problem was associated with a rather subtle condition. When film is removed from the reaction vessel it still contains a considerable amount of benzene. The roll is therefore allowed to stand and after it has dried the interlayer and film are separated. If the drying period, i.e. the time from removal of the film from the tank to when it is unrolled is excessive (about one week) the roll thends to dry completely and the homopolymer on the film and mesh adhere more thightly than when the bundle is unwound after one day. This "adherence" causes some embrittlement and cracking of the edges during unwinding. On washing this film excessive tearing occurs. This condition occurred with runs number 13 and 14. Runs number 19 and 20 which were identical but were unwound within two days after being taken from the reaction tank were washed very easily. No tears were experienced and film lengths were cut every 250 feet. This was done purposely since each roll contained only this quantity of film.

Threading film through the wash tanks, which were maintained above 90°C is a formidable problem and initially caused considerable down time. This was simply solved by placing nylon belting in each tank. The belting was festooned in each tank in the same sequence as the film. The ends of the nylon belt were open and the ends were left out of the tank. If a break occurred the open ends of the belt were passed through the nip rollers and then fastened. This would drive the belt continuously through one tank and the nip preceeding the tank. Film was then knotted and tied to the belt and driven through the tank and nip. At the break point a splice was made and the washing continued.

After finishing washing a thin line of nylon cord was tied from a spool to the end of the film entering the first wash tank. The line traversed all five tanks and was left in place while the tanks were drained, cleaned and refilled. The following day film was tied to the nylon chord and fed through the heated tanks. The nylon belting and chord shrink considerably when the tanks are heated; with the belting about 4 feet of shrinkage was evident with twenty four feet of belt maintained in the conversion tank as it went from room temperature to 95°C.

All tanks must be thoroughly washed after each shift since the homopolymer formed can cause considerable problems particularly on the nip rollers.

The dried homopolymer on the film after it is removed from the reaction vessel is powdery in form but tends to build up slightly on the edges of the film. The film in this form is a problem to handle since the powder tends to "atomize" and float in the air. The unwinding of film from the bulk roll must be done in a hooded area with a strong draft. Once removed the film still contains considerable homopolymer. If washed in this condition the first two tanks can not be used for washing more than 1500-2000 feet before changing the wash water. As noted, a simple brushing removes the bulk of the homopolymer and results in maintaining the first two rinse tanks cleaner. Work subsequent to this contract will be directed toward improving the grafting reaction to reduce the homopolymer formed during the grafting reaction. This is possible and one of the runs, No.3, made during this program resulted in a grafted film with no homopolymer. This was discussed in a previous section.

The most difficult problem in washing is associated with the tendency of the film to curl. This was found to occur only on occasion. Runs Nos. 13 and 14 both of which had poor edges and neither of which were brushed prior to washing curled to a significant extent. Curling, when it occurs, develops in the conversion tanks and becomes more pronounced in the two final wash tanks. When this happens it is necessary to physically open the film to a flat condition as it enters the nip. This requires placing a man by each of two nips and one by the heating unit.

This condition was absent on washing rolls #19 and 20 both of which had clean cut edges and were brushed off homopolymer. These two rolls also appeared cleaned after leaving the first wash tank. The curling seems to be associated with the edge effect due to poor cutting and to excess homopolymer on the film as it enters the conversion tank. This could in turn be related to poorer conversion of the edge of the film and an uneven swelling. No evidence other than association supports this conclusion. We do find the resistance of the edges of the film to be equal to other parts of the film indicating the conversion is not different. Suffice to note than when the grafted film is treated like Runs Nos. 19 and 20 no curling occurs.

2.8 TASK NUMBER EIGHT: QUALITY ASSURANCE TESTING AND DEVELOPMENT

This task was in force throughout the program. Results were used in guiding manufacturing process development and in establishing controls for the acceptance of incoming material and the final product. From the results of these tests, product and manufacturing specifications were established. The task consists of three sections:

1. Incoming Raw Materials
2. In Process testing
3. Final Product Testing

2.8.1 Incoming Raw Materials Testing

A. Film Resin: Prior to extrusion of the resin into film form, the resin is qualified by the following testing.

a) Gel Permeation Chromatography (GPC) This test is used to establish the number and weight average molecular weight, as well as the molecular weight distribution of the resin. It is known that the efficiency in crosslinking polyethylene is sensitive to the average molecular weights and its distribution. The GPC test can be used to determine these properties. The resins were analyzed by Waters Associate Inc. using the condition given below:

Solvent 1.2.4 trichlorobenzene
Columns: Styragel with contour chain length exclusion values of 10^6, 10^5, 10^4, 10^3 Å (in series)
Temperature: 138°C
Flow rate: 1cc/minute
Concentration: 0.25% polymer solution

These conditions were set in order to use the calibration curve as published by Wild and Guliana (9)

The molecular weight distribution index was obtained by dividing the weight average molecular weight by the number average molecular weight.

The chromatogram developed shows a basic log normal molecular weight distribution. Typical chromatograms are shown in Figure 8-1 and Figure 8-2 for film extruded by Sea Space Company and Shoreline Industries. The calibration curve used is given in Figure 8-3. Particular attentions must be given to the high and low molecular weight tails. In case the same experimental conditions cannot be reproduced, it is necessary to run the GPC sample together with a known material such as the Sea Space film for internal comparison. The molecular weight distribution index of each should not differ by more than 10%. The calculations for molecular weight fraction are shown in Table 8-1 where Hi is the height of the curve from the baseline at count i and Ai is the chain length equivalent in angstrom from the calibration curve.

b) <u>Infrared Spectra</u>

The infrared spectrum is a fingerprint of the polymer resin. Not only for the characteristic functional groups but also accidental impurities will show up in the IR spectrum. The infrared spectrum of a polyethylene film made from DFD-0602 resin is shown in Figure 8-4. There are three major bands characteristic of the polyethylene, the 2850-2950 cm^{-1} region for C-H stretching frequency, the 1450-1470 cm^{-1} for C-H deformation, and the 750-720 cm^{-1} region for the $(CH_2)n$ skeletal vibration. In addition, absorptions at 3050-3300 cm^{-1} (unsaturated C-H), 1750-1650 cm^{-1} (carbonyl-C=0) and 1000-800 cm^{-1} (vinylidene) should be studied carefully. The spectrum was taken with a Perkin Elmer IR 21 spectrophotometer.

The ultraviolet spectra of polyethylene would be rather featureless since CH_2 units absorb only in the far UV region. It could detect double bond conjugation in the UV region. A typical spectrum is shown in Figure 8-5 where no absorption throughout the frequency range is observed. However, any coloring matter or UV stabilizer added to the resin would be detected. Spectra were taken with a Beckman DBG model using procedures described in the manual.

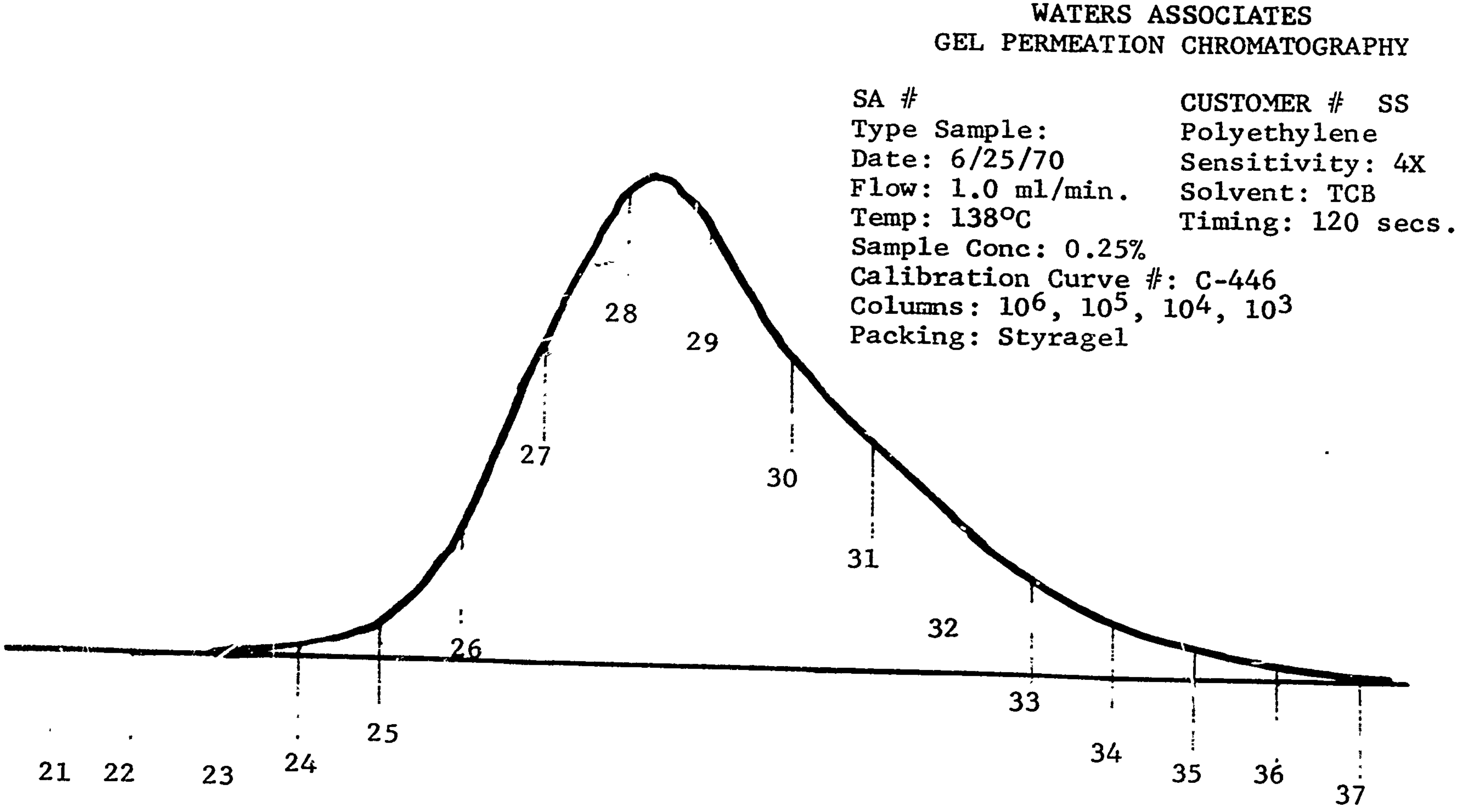


Figure 8-1. GPC Spectrum of Sea Space Film.

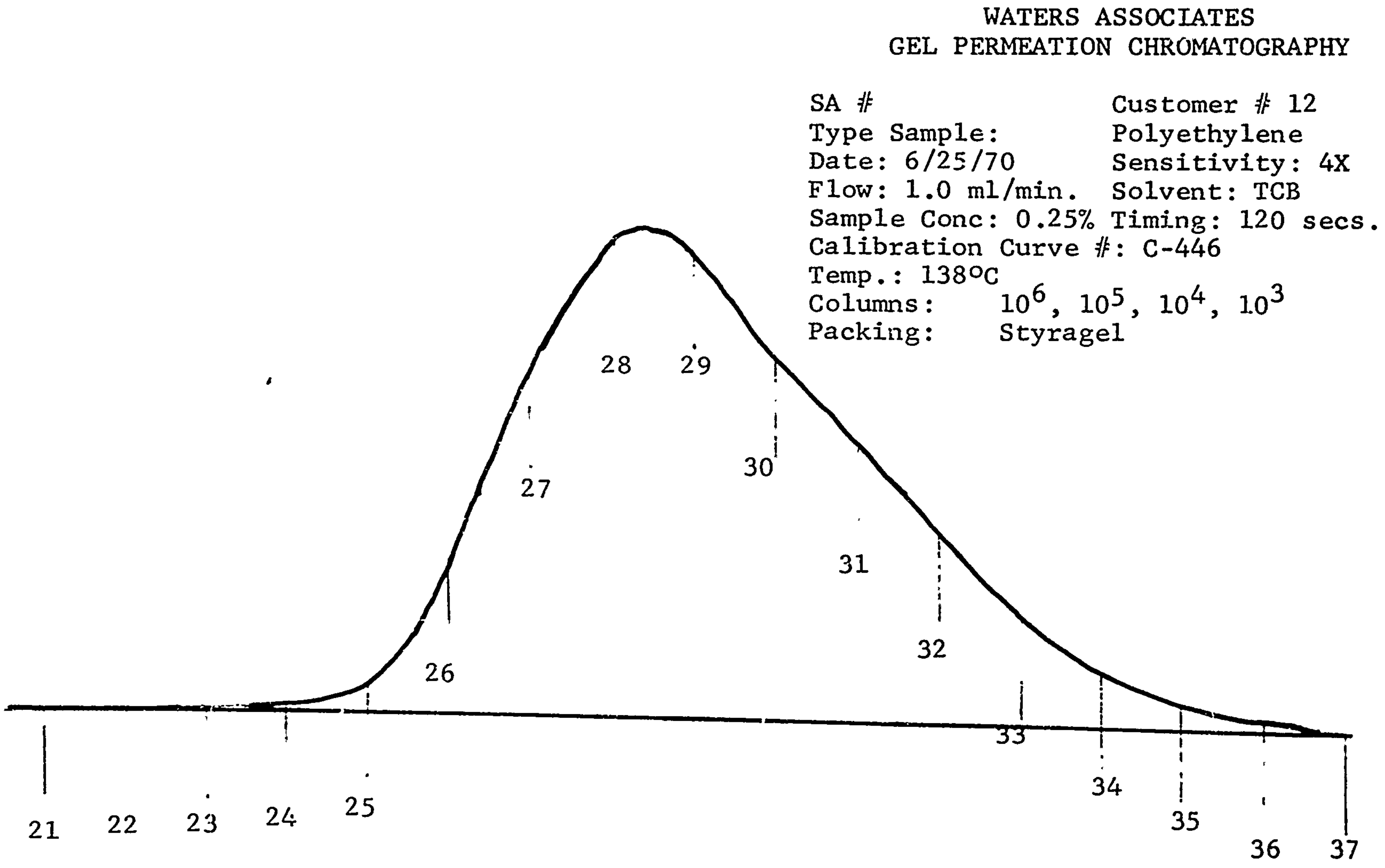
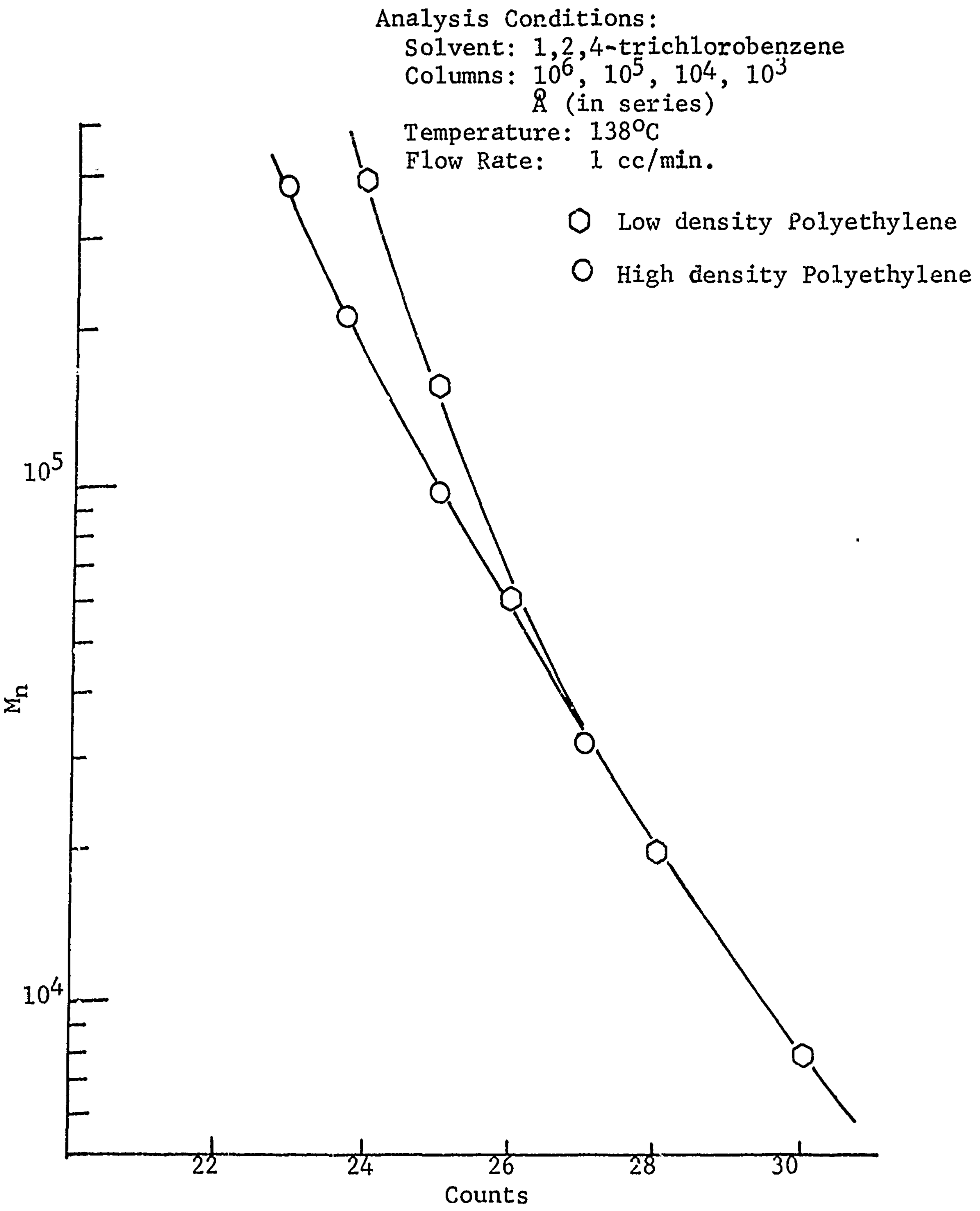


Figure 8-2. GPC Spectrum of Shoreline Film.



Analysis Conditions:
Solvent: 1,2,4-trichlorobenzene
Columns: 10^6, 10^5, 10^4, 10^3 Å (in series)
Temperature: 138°C
Flow Rate: 1 cc/min.

Figure 8-3. Standardization Curve for GPC.

TABLE 8-1

Molecular Weight Distribution Calculations For Shoreline Industries Film

Count	Hi	Ai	$^{Hi}/Ai$	Hi Ai
22	0	-		
23	0	-		
24	0.0312	400,000	0.00000008	12,480
25	0.1875	150,000	0.00000125	28,125
26	1.000	62,000	0.0000161	62,000
27	2.2500	34,000	0.0000662	76,500
28	3.1250	20,000	0.000156	62,500
29	3.0625	12,500	0.000245	38,281
30	2.3750	8,000	0.000297	19,000
31	1.8125	5,300	0.000342	9,606
32	1.2500	3,500	0.000357	4,375
33	0.6875	2,400	0.000286	1,650
34	0.3125	1,600	0.000195	500
35	0.1250	820	0.000152	102.5
36	0.0625	600	0.000104	37.5
37	0			
$\sum$	16.2812		0.0022176	315.157

$$Mw = \frac{\sum Hi}{\sum Hi/Ai} = \frac{16.2812}{0.0022176} = 7.342\text{x}10^3$$

$$\frac{Mw}{Mn} = \frac{19357}{7.342} = 2.64$$

$$Mn = Hi\ Ai = \frac{315157}{16.2812} = 19{,}357$$

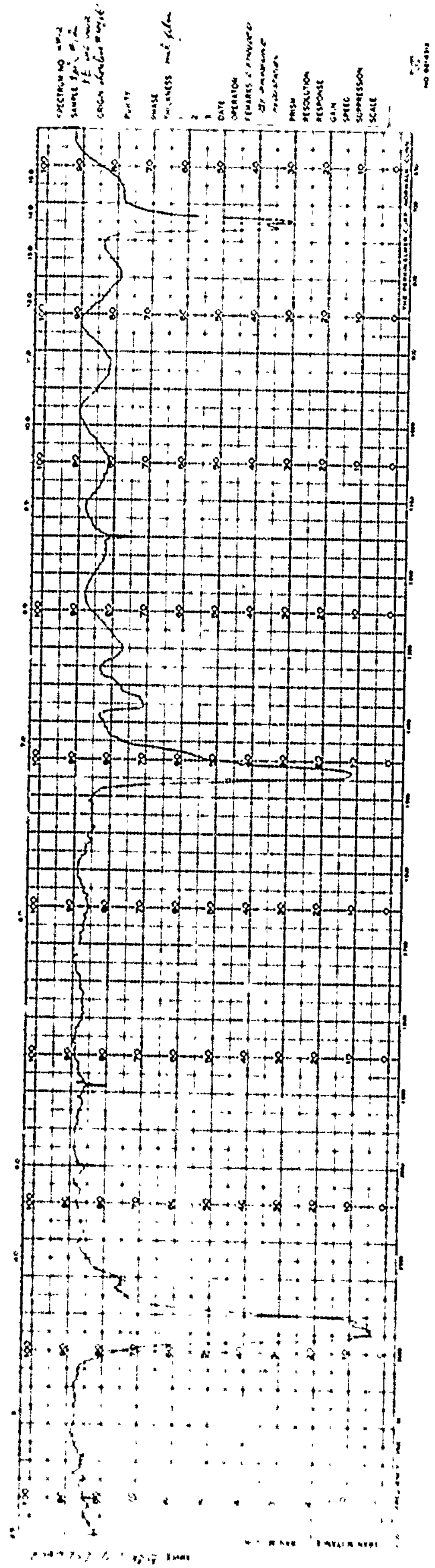


Figure 8-4. IR Spectrum of Bakelite DFD-0602 (Shoreline Industries).

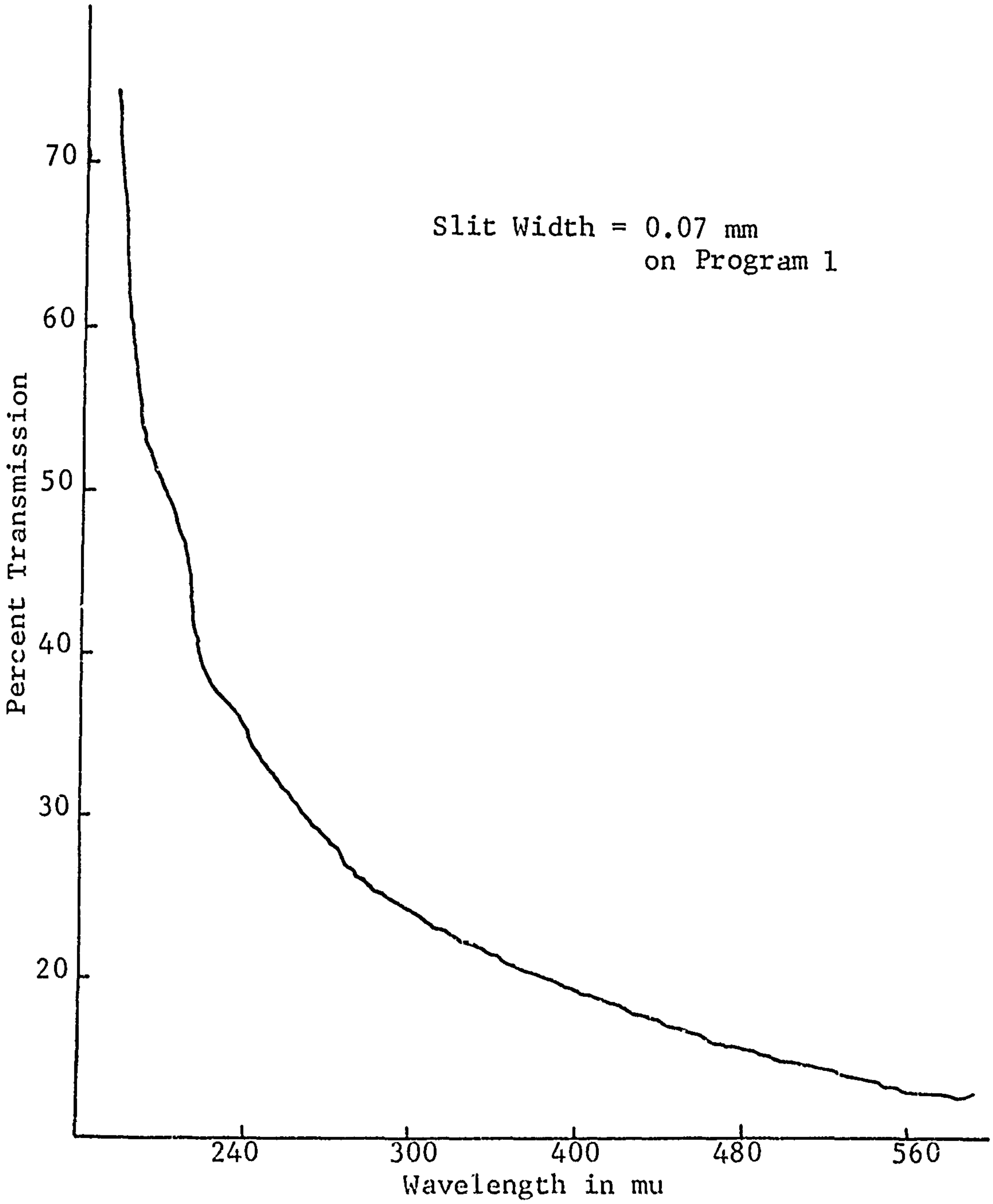


Figure 8-5. Visible and UV Spectra of PE Film.

c) Atomic Absorption Spectrosopy

This test is used to determine metal traces present in the resin or film. For a qualitative picture of metals present in the resin, a semi-qualitative emission spectrum was done by the Schwazkpoff Microanalytical Laboratories. The analysis is given in Table 8-2. The polyethylene has a nonvolatile residue of 0.12%, the majority of which is believed to be silica, a slip agent. In the metal trace analysis, the iron content is of primary concern in the manufacture of separators. In the present case, the iron varies from 0.0012% - 0.012% of the film's weight.

Ash = 0.12% ± 0.03%
Fe = 0.012 - 0.0012% (on film's weight)

d) Density

The density of the film is an important parameter because it relates to the crystallinity and structure of polyethylene. This test is performed according to the ASTM-D1505-60T, Density of Plastics using the Density-Gradient Technique. The density gradient tube is equilibrated at 23 ± 0.5°C for 24 hours. Standard floats are introduced into the column, and the height of the floats are read with a cathometer to 0.01 cm. The calibration curve, shown in Figure 8-6, illustrates that the gradient is linear. Samples are then put into the column and their density read from the calibration curve.

Desnity $^{(23^oC)}$ = 0.922 ± 0.009 gm/cc

e) Differential Thermal Analysis

DTA is useful in measuring the transition points of polymers. This test was done by Sadtler Research Corporation, using a DuPont 900 analyzer. The DTA curve for the Bakelite DFD-0602 polyethylene is shown in Figure 8-7. The major exotherm identified as the melting point (Tm) of the polymer occurs at 113°C. The width of the baseline under the peak measures the melting range. The presence of other peaks indicate impurities and too wide a melting range indicates non-homogenity in the polymer.

Tm = 110 ± 4°C

TABLE 8-2

Semi-Quantitative Emission Spectrum on Extruded Bakelite DFD-0602 Film.

Aluminum	ML	Magnesium	m	Titanium	mL
Arsenic	ND	Manganese	mL	Trungsten	ND
Antimony	ND	Mercury	X	Urandum	X
Barium	ND	Molybdenum	ft	Vanadium	ND
Boron	ND	Niobium	ND	Zinc	ND
Bismuth	ft	Nickel	t	Zirconium	ND
Cadmium	ND	Phosphorus	X		
Calcium	m	Potassium	X		
Carbon	X	Sodium	mL	Percent Ash	
Chromium	tL	Sulfur	X		
Cobalt	ND	Silicon	P	0.12%	
Copper	mL	Silver	ft		
Iron	ML	Tantalum	ND		
Lead	tl	Tellurium	X		
Lithium	ND	Tin	ft		

P - 10 (0.012-0.12%)
M - 1 (0.0012-0.012%)
m - .1 (0.00012-0.0012%)
t - .01 (0.000012-0.0012%)
* - less than figure shown
H - upper half of range
ft - less than 0.01% (0.000012%)
L - lower half of range
ppm - parts per million
ND - not detected
X - not tested
vft - very faint trace

The figures in the brackets are the weight percent of the metal present in the film which has 0.12% ash. It appears that some kind of silicate was used as the slip agent in this film. The iron present in this film is <0.012% and >0.0012%.

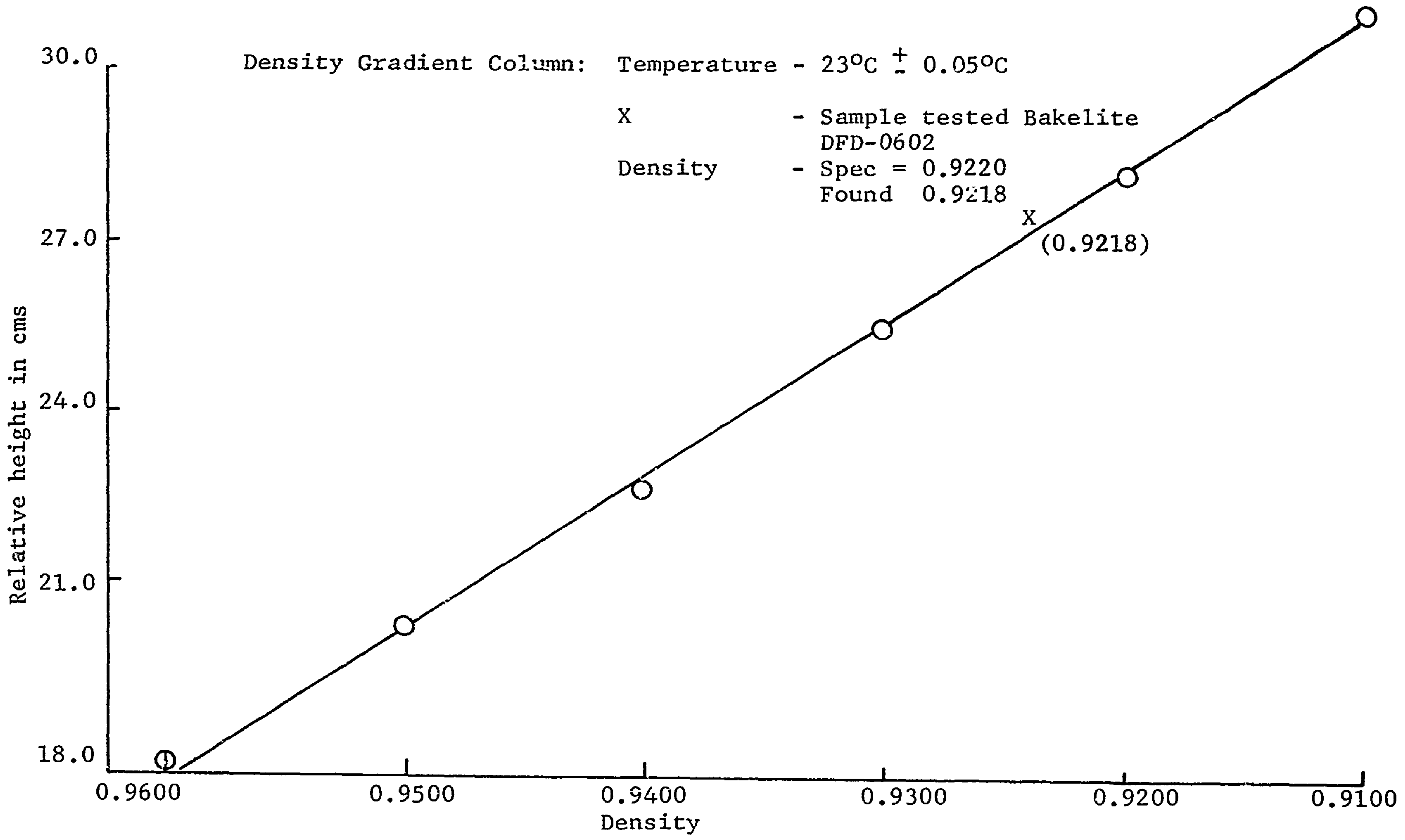


Figure 8-6. Density Gradient Standard Curve.

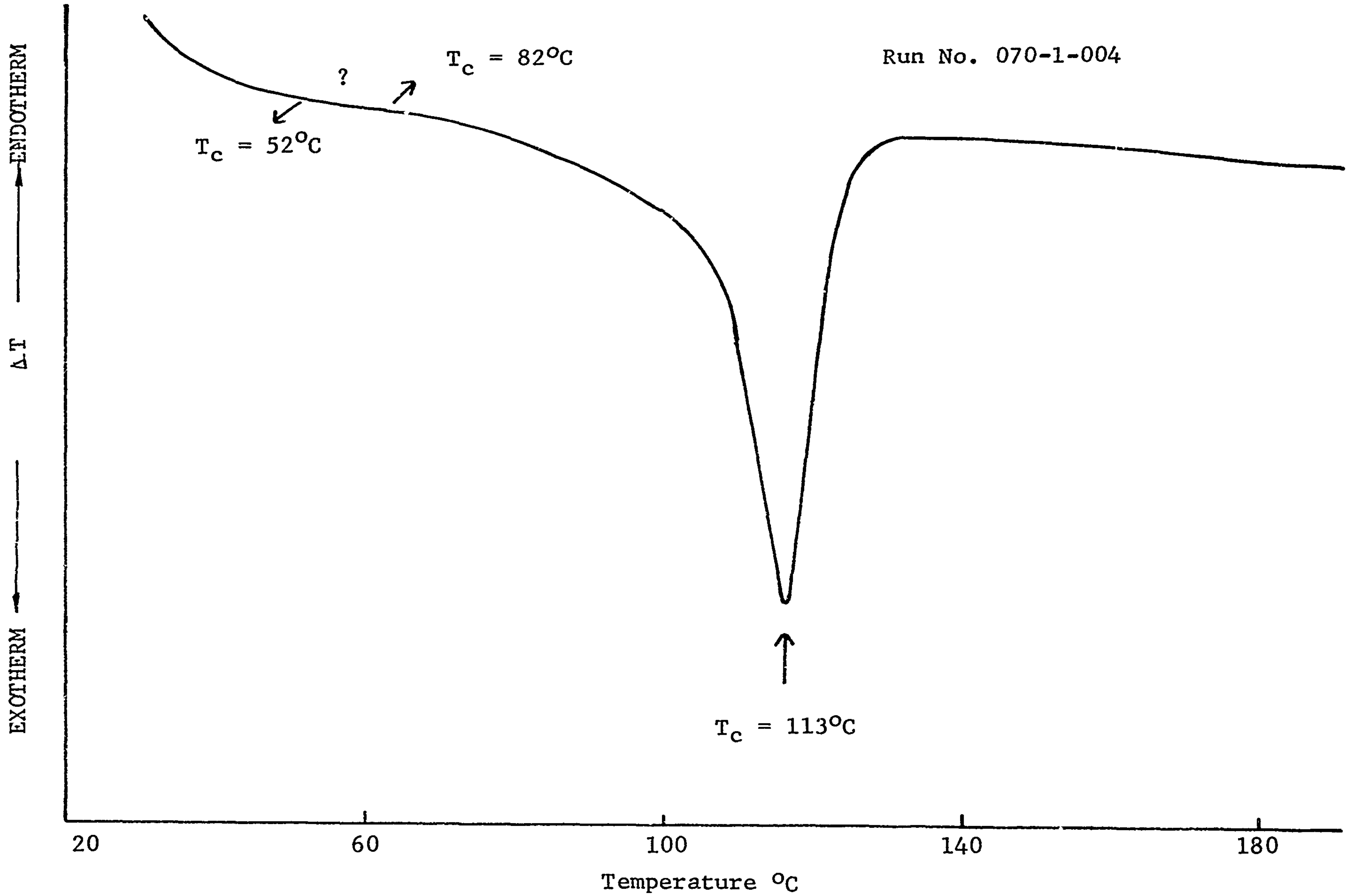


Figure 8-7 DTA Curve for Bakelite DFD-0602

B. **Extruded Film:** The extruded film is also qualified using test indicated in A above. The only other additional tests not related to the film resin which are made are thickness and tensile strength.

a) Thickness

The thickness of the extruded film is an important parameter. Thickness is measured with a constant weight head gauge (Federal Products Corporation). At least 25 measurements were made for a 10 foot section of the film, and for as many different locations as practical. The average thickness is given by the arithmetic mean. Sample data is shown in Table 8-3.

Thickness = 1.0 ± 0.1 mil

TABLE 8-3

Thickness Measurements of Extruded Film

Phillips Joanna Film	Linear Feet/Roll	Average Thickness (mil)	Mean Error a	Standard Deviation σ	Probable Error γ
Roll # 1	11,220	1.00	0.06	0.08	0.06
2	12,000	0.95	0.07	0.09	0.06
3	12,000	0.99	0.07	0.09	0.06
4	12,000	0.92	0.07	0.09	0.06
5	12,000	0.96	0.07	0.10	0.07
6	12,000	0.97	0.07	0.10	0.07
7	12,000	0.98	0.08	0.10	0.06
8	12,000	0.95	0.07	0.08	0.06
9	12,000	1.00	0.06	0.09	0.06

b) Tensile Strength

The tensile strength of the film is the resultant effect of crystallinity, molecular weight and orientation. As such, the interpretation is complex. However, the tensile strength can be a useful quality control test. The tensile properties are determined according to ASTM D638-60T using a table Instron. A sample calculation is given in Table 8-4

Tensile Strength = 3200 ± 200 psi

TABLE 8-4

Tensile Strength For 1 mil Bakelite DFD-0602 Film from Shoreline Industries

Roll No.	Average Tensile (psi)	d*	d^2
1	3269	8	64
2	3448	171	29241
3	3320	43	1849
4	3370	93	8649
5	3160	117	13689
6	3020	257	66049
7	3290	13	169
8	3374	97	9409
9	3440	163	26569
10	3050	227	51529
11	3460	183	33489
12	3120	157	24649
Average	3277 psi		

* d = deviation from average

Arithmetic mean = $\alpha = \frac{\sum d}{\eta} = \frac{1529}{12} = \pm 127$ psi

Standard Deviation = $\sigma = \sqrt{\frac{\sum d^2}{\eta-1}} = \sqrt{\frac{265355}{11}} = \pm 155$ psi

Most Probable Error = $\gamma = 06745 \sqrt{\frac{\sum d^2}{\eta-1}} = \pm 105$ psi

C. Solvents: The solvents used in grafting are benzene and carbon tetrachloride. They are qualified by manufacturer's grade, refractive index, density and infrared spectra.

a) Benzene

Grade: This is sold by the Peerless Oil Chemical Company as the "nitration grade."

Refractive Index: The refractive index of benzene has been recorded in the literature. The index is measured using an Abbe Refractometer at 20°C (Sodium line).

N_D^{20} (literature) = 1.5011
(found) = 1.5005 ± 0.0007

Density: The density of benzene is also recorded in the literature. The density is measured using a pycnometer at 25°C.

density (literature) = 0.876 gm/cc (25°C.)
(found) = 0.879 gm/cc ± 0.004

Infrared Spectra: The IR spectra is taken with a Perkin Elmer 21. The spectra should not show absorptions at 2990-2800 cm^{-1}, and 1750-1650 cm^{-1} region. Major peaks are present at 3050, 1500 and 1050 cm^{-1}.

b) Carbon Tetrachloride

Grade: This is supplied by Metro Scientific, Inc., as the "Industrial Grade."

Refractive Index: The refractive indices given in the literature and found are:

N_D^{20} (literature) = 1.4607
(found) = 1.4608 ± 0.0005

Density: The density of carbon tetrachloride given in the literature and found are:

density (literature) = 1.585gm/cc (25°C)
(found) = 1.590 ± 0.008

Infrared Spectra: Major peaks appear at 760, 1550, 1250 and 1000 cm^{-1}. There should be no absorptions from 1600 - 4000 cm^{-1} region.

D. Monomer: The monomer used for grafting is Methacrylic acid, supplied by the Rohm & Haas Company. It is qualified by the manufacturer's specification, refractive index, density, and viscosity.

Grade: "Glacial Methacrylic Acid," with 250 ppm MEH Q as inhibitor. Any change in inhibitor or its concentration must be approved before grafting. MEH Q stands for monoethyl ether of hydroquinone.

Refractive Index: The refractive index in the literature is:

N_D^{20} (literature) = 1.4314
(found) = 1.4311 ± 0.0005

Density: The density of methacrylic acid is:

density (literature) = 1.015 gm/cc at 25°C.
(found) = 1.013 ± 0.004

Viscosity: The viscosity of the monomer is an important parameter because it gives an indication of the degree of polymerization, as due to storage, temperature and inhibitor effects. The kinematic viscosity of methacrylic acid at 25°C is:

kinematic viscosity (literature)= 1.30 centistokes
(found) = 1.38 ± 0.09

The viscosity is easily measured from a calibrated Ubbelohde viscometer. The flow time is converted into kinematic viscosity by multiplying by a constant.

Kinematic Viscosity (Centistoke) = Flow time (seconds) x 0.00988

E. Cheesecloth: Cheesecloth was the interlayer used for grafting. Recently paper mesh, Lenonet, from Bemis Bros. Bag Co. has been successfully employed. The qualifying tests for mesh are, however, related to cheesecloth. They include the manufacturer's specification, extractables, tensile strength, thickness, trace metals and moisture content.

Manufacturer's Grade: The cheesecloth was supplied by the Marsales Company as grade 20-12 bleached cloth.

Extractables: By water, not to exceed 0.16% by weight. By Benzene, not to exceed 0.45% by weight. The cheesecloth was weighed and introduced to the Soxhlet extractor. After adding the appropriate solvent, it was extracted by refluxing for 24 hours. The cheesecloth was dried and again weighed. The weight loss was expressed as

$$\% \text{ extractable} = \frac{W_o - W}{W_o} \times 100$$

where W_o, and W are the original and final dry weights.

Tensile Strength: 7996 ± 500 psi (for 12 threads)

Thickness: = 5.0 ± 0.5 mil.

Trace Metals: A typical metal analysis is shown in Table 8-5. The major metals found are calcium, sodium, and silicon. The ash content is 0.16% which agrees with the maximum water extractables.

TABLE 8-5

Semi-Quantitative Emission Spectrum of Cheesecloth 20/12

Aluminum	ML	Magnesium	M	Titanium	mL
Arsenic	ND	Manganese	t	Tungsten	ND
Antimony	ND	Mercury	X	Uranium	X
Barium	ND	Molybdenum	ND	Vanadium	ND
Boron	ND	Niobium	ND	Zinc	mL
Bismuth	ND	Nickel	ft	Zirconium	tL
Cadmium	ND	Phosphorus	X		
Calcium	P	Potassium	X		
Carbon	X	Sodium	M	Percent Ash	
Chromium	ND	Sulfur	X		
Cobalt	ND	Silicon	PL	0.16%	
Copper	tL	Silver	ND		
Iron	ML	Tantalum	ND		
Lead	t	Tellurium	X		
Lithium	ND	Tin	t		

P - 10 to 100% (0.016-0.16%)
M - 1 to 10% (0.016-0.0016%)
m - .1 to 1.0% (0.0016-0 00016%)
t - .01 to 1% (0.00016-0.000016%)
* - less than figure shown
H - upper half of range
L - lower half of range
ft - less than 0.01%
ppm - parts per million
ND - not detected
X - not tested
vft - very faint trace

Moisture Content: Heating at 80°C under vacuum for five hours gives a weight loss of 5%. Weight loss by heat can be other than water. The Carl Fisher titration gave:

Moisture = 2.9 ± 0.5%

F. Leonet Paper Mesh: The Leonet paper mesh is the interlayer being used for grafting instead of the cheesecloth. The qualification for this material will be manufacturer's specification, thickness, atomic absorption and moisture content.

Grade: The mesh is supplied by the Bemis Company, Inc., as "28" wide weave, natural Lenonet, plain without Drawtapes." A picture of the interlayer is shown in Figure 8-8.

Thickness: The gauge of the Lenonet is over 30 mils. The average thickness on the single thread is 33.4 mil, and on the double thread is 46.8 mil, ± 10%.

Trace Metals: A typical metal trace analysis is shown in Table 8-6. In contrast to the cheesecloth, the major traces in Lenonet are aluminum, sodium and silicon. The ash content is 0.62% much higher than that of the cheesecloth which is 0.16%.

Moisture Content: The Carl Fisher titration gives:

Mositure Content = 4.0 ± 0.5%

2.8.2 In-Process Testing

A. Crosslinking

Film crosslinked to 90 Mrads is qualified by three tests, namely, the gel content, the molecular weight between crosslinks, (Mc) and the infrared spectrum.

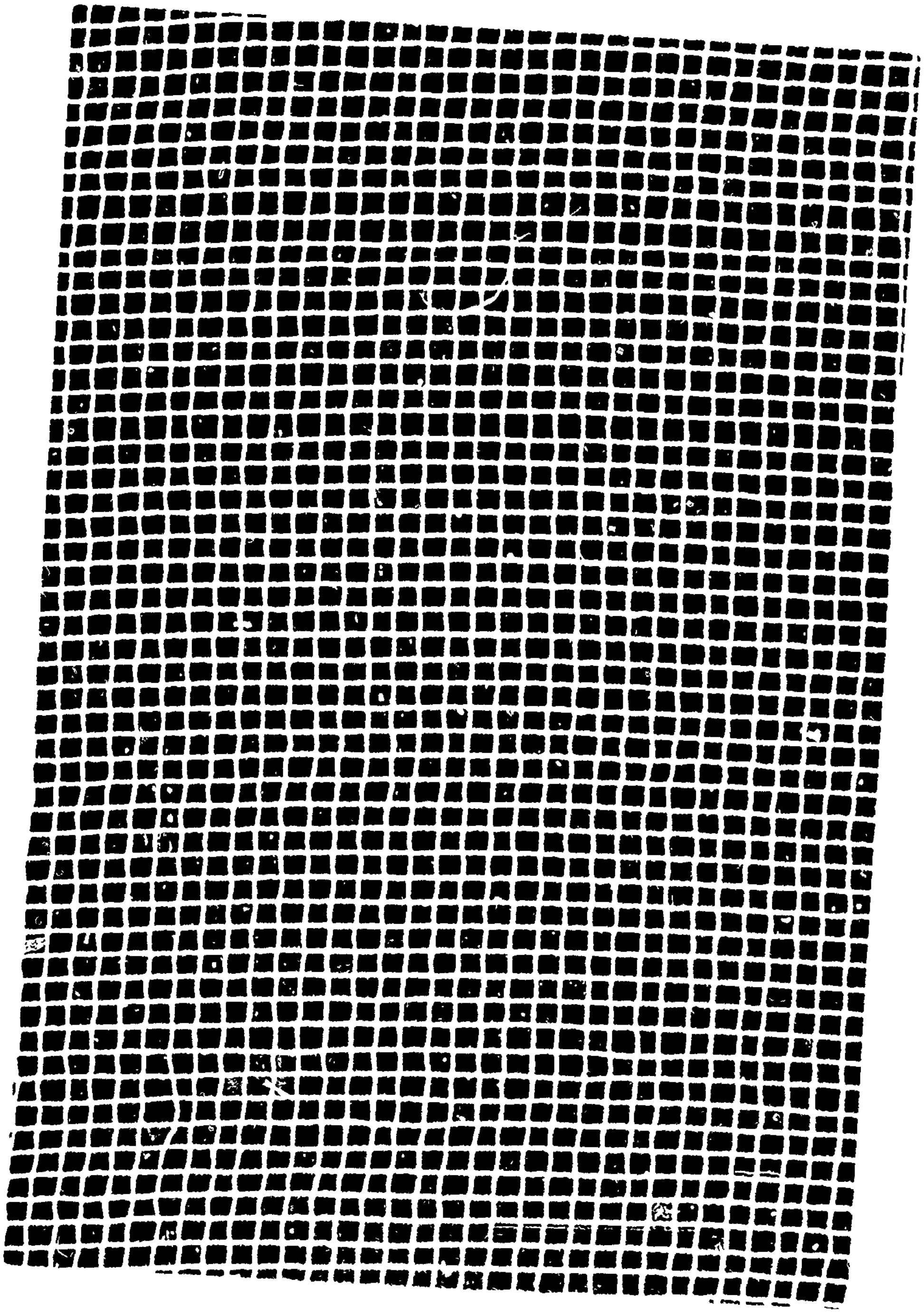


Figure 8-8. Lenonet Interlayer.

TABLE 8-6

Semi-Quantitative Emission Spectrum of Lenonet Paper Interlayer

Aluminum	P	Lead	t	Silver	ft
Arsenic	ND	Lithium	ND	Tantalum	ND
Antimony	ND	Magnesium	mH	Tellurium	X
Barium	ND	Manganese	mL	Tin	ND
Boron	mL	Mercury	X	Titanium	ML
Bismuth	ND	Molybdenum	ND	Tungsten	ND
Cadmium	ND	Niobium	ND	Uranium	X
Calcium	mL	Nickel	ft	Vanadium	ND
Carbon	X	Phosphorus	X	Zinc	tL
Chromium	ft	Potassium	X	Zirconium	t
Cobalt	ND	Sodium	PL		
Copper	ft	Sulfur	X		
Iron	ML	Silicon	M		

Percent Ash: 0.62%
Results are given on the ash basis.

P - 10 to 100%
M - 1 to 10%
m - .1 to 1.0%
t - .01 to 1%
* - less than figure shown
H - upper half or range

L - lower half of range
ft - less than 0.01%
X - not tested
ND - not detected
vft - very faint trace
ppm - parts per million

a) <u>The gel content</u>: The gel content is indicative of the network formation in polymeric substances. The crosslinks present in the film are believed to give the separator its longer cycle life, slower diffusions, and decrease swelling characteristics. A sample of irradiated film was put into a stainless steel cage, which in turn was placed into a 4 oz. jar filled with xylene. The xylene contained 0.1% B-phenyl-naphthylamine to prevent oxidative degradation of the film during extraction. The jar was maintained at 115-120°C in an oil bath, and the solvent changed daily for two days. After the extraction was completed, the film was vacuum-dried at 90°C for 24 hours, weighed, and the gel content calculated from the equation.

$$\% \text{ gel} = \frac{W_G}{W_O} \times 100$$

where W_G is the dry weight of the insoluble fraction (i.e., gel) and W_o is the initial weight of the film before extraction. A sample calculation is shown in Table 8-7.

TABLE 8-7

Gel-Studies of 90 Mrad Crosslinked Film

Code No.	Film Location	Cage Wt	Cage + Film	Cage + Gel	% Gel
1006-143	Top	4.7592g	4.9455g	4.9078g	79.7
1006-143	Top	4.7358	4.8983	4.8645	79.2
1006-143	Center	4.6385	4.8794	4.8186	81.4
1006-143	Center	4.6681	4.8534	4.8190	81.4
1006-143	Bottom	4.7432	4.9837	4.9367	80.5
1006-143	Bottom	4.6600	4.9039	4.8586	81.4

Based on the above data the minimum acceptable gel content is 79%.

b) Mc Value: When polyethylene is subjected to a crosslinking dose greater than thirty megarads, the gel content is no longer of significant value in determining the crosslink density. To note the change in crosslink density at higher irradiation dose, the molecular weight between the crosslinks was determined. There are two ways of determining the Mc value. The first method involves the sol-dose plot from which the slope yields $1/q_oU$. The Mc is given by

$$M_c = \frac{w}{q} = \frac{w}{q_o r}$$

Where w is the molecular weight of the repeating unit in the polymer, q_o is the crosslinking density per unit dose, and $q=q_o r$ where r is the dose in megarads. This approach had been used in the research effort preceeding this contract(1). The second approach involves determing the hot elastic modules of the polymer above its melting point. This has been widely employed in this contract. The equation relating E to the Mc value is:

$$E = 3\rho RT/M_c$$

Where E is the hot modulus, ρ the density of the polymer at T, the temperature and R is the gas constant. For low degrees of extension, the above equation is adequate. With the sample evaluated, the actual extension of the polymer is about 5%. The modulus is measured using a table Instron with a thermo-cabinet set at 140 ± 2°C. Sample calculation of the Mc is given in Table 8-8.

TABLE 8-8

Mc Values of 90 Mrad Crosslinked Film

Code No.	Film Location	E	ρ	R	T	Mc
1006-143	Top	432psi	0.920g/cc	8.34×10^7	413°K	3194
1006-143	Top	426	0.920g/cc	erg/mole-°K	413°K	3239
1006-143	Center	399	0.920g/cc	erg/mole-°K	413°K	3459
1006-143	Center	412	0.920g/cc	erg/mole-°K	413°K	3350
1006-143	Bottom	403	0.920g/cc	erg/mole-°K	413°K	3427
1006-143	Bottom	429	0.920g/cc	erg/mole-°K	413°K	3217

The Mc value here represents an upper limit since ρ the density above the melting point of the polymer should be smaller than the density at 23°C. The difference is expected to be small. The maximum acceptable Mc value from this data is 3500.

c) Infrared Spectrum for Crosslinked Film: The infrared spectrum has been measured for a non-crosslinked film. It represents a "fingerprint" of the material. The spectrum is used here to detect any oxidation of the film during crosslinking. Irradiation in the presence of oxygen results in an increase of unsaturation and oxidation. Since the crosslinking was done under nitrogen atmosphere, no such effect was expected. This was confirmed by infrared spectrum, a typical one is given in Figure 8-9. The frequency ranges of interest in the spectrum are 890cm^{-1} (pendent methylene); 910cm^{-1} (terminal vinyl); 970cm^{-1} (trans-vinylene) and 1700cm^{-1} (carbonyl). Comparison of Figure 8-9 with un-irradiated polyethylene spectrum Figure 8-4 reveals no significant oxidative effect occurred.

B. DOSIMETRY

The dosimetry of the cobalt-60 source was measured using Fricke Dosimeters according to ASTMD-1671-59T. This method measures the absorbed gamma radiation dose in the range of 2 x 10^3 to 4 x 10^4 rads by the oxidation of ferrous ion to the ferric ion. The ferric ion is related to the exposed radiation dose by:

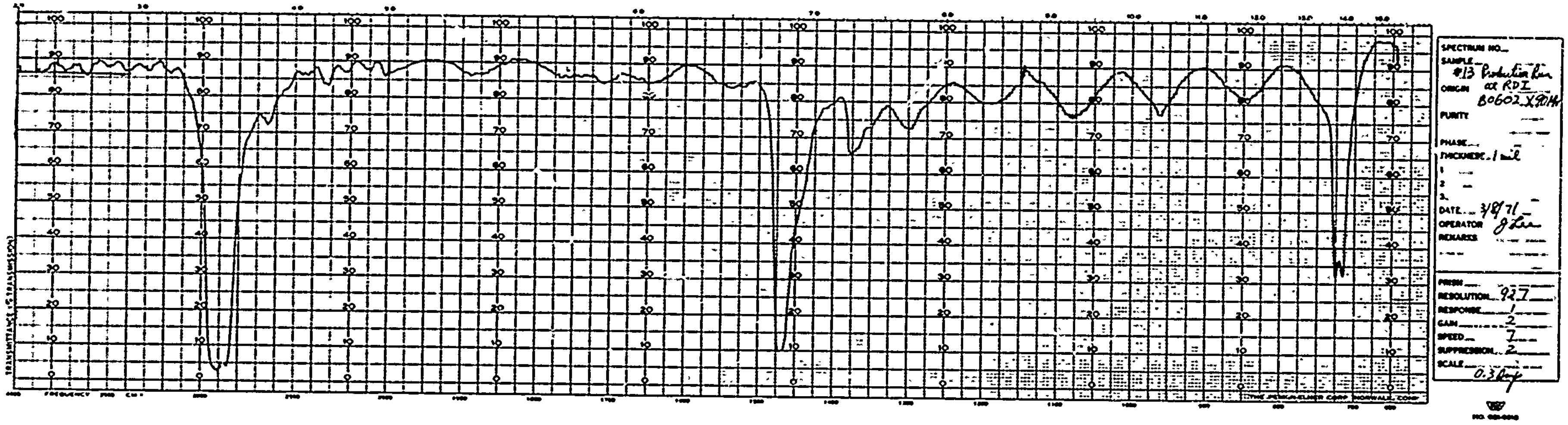
$$\text{Rads} = \text{micromoles of } Fe^{+++} \text{ per liter} \times 60.9$$

In practice, a calibration curve of a known ferric ion concentration and the optical density of the known solution is set up. The actual ferric ion in the exposed solution is compared to the calibration curve from which the absorbed dose is calculated. Results of the calibration are given in Table 8-9.

TABLE 8-9

Optical Density of Dosimeter Solution and The Equivalent Absorbed Dose at 26°C.

Ferric Ion Concentration (Moles)	Optical Density	Equivalent Dose (rads)
0.099×10^{-4}	0.024	600
0.20×10^{-4}	0.095	1,218
0.60×10^{-4}	0.142	3,898
0.80×10^{-4}	0.180	4,872
0.99×10^{-4}	0.232	5,999
1.60×10^{-4}	0.370	9,744
2.95×10^{-4}	0.720	17,965
3.20×10^{-4}	0.740	19,488
5.90×10^{-4}	1.40	35,931
8.00×10^{-4}	1.70	48,720
9.90×10^{-4}	2.00	59,986



SPECTRUM NO.
SAMPLE #13 Production Run
ORIGIN at RDI
B0602 X90H
PURITY
PHASE
THICKNESS 1 mil
1
2
3
DATE 3/8/71
OPERATOR J Lee
REMARKS

PRISM
RESOLUTION 927
RESPONSE 1
GAIN 2
SPEED 7
SUPPRESSION 2
SCALE 0.3 Amp

Figure 8-9 Infrared Spectrum of Crosslinked Polyethylene Film

Since this method is applicable from a range of 2,000 to 40,000 rads, the ferric ion concentration range should be about 0.3 x 10^{-4} to 6.0 x 10^{-4}M. The irradiation time should be adjusted accordingly. The calibration curve is shown in Figure 8-10. The optical density is linear with the concentration of ferric ion up to the ranges studied.

The dose rate at a point 27 inches above the floor and at a distance of 4 foot from the source was determined in Task 1. The rate was 10,100 rads/hr on February 18, 1971. The dosimetry inside the film reactor was also measured. The center of the reactor is 4 feet from the source. Dosimeters were placed inside the reactor so that they divided the circumference of the reactor into four equal portions. The nearest distance to the source is 33" and the farthest distance is 64.5", as shown in Figure 8-11.

The data is given in Table 8-10. It is seen that the front and the rear dose differ greatly due to the difference of distance from the source.

TABLE 8-10

Dosimetry Inside the Film Reactor

Height above Floor	Distance from Source 33"	64.5"	53.1"	53.5"
40"	15,471rad/hr	4,126rad/hr	6,446rad/hr	5,930rad/hr
33"	16,760	4,126	6,834	6,446
27"	18,049	4,899	7,092	7,092
20.5"	17,791	4,384	7,092	6,834

If the dose rates at all 27" points are summed and then divided by the number of points, an average dose rate would be obtained for the 27" point. This gives (18,049 + 4,899 + 7,092 + 7,092)/4 9,283 rads/hr. This average dose rate is obtained in a static non-moving condition. A more meaningful average would be obtained if the dosimeter is rotating inside the film reactor. A bundle of Lenonet paper mesh was used. The dosimeters were placed inside a glass tube sealed at one end, and slid inside the bundle which was rotated at a speed of 2 revolutions per minute (rpm). The glass tube was 13 5/8" from the center of the rotating bundle. Data is

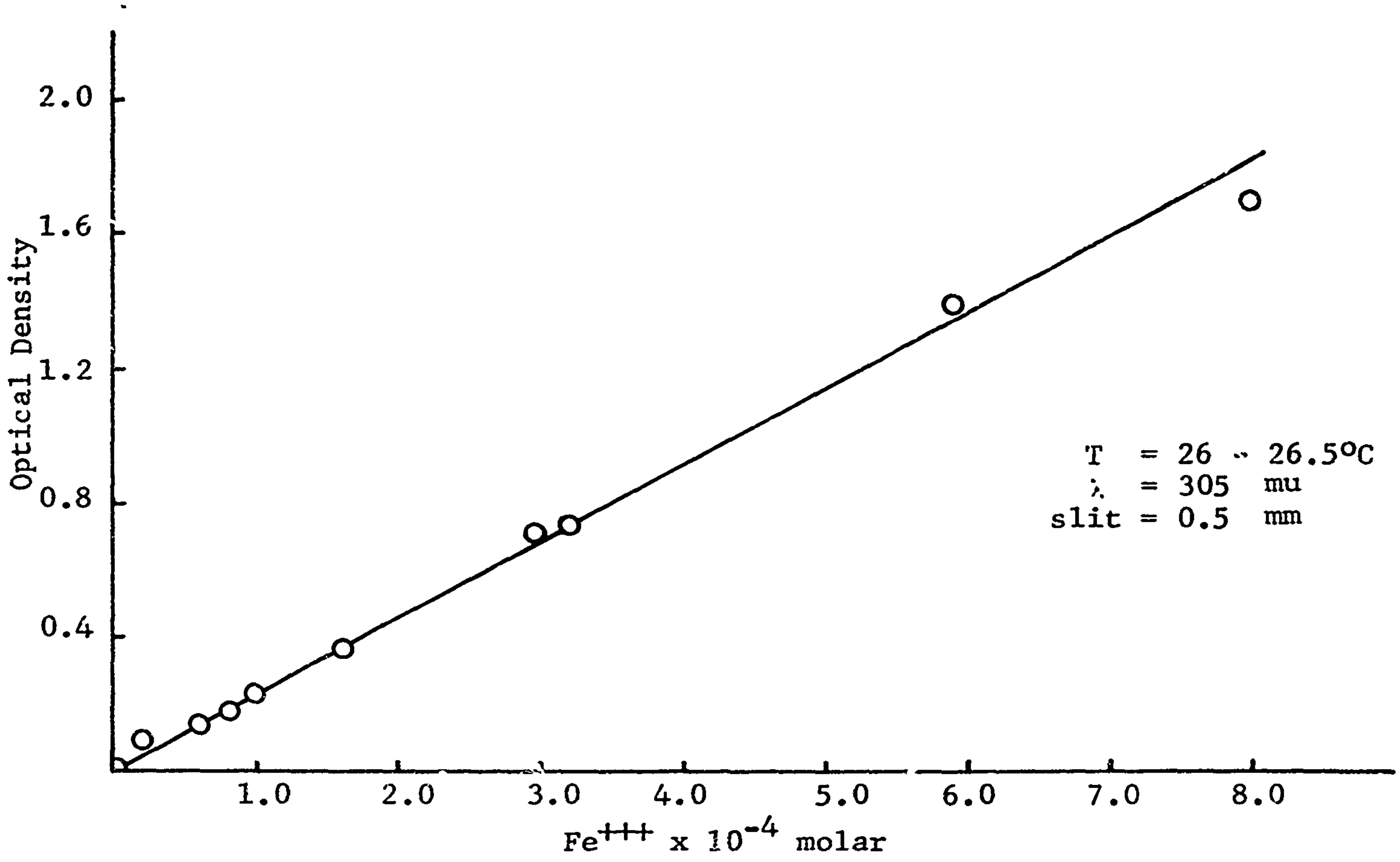


Figure 8-10. Calibration Curve for Ferric Ion Dosimetry Solutions.

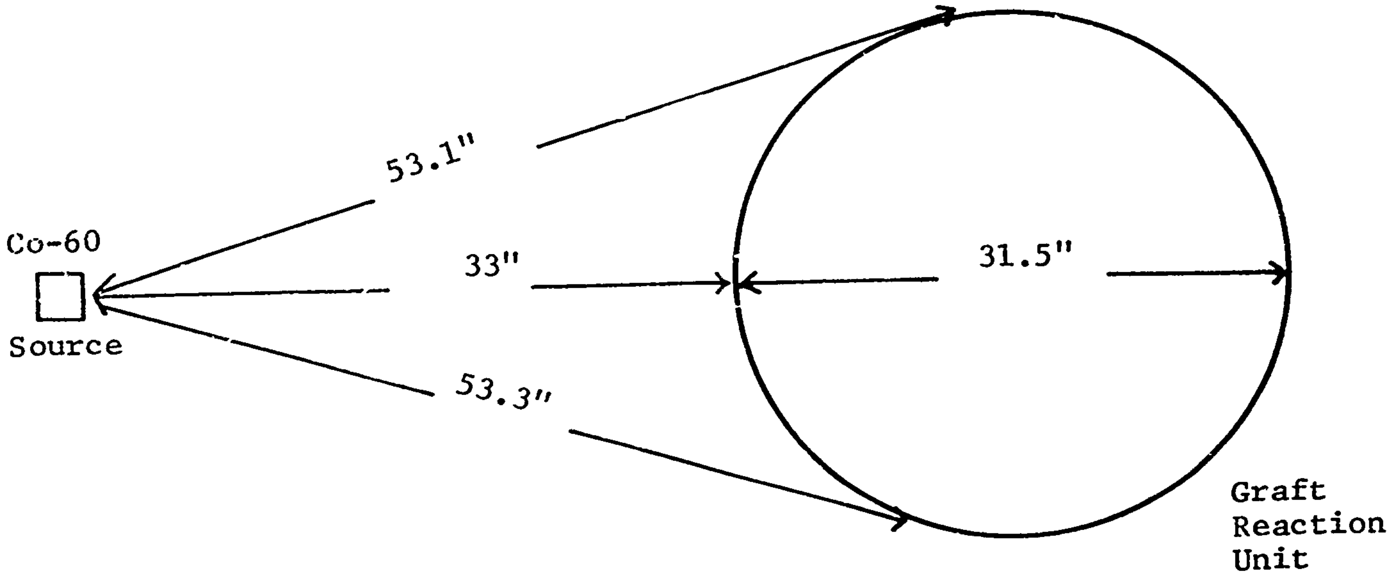


Figure 8-11. Radiation Dosimetry of Grafting Reactor Unit.

presented in Table 8-11.

TABLE 8-11

Dosimetry in a Rotating Bundle

Height Above Floor	48" ± 13 5/8" Distance From Source
36 3/4"	8,120 rad/hr
33 3/4"	8,729
30 3/4"	8,729
27.3/4"	8,720
24.3/4"	8,729
21.3/4"	8,120
18.3/4"	8,120

The dose rate at the 27" point is 8,729 rads/hr when the bundle rotates as compared to an average of 9,283 rads/hr when it is not moving. The rotating value is considered more reliable since it duplicates the condition which will be applied during grafting.

C. Solution of Monomers

The initial composition of the grafting solution was monitored by refractive index. In theory, any change in physical properties can be used to follow the monomer concentration during the grafting reaction. In practice, it is somewhat complicated. The monomer solution actually consists of benzene, carbon tetrachloride, and methacrylic acid, and as the reaction proceeds, there is an increase in viscosity and precipitation of a homopolymer slurry. In a three component system, one refractive index measurement does not define the composition unless one of the components is known, as can be seen in the refractive index diagram of the teriary mixture in Figure 8-12. There is a region where different compositions may have the same refractive index. For example, 0.21 mole fraction of MA, 0.19 mole fraction of CCl_4 and 0.60 mole fraction of benzene has an index of 1.478, but so will 0.25 mole fraction of MA, 0.12 mole fraction of CCl_4 and 0.63 mole fraction of benzene. To determine which is which, the mole fraction of one of the three components need to be known. The standard grafting solution at the time this was developed, had an initial composition of 70.0% benzene, 3.6% carbon tetrachloride and 26.4% methacrylic acid and a index of 1.481 according to the diagram. The experimental index found was 1.480. Agreement is quite satisfactory. The grafting solution for the production runs now consists of 80.2% benzene, 2.3% carbon tetrachloride and 17.5% methacrylic acid. The index from the diagram is 1.488 and the experimental value is 1.485. As a check for initial composition, the refractive index method is sufficient. As a means to follow the composition during the reaction, the direct titration of methacrylic acid is preferred. This was discussed in Task 6.

D. Equilibrium Swelling Time

The time required for the diffusion of monomer into the basefilm was determined by swelling the film in the monomer solution and determining the weight gain as a function of time. Bakelite DFD-0602 film, precrosslinked to 90 Mrads was submerged into the standard grafting solution in a constant temperature bath kept at 25 + 1°C. The % weight gain was taken as the monomer solution pick-up.

$$\%\ \text{weight gain} = \frac{W_t - W_o}{W_o} \times 100$$

where W_o and W_t are the weight of film at time zero and t. Data is given in Table 8-12, and the change in weight with time is shown in Figure 8-13. The weight pick-up is almost instantaneous and levels off after about 15 hours. The equilibrium weight gain is approximately 4%. A swelling time of 24 hours is therefore considered more than adequate for swelling. This also indicates that intermittent grafting may be a preferred procedure for grafting. This supposition could not be pursued under the present contract.

E. Wash Temperature, Concentration and pH

Findings subsequent to the Delco-Remy contract, ref. (1), indicated that the electrical resistance of a grafted membrane is a function of wash temperature. Evaluation is made here of grafted membrane produced under Task 6. The film was grafted at 85°F and washed at different temperatures at a fixed KOH concentration of 4%. Table 8-13 shows the relationship between wash temperature and electrical A.C. resistance. This is also graphically illustrated in Figure 8-14.

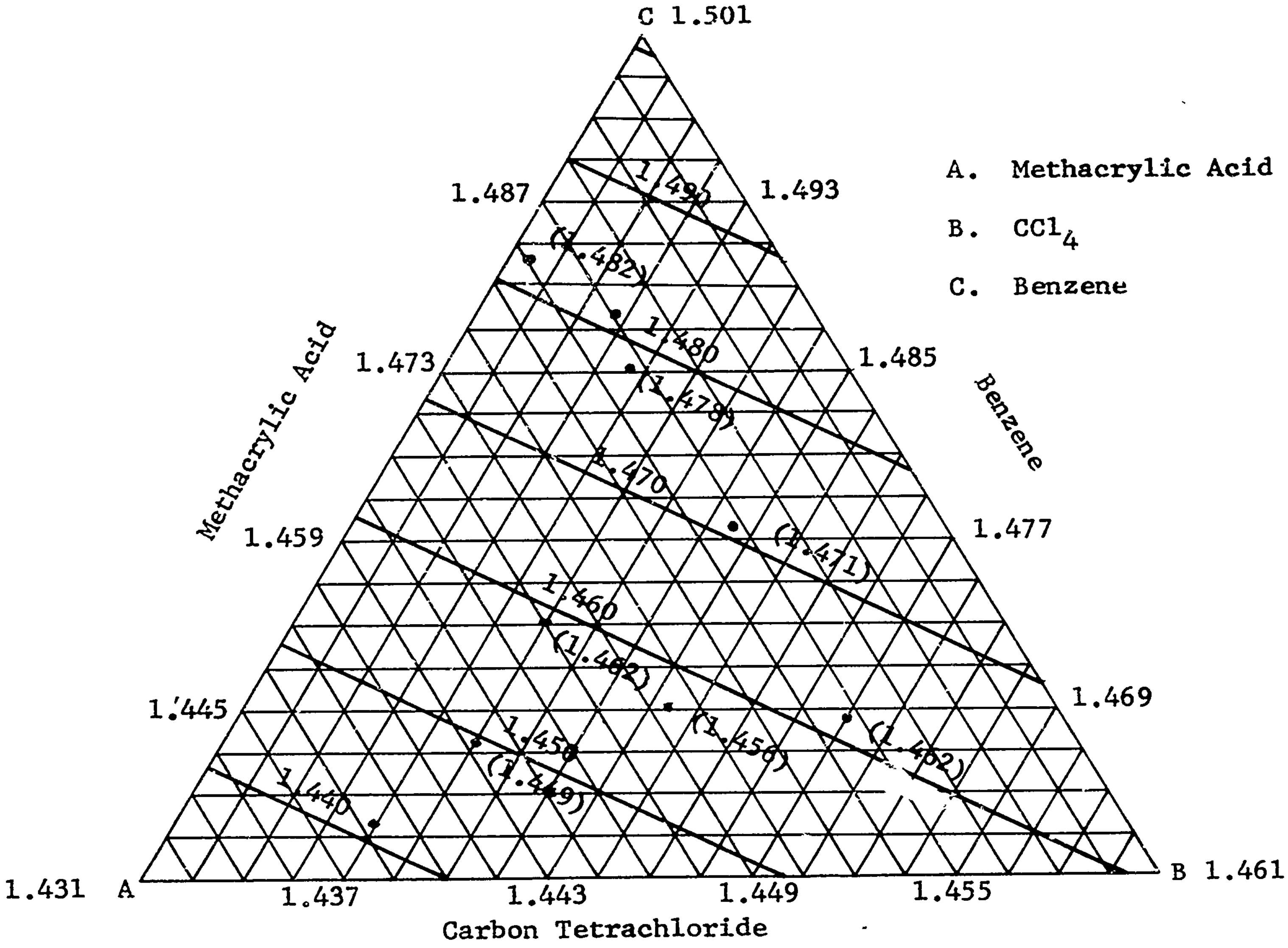


Figure 8-12. Refractive Index for Three Component System Methacrylic Acid, Carbon Tetrachloride and Benzene.

TABLE 8-12

Equilibrium Swelling Study

Swelling Time	% Weight Gain
0.5	1.86
0.5	2.95
1.0	2.32
1.0	2.15
2.0	3.58
2.0	2.73
4.0	3.25
4.0	2.10
7.0	2.88
7.0	2.68
16.0	4.34
16.0	3.94
24.0	3.94
24.0	3.77
48.0	4.20
48.0	3.80

TABLE 8-13

Washing Temperatures and Electrical Resistance - Film No. WP 231-46

Temperature (°C)	Resistance (milliohm/in^2)
23	148
40	96
60	64
80	38
100	24

The KOH concentration is 4% (w/v), and the film is kept at the temperature indicated for 15 minutes before cooling.

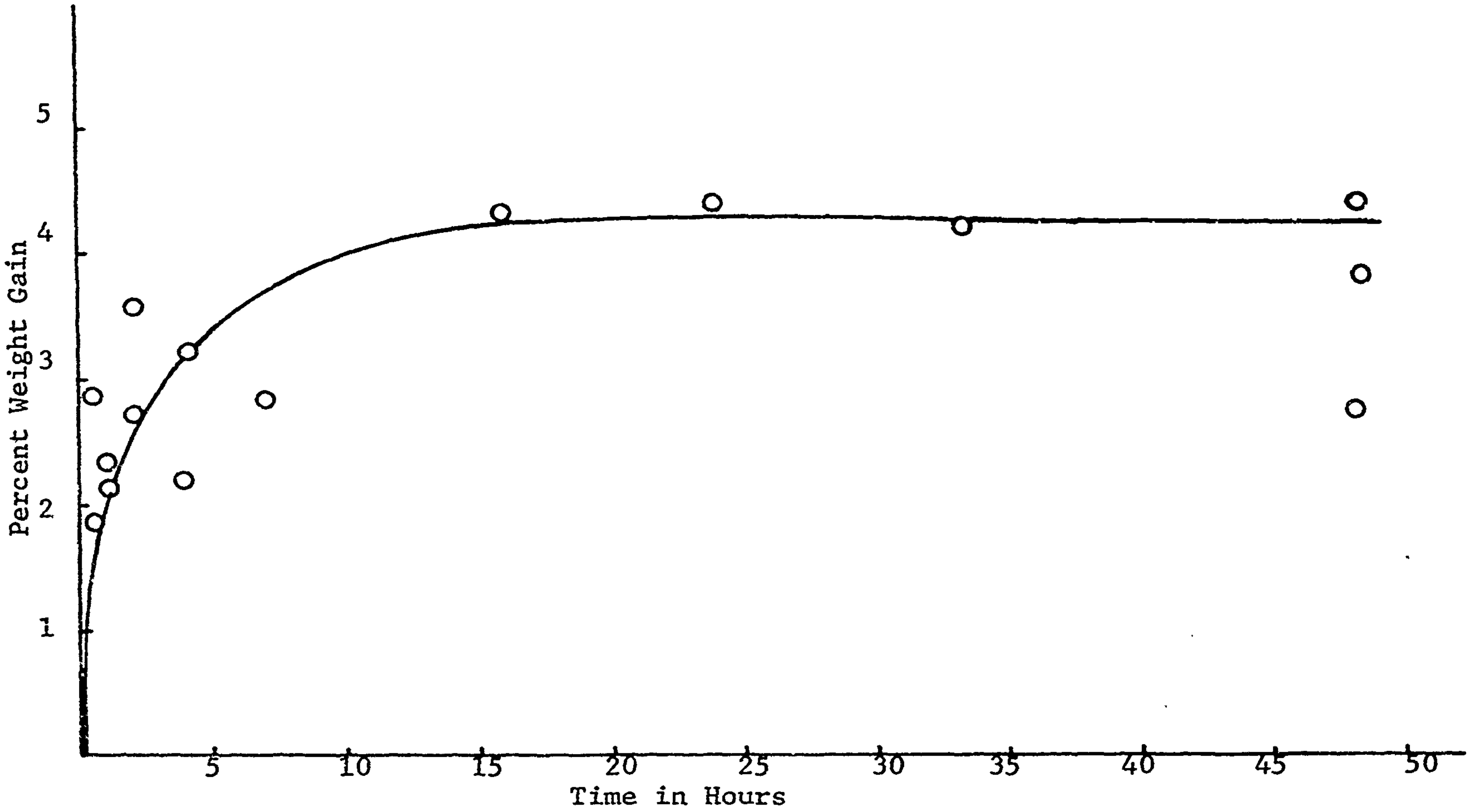


Figure 8-13. Equilibrium Swelling Weight Pick-up vs Time.

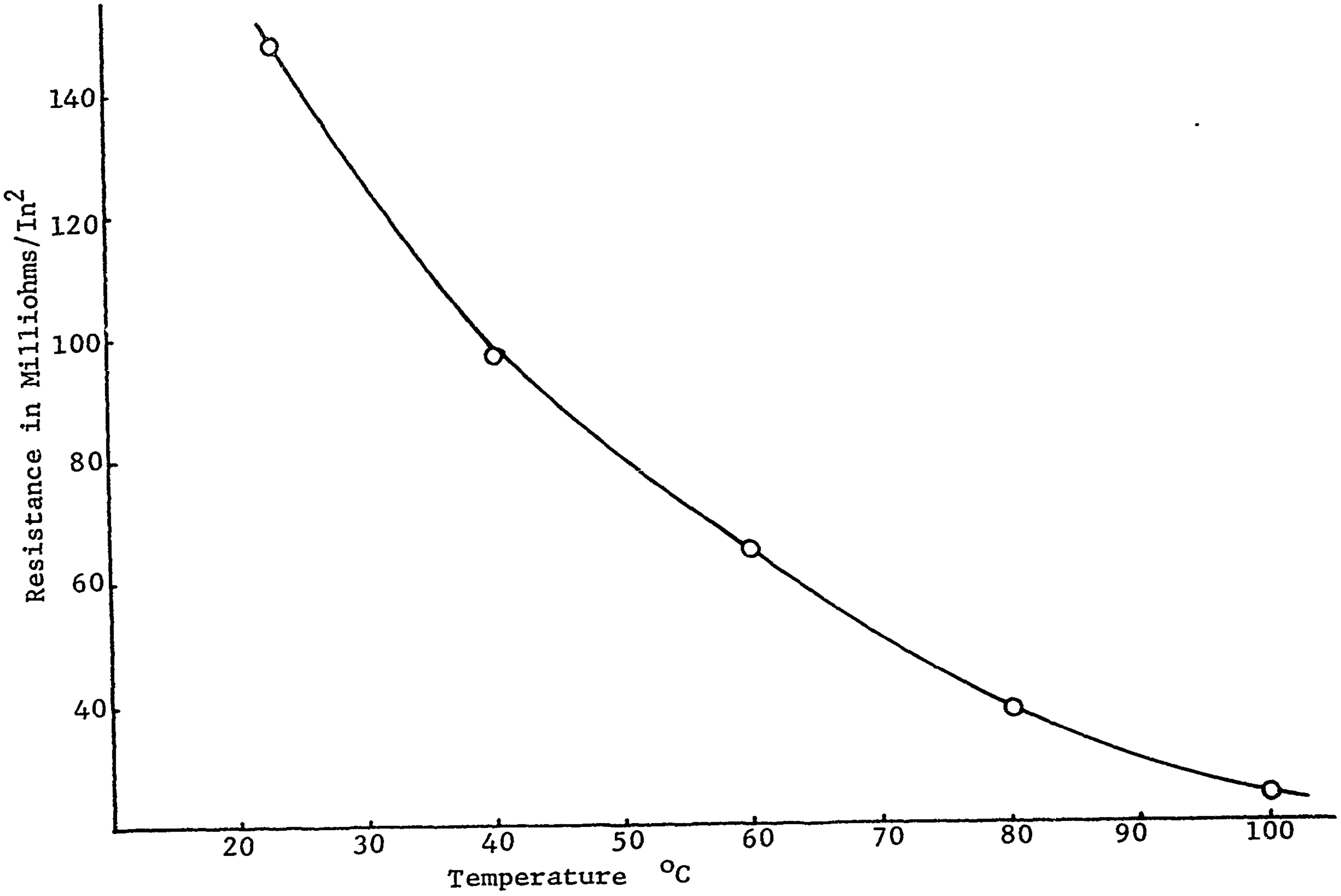


Figure 8-14. AC Resistance for P-2291 (WP 234-46) at Various Temperatures and 4% KOH Wash.

The electrical resistance of the film decreases rapidly as the wash temperature increases. The same film was also washed at a fixed temperature while varying the KOH concentration. Results are given in Table 8-14.

TABLE 8-14

Effect of KOH Concentration on Electrical Resistance - Film No. WP 231-46

KOH Concentration (% w/v)	Resistance (milliohm/in^2)
65	62
40	47
20	30
10	16
5	4
2.5	7
1.25	26
0.1	32
0.05	54

The film was boiled in the KOH solution for two minutes.

Figure 8-15 indicates that there is an optimum KOH concentration at which the electrical resistance of the grafted membrane is a minimum. The optimum range centers around 4-5% KOH. The above results clearly indicate that both the KOH concentration and the wash temperature are significant parameters in processing. This is due to the intrinsic character of the acid graft. The KOH serves to neutralize the acid and expand the grafted side chain while also acting as a salt to shield the charged sites along the side chain. The higher temperature serves to increase the ionization constant of the methacrylic acid so that more acid can be neutralized. However, increased salt formation, and hence higher ionic strength tends to inhibit expansion of the grafted side chain and increase the electrical resistance. These factors probably give rise to the optimum KOH concentration and the gradual decrease of resistance with temperature. When the log of conductivity of the film is plotted against 1/T as in Figure 8-16, a straight line is obtained with a

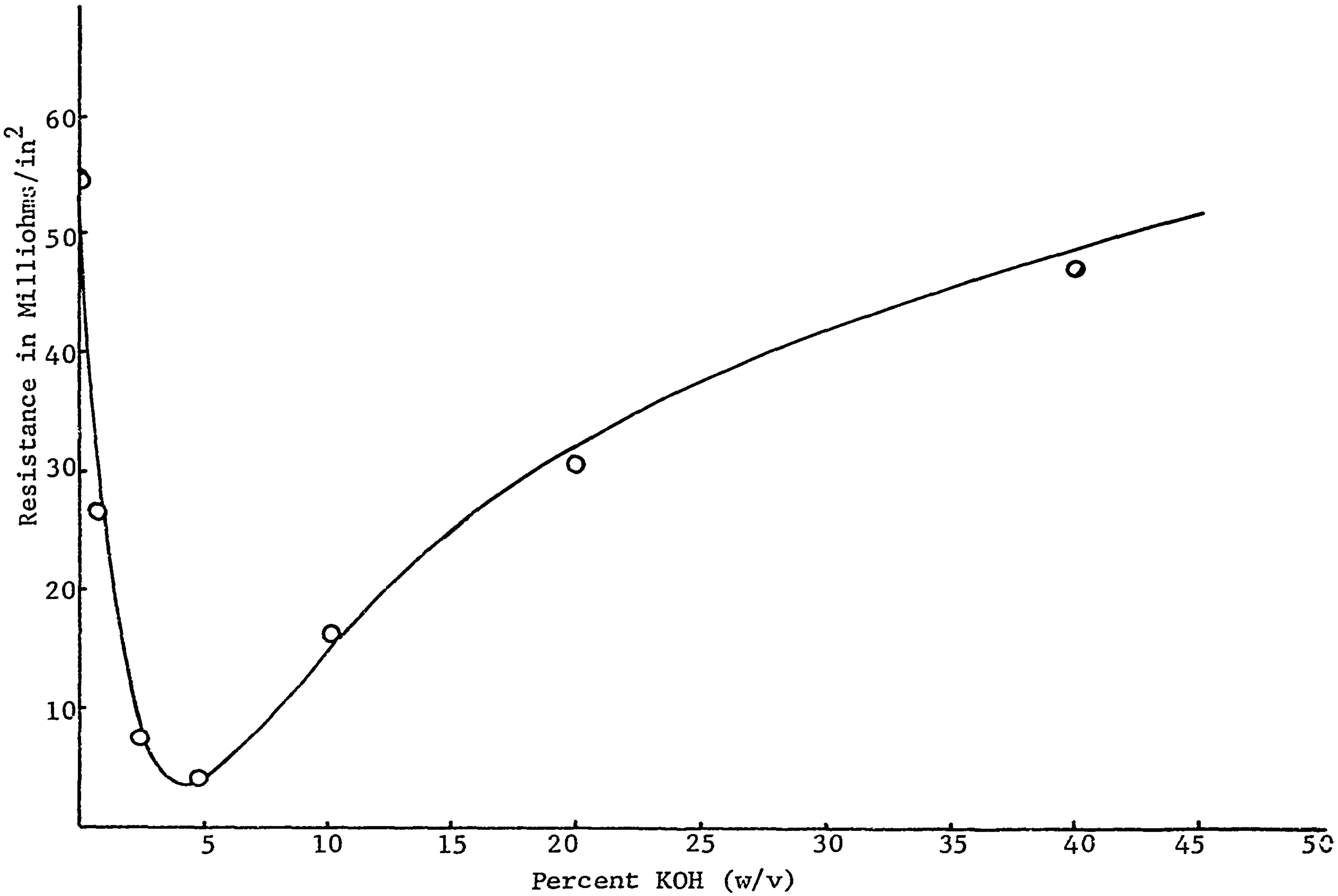


Figure 8-15. AC Resistance vs KOH Wash Concentration for P-2291 (Top 231-46).

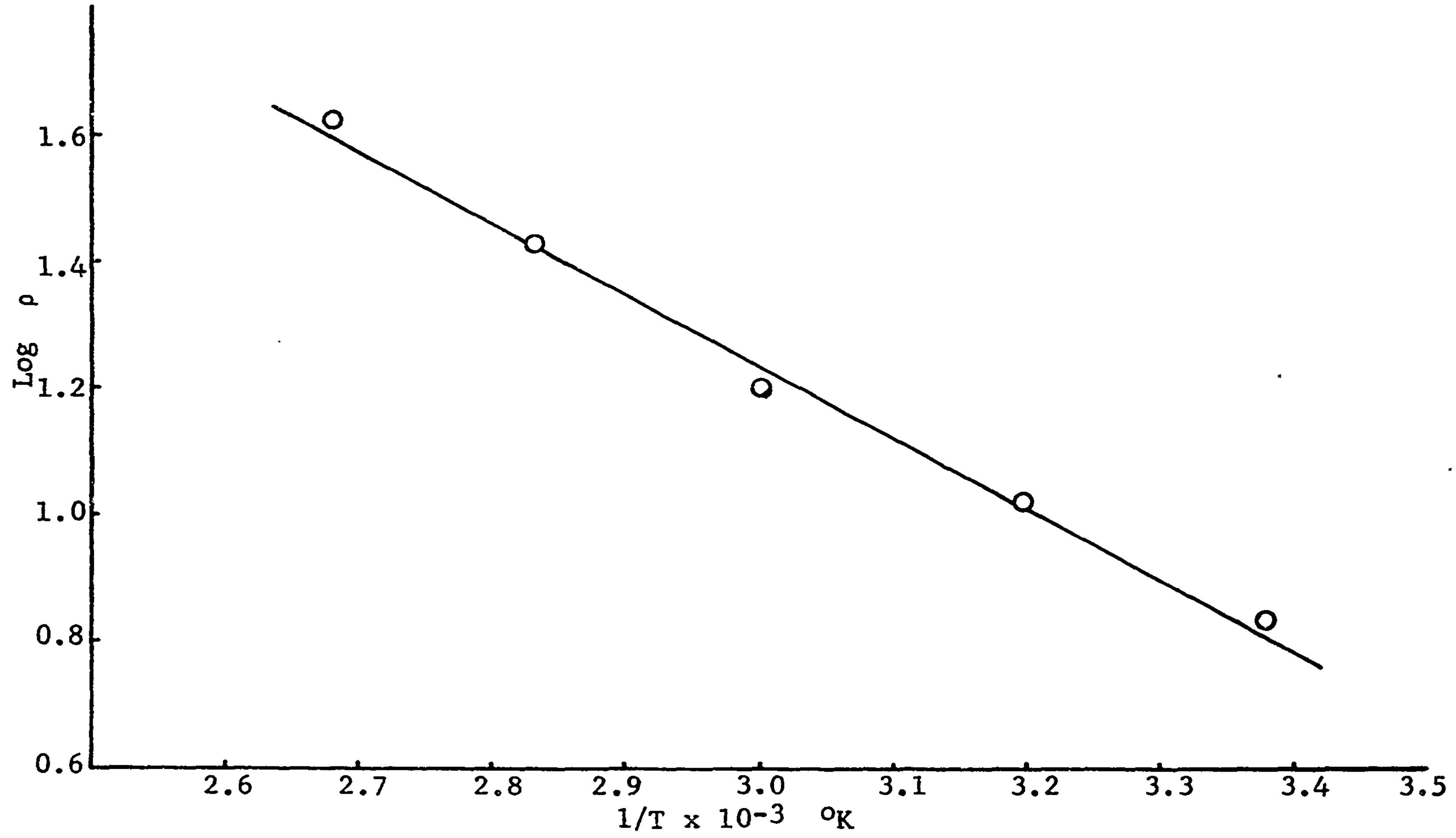


Figure 8-16 Arrhenius Plot of Salt Formation of the Grafted Membrane

slope which is characteristic of the salt formation process. The Arrhenius activation energy calculated from the slope is 2.53 Kcal/mole. This activation energy is quite small. It may reflect the increase of dissociation with temperature since the titration of acid and base involves no energy of activation. It is not the activation energy of conductivity since the conductivity of the membranes was taken at room temperature in 40% KOH.

2.8.3 Final Product Testing

A. Grafting Uniformity

A preliminary procedure for the determination of graft uniformity made use of light absorption and related it to the percent graft. The objection to this is that at high percent grafts, Beer's law is not obeyed, and the correlation of graft to absorption is not accurate. A new procedure was developed under Task 6 such that graft uniformity was determined directly. Weighed one square foot pieces of base film were inserted throughout the film bundle. Since the bundle was made up of 3,300 to 3,500 square feet of film, the one square foot pieces represent the true percent graft throughout the bundle and hence give an accurate picture of graft uniformity. The electrical resistance of the film is directly related to the percent graft, and uniform electrical resistance of the film is dependent on a relatively uniform graft. Typical data from Run #12 (WP 231-83) is presented in Table 8-15. Figure 8-17 indicates that from the 4" to 10" diameter of the roll, the film has a graft range from 47% to 43% with a range of electrical resistance from 28 to 32 milliohms/in^2. There are 1,684 square feet of membrane inside this diameter range. From 2" to 12" diameter, the % graft would be 52 to 41%, and the resistance is 27 to 35 milliohm/in^2, and the amount of film would be about 2,600 square feet. It should be noted within these ranges, the electrical resistance varies from 27 to 35 milliohm/in^2 although the graft range varies from 52% to 41%. If the beginning and the end of roll are included, the electrical resistance ranges from 23 to 44 milliohm/in^2 while the graft ranges from 35 to 66%.

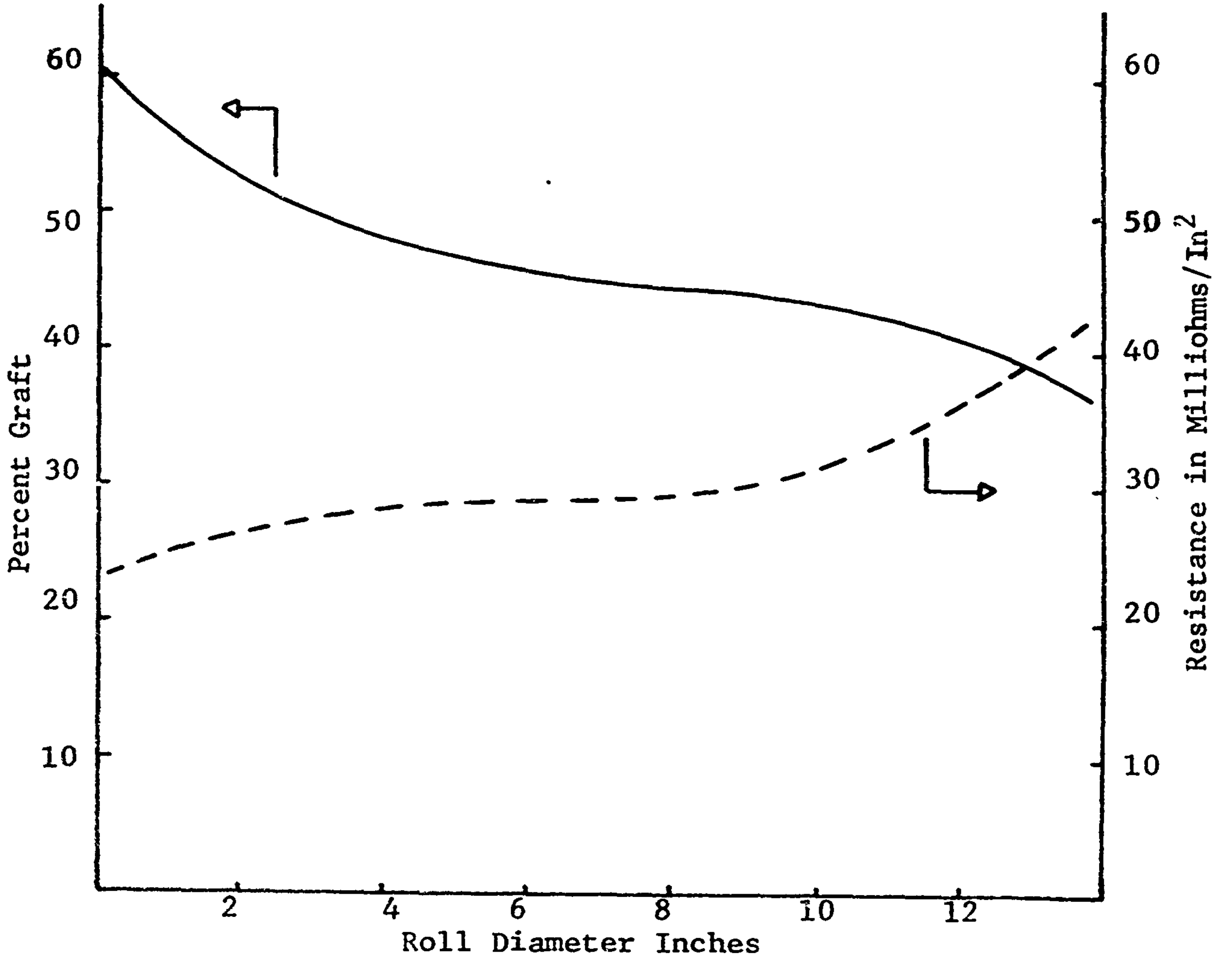


Figure 8-17. Percent Graft and Resistance as Function of Roll Diameter.

TABLE 8-15

Graft Uniformity and Electrical Resistance (WP 231-83)

Part of Bundle	Diameter into roll	% Graft	Electrical Resistance 40% KOH milliohm/in^2
Bottom	0"	55.0	25
Bottom	4½"	47.4	27
Bottom	9"	44.4	29
Bottom	13½"	38.5	44
Top	0"	66.3	23

B. Thickness

The thickness of the grafted film was measured with a constant weight head gauge (Federal Model 691B-R2) graduated in 0.0001". A large number of measurements were taken across a 10 foot film so as to obtain a reasonable average reading. The uncertainties in the measurements were expressed as average error α, as standard deviation σ, and as probable error γ.

$$\alpha = \pm\ 0.07$$

$$\sigma = \pm\ 0.09$$

$$\gamma = \pm\ 0.06$$

Where d is the deviation from the arithmetic mean and n is the number of measurements. Typical data is shown in Table 8-16.

TABLE 8-16

Thickness Measurement of Grafted Membranes

Thickness Mills	d[a]	d^2	Thickness Mills	d	d^2
1.30	0.07	0.0049	1.15	0.08	0.0064
1.30	0.07	0.0049	1.15	0.08	0.0064
1.38	0.15	0.0225	1.15	0.08	0.0064
1.38	0.15	0.0225	1.15	0.08	0.0064
1.30	0.07	0.0049	1.25	0.02	0.0004
1.25	0.02	0.0004	1.30	0.07	0.0049
1.25	0.02	0.0004	1.35	0.12	0.0144
1.15	0.08	0.0064	1.35	0.12	0.0144
1.20	0.03	0.0009	1.30	0.07	0.0049
1.15	0.08	0.0064	1.31	0.08	0.0064
1.38	0.15	0.0225	1.35	0.12	0.0144
1.35	0.12	0.0144	1.20	0.03	0.0009
1.35	0.12	0.0144	1.10	0.13	0.0169
1.35	0.12	0.0144	1.15	0.08	0.0064
1.35	0.12	0.0144	1.10	0.13	0.0169
1.35	0.12	0.0144	1.30	0.07	0.0049
1.28	0.05	0.0025	1.15	0.08	0.0064
1.38	0.15	0.0225	1.15	0.08	0.0064
1.25	0.02	0.0004	1.15	0.08	0.0064
1.23	0.00	0.0000	1.35	0.12	0.0144
1.25	0.02	0.0004	1.15	0.08	0.0064
1.28	0.05	0.0025	1.21	0.02	0.0004
1.20	0.03	0.0009	1.20	0.03	0.0009
1.30	0.07	0.0049	1.20	0.03	0.0009
1.25	0.02	0.0004	1.20	0.03	0.0009
1.20	0.03	0.0009			
		Total	63.83	3.84	0.3786

a. d is the absolute value

The arithmetic mean thickness is given by:

$$\text{Mean} = \frac{63.83}{52} = 1.23 \text{ mil}$$

$$\alpha = \pm \frac{3.84}{52} = 0.07 \text{ mil}$$

$$\sigma = \pm \frac{0.3786}{51} = 0.09 \text{ mil}$$

$$\gamma = \pm 0.6745 \times 0.09 = 0.06 \text{ mil}$$

C. Resistance

The electrical resistance of a separator is one of the most important properties because it is a valuable indicator of the performance of the separator in the working cells. The electrical resistance of a battery separator can be measured by several methods. We have evaluated the Alternating Current method and the Direct Current Method, which were described in the "Screening Methods of Battery Separator" by Cooper and Fleischer.

Using the AC method, electrical resistance of the grafted film was measured in 40% KOH at room temperature using a plexiglass cell as shown in Figure 8-18. The circuitry for the resistance measurement apparatus is shown in Figure 8-19. The resistance of the separator is obtained as the difference between the cell resistance with and without the separator, in milliohm/in^2. The resistance was determined as follows:

$$R_{\text{separator}} = R_{(\text{cell = separator})} - R_{(\text{cell out separator})}$$ where

R stands for the electrical resistance of the material. Resistance is measured using an AC bridge at 1,000 cycles.

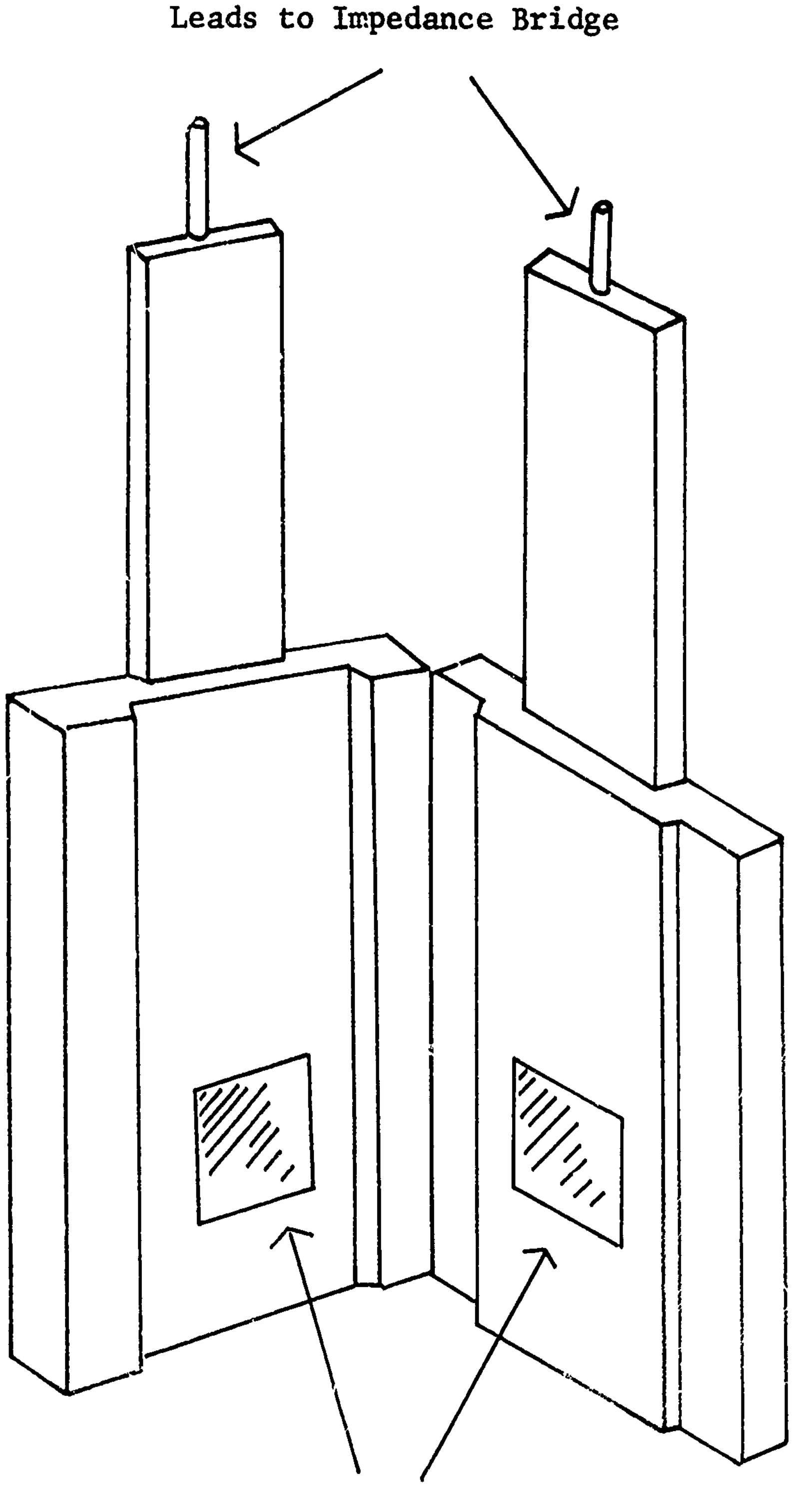


Figure 8-18 Resistance Cell

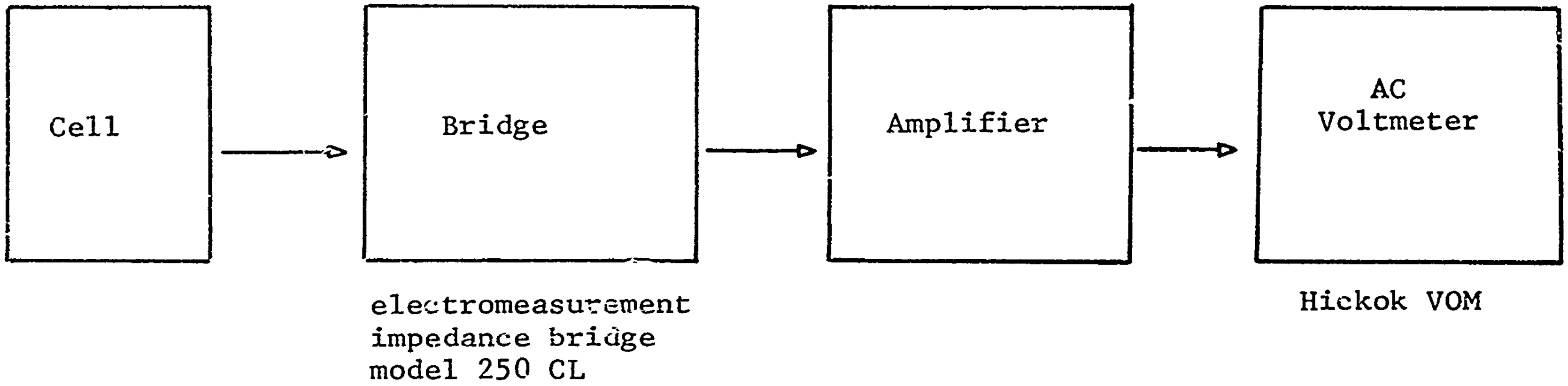


Figure 8-19. Membrane Resistance Measurement Apparatus.

TABLE 8-17

A.C. Electrical Resistance of Grafted Membrane at Various Parts in a Roll, at Room Temperature

Roll No.	Diameter into Roll	R Cell + Separator	R Cell	R Separator
7	3" Top	240	219	21
	6" Top	230	219	11
	9" Top	233	219	14
	12" Top	230	219	11
7	3" Bottom	220	210	10
	6" Bottom	224	210	14
	9" Bottom	225	210	15
	12" Bottom	225	210	15
8	1" Top	Varies	210	-
	5½" Top	222	211	11
	9" Top	224	211	13
	12" Top	261	211	50
8	1" Bottom	5500	211	5,289
	5½" Bottom	222	211	11
	9" Bottom	226	211	15
	12" Bottom	253	211	42
9	0" Top	11800	213	11,587
	5½" Top	8380	213	8,167
	10½" Top	763	213	50
	13 5/8" Top	5850	213	5,637
9	0" Bottom	5300	213	5,087
	5½" Bottom	472	213	259
	10½" Bottom	290	213	77
	13 5/8" Bottom	5000	213	4,787
10	0" Top	315	210	105
	4½" Top	271	210	61
	9" Top	285	210	75
	13 1/3" Top	255	210	45
10	0" Bottom	490	210	280
	4½" Bottom	261	210	41
	9" Bottom	281	210	71
	13 1/3" Bottom	385	210	175

TABLE 8-17 (Continued)

Roll No.	Diameter into Roll	R Cell + Separator	R Cell	R Separator
11	0" Top	340	218	122
	4½" Top	255	218	37
	9" Top	265	218	47
	13½" Top	285	218	67
11	0" Bottom	768	218	550
	4½" Bottom	264	218	46
	9" Bottom	304	218	86
	13½" Bottom	262	218	44
12	0" Top	229	206	23
	4½" Top	233	206	27
	9" Top	236	206	30
	13½" Top	243	206	37
12	0" Bottom	232	206	26
	4½" Bottom	233	206	27
	9" Bottom	235	206	29
	13½" Bottom	250	206	44
Control				
Visqueen		235	210	35
Pudo		228	210	18

Typical resistance data is given in Table 8-17 which indicates the resistance of different parts of the grafted roll.

Figure 8-20 presents a graph of the electrical resistance of the separator vs the percent graft. Below 30% graft, the resistance increases rapidly and levels off to a minimum above 80% graft. The graft was converted to the salt form with 4% KOH at 100°C, and the resistance was measured in 40% KOH at ambient temperature. In the 35% - 65% graft region, the resistance will vary from about 35 to 20 milliohms/in^2. The curve can be used to predict the resistance of the separator if the percent graft is known.

The electrical resistance determined by a direct current method was measured according to the procedure of Lander and Weaver.[10] Certain modifications of the instruments were made. These are noted in the schematic which is given in Figure 8-21. A Vibron electrometer was used in place of the potentiometer. The 0.25 inch hole was enlarged to accept the reference Hg/HgO electrodes, and a cover was added to avoid exposure to air of KOH solution. A Weston milliameter, Model 911 with scales 0-10, 30, 100, 1,000 ma. was used. The resistance was calculated from

$$R'' = \frac{(E' - E)A}{I}$$

where R" is the resistance of the separator, E' the voltage drop with the separator, E without the separator, A the area of the separator exposed (0.049 in^2) and I the current, which was held constant at 20 ma. A comparison of AC and DC resistance on the P-2291 membrane is given in Table 8-18. A Visqueen and a Permion 2291 film were also evaluated; the results in 45% KOH are given below. The DC resistance of Permion 2291 and a Visqueen are given in Table 8-19.

TABLE 8-18

Comparison of AC and DC resistance of methacrylic acid grafted membrane.

Distance Across (Inches)	D.C. RESISTANCE E′ (mv)	E (mv)	R (milliohm/in^2)	A.C. RESISTANCE R_{c+s}	R_c	R_s (milliohm/in^2)
1.5	20.8	4.1	41	270	225	45
3.0	21.6	4.1	43	278	225	53
4.5	22.5	4.1	45	276	225	51
6.0	20.4	4.1	40	274	225	49
7.5	20.8	4.1	41	275	225	50
9.0	20.8	4.1	41	274	225	49
10.5	18.4	4.1	35	275	225	50
12.0	18.8	4.1	36	272	225	47
13.5	19.6	4.1	38	265	225	40
15.0	20.0	4.1	39	260	225	35

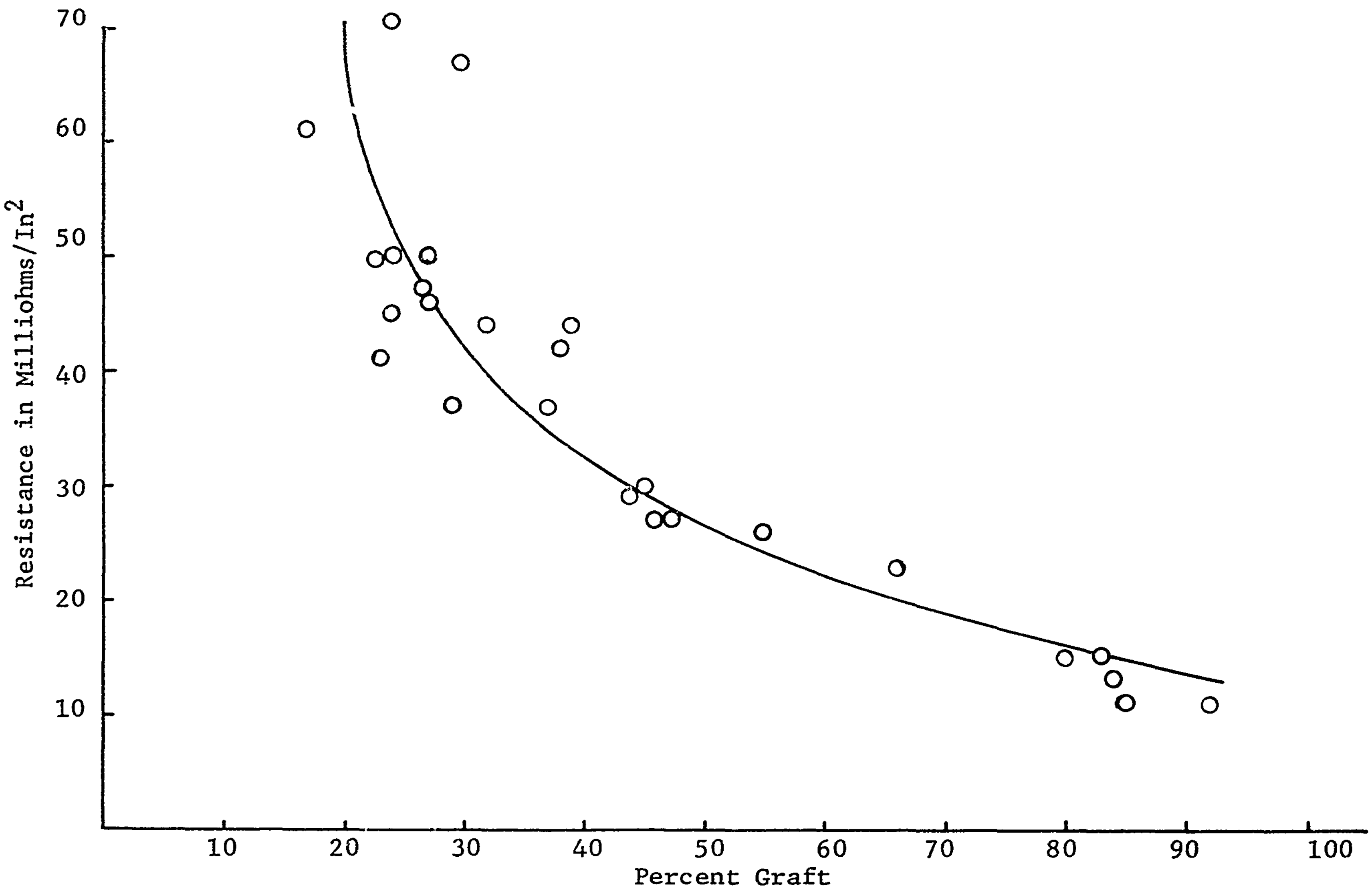


Figure 8-20. Percent Graft vs AC Resistance.

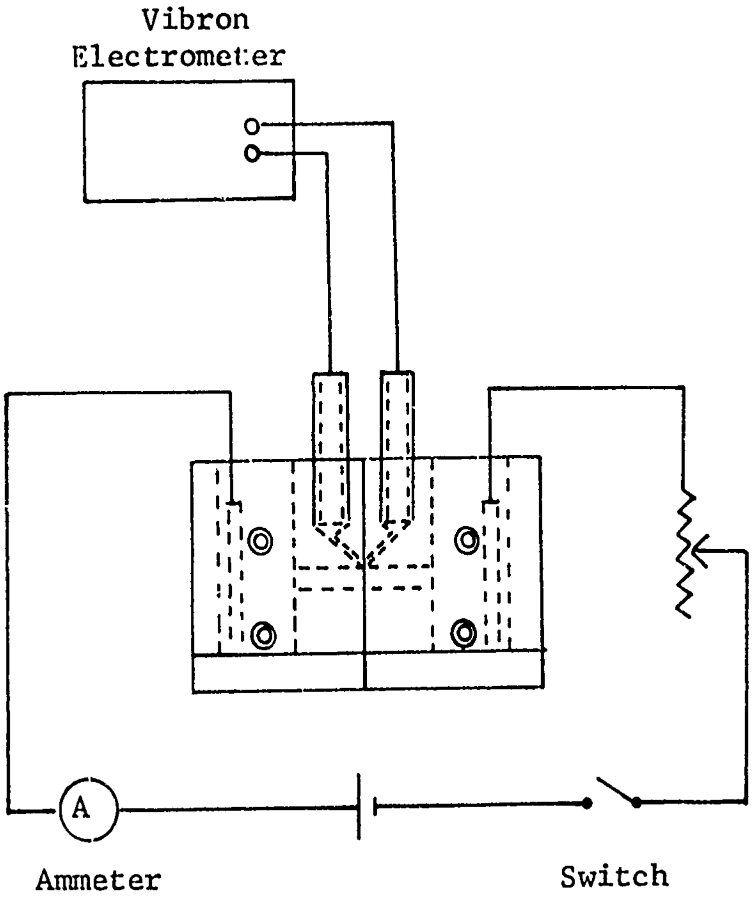


Figure 8-21. Schematic for DC Test Method.

TABLE 8-19

D.C. Resistance of P 2291 Separators

Distance (inches)	Visqueen E' (mv)	Visqueen E (mv)	Visqueen R" (milliohm/in^2)	Permion 2291 E' (mv)	Permion 2291 E (mv)	Permion 2291 R" (milliohm/in^2)
2	5	1	10	17	1	39
4	5	1	10	22	"	51
6	"	"	"	31	"	73
8	"	"	"	54	"	130
10	"	"	"	63	"	152
12	"	"	"	48	"	115
14	"	"	"	9	"	20

Two properties of the separators were observed. First, it takes more than ten minutes for a dry Visqueen to reach an equilibrium resistance value. The initial resistance is quite high but drops rapidly with time. It takes about ½ minute for Permion 2291 to reach its equilibrium value. Second, the resistance across the width of the Visqueen film is very uniform being about 10 milliohm/in^2 whereas Permion 2291 shows a high resistance area in the middle of its width and lower resistances at both edges, indicating that the separator tested was not uniform. As a comparison, the D.C. resistance of a grafted membrane (WP 231-24) which was previously known to be uniform, was measured and compared with the A.C. method. The results are comparable as seen in Table 8-18.

D. Exchange Capacity

The exchange capacity is the number of ionic sites capable of exchanging with other ions (cations in this case) per unit weight of the separator. This is usually expressed as milliequivalents per gram of film, and indicates the percent conversion into the salt form from the acid graft. As such, it is sensitive to the temperature of washing, the concentration of KOH in the washing tank, salt impurities, and would be expected to be directly related to the graft level. The exchange capacity of a Permion 2291 film was measured at five different positions. Results are given in Table 8-20 and shown in Figure 8-22.

TABLE 8-20

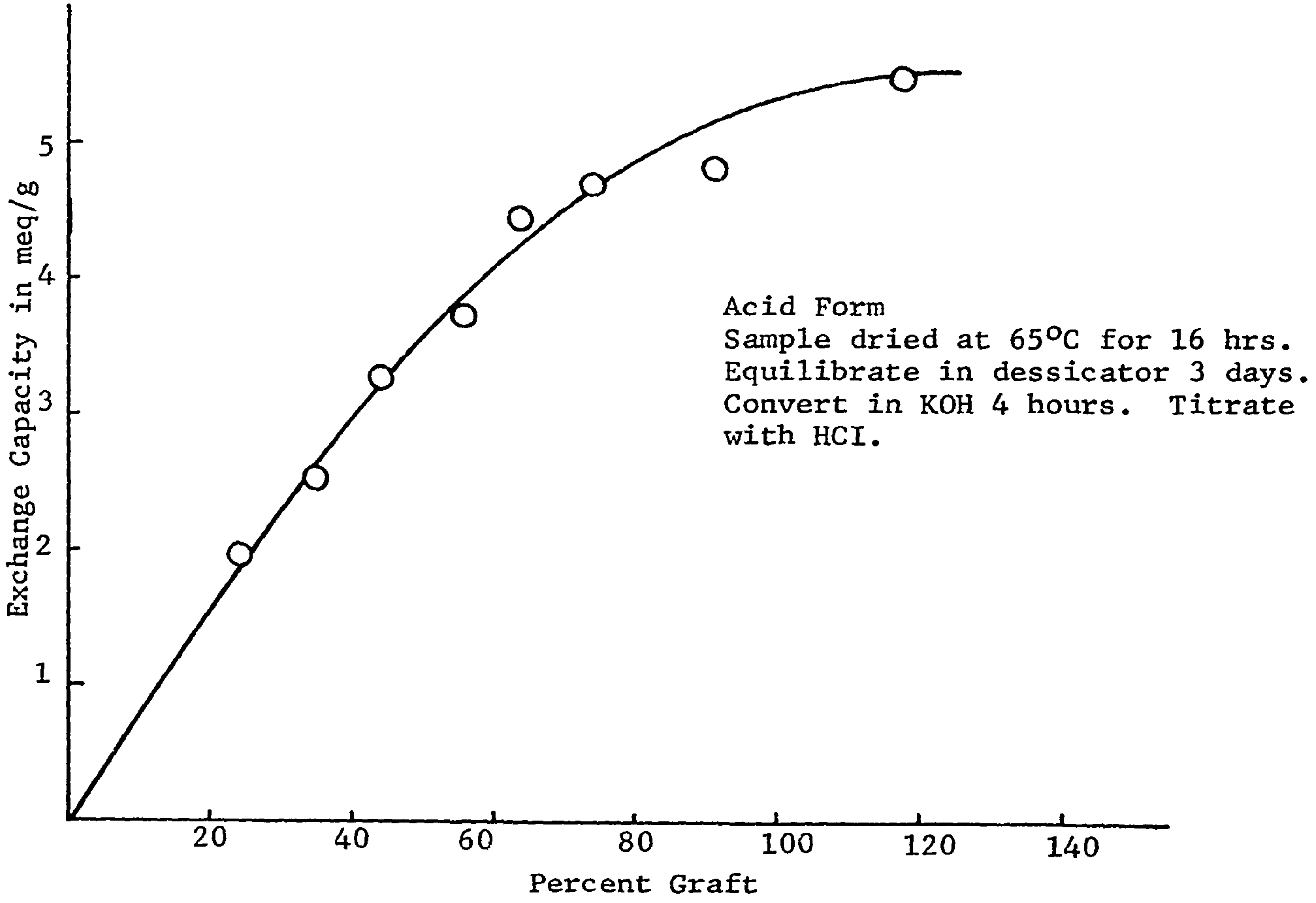
Exchange Capacity of Permion 2291 at Room Temperature

Expt. No.	Exchange Capacity (meq/g)	d*
1	4.66	0.18
2	4.94	0.10
3	4.72	0.12
4	4.73	0.11
5	5.17	0.33
Average	4.84 meq/g	

* d = deviation from average

$$\alpha = \frac{\sum d}{\eta} = \frac{0.85}{5} \pm 0.17$$

The percent graft in this 2291 sample was not known. Experiments were carried out where the exact percent graft was known. The amount of potassium in the separator after it was converted into the salt form was determined by atomic absorption spectroscopy. The washed film was dried in the acid form, weighed, boiled in 4% KOH solution , washed thoroughly and finally ashed in an oven kept at 850°C. Anhydrous potassium carbonate melts at 891°C. The alkali fusion crucible was cooled and then weighed. The ash was dissolved in 1,000 ml of distilled water and diluted before atomic absorption determinations were made. The amount of potassium found and the exchange capacity were then calculated. This was then compared with the exchange capacity calculated from the percent graft alone. The exchange capacity as determined by atomic absorption is always smaller than that calculated from the percent graft, indicating that even at the optimum conversion conditions, not all grafted acid was converted into the salt form. This is easily seen in Table 8-21. If all the grafted acid groups were converted to the potassium salt, then the potassium found by



Acid Form
Sample dried at 65°C for 16 hrs.
Equilibrate in dessicator 3 days.
Convert in KOH 4 hours. Titrate
with HCI.

Figure 8-22. Exchange Capacity vs Percent Graft atomic absorption should agree with the value calculated from percent graft alone. The low findings are consistant with the polyelectrolyte theory since to neutralize every acid molecule in the graft, considerable work has to be done to overcome the force of electrostatic repulsion between the negative carboxylate and the negative hydroxyl anion after 50% neutralization. It may be achieved at high temperatures. The percent K^+ and exchange capacity were calculated from the graft by:

$$\% \ K^+ \text{ in dry film} = \frac{\% \text{ graft}}{86} \times \frac{39.1}{(100 + \% \text{ graft})}$$

$$\text{Exchange capacity meq/g} = \frac{\% \text{ graft}}{86} \times \frac{1{,}000}{(100 + \% \text{ graft})}$$

The results show that from 60 to 87% of the acid could be converted to salt under the experimental conditions.

TABLE 8-21

Potassium Content in Separator Determined by Atomic Absorption Method

% Graft	Resistance in 40% KOH milliohm/in^2	%K by AA	%K Calc.	Exchange Capacity by AA(meq/g)	Exchange Capacity Calc.	Percent Theoretical
22.8	50	7.34	8.44	1.88	2.16	87.0
38.6	42	7.80	12.70	1.98	3.24	61.6
84.6	11	13.08	20.80	3.35	5.33	62.9
102.2	21	19.22	23.00	4.92	5.87	83.4
125.7	11	20.85	25.30	5.33	6.47	82.3
126.3	14	19.20	25.40	4.91	6.48	75.6

A plot of the exchange capacity as a function of percent graft is shown in Figure 8-22. The curve is almost linear up to 60% graft and then slowly levels off with higher percent graft, indicating more difficulty in exchanging the acid groups as the percent graft increases.

E. Moisture Control

The moisture content of the films grafted at 85°F was determined by Karl Fisher titrations. The films were dried at 40°C overnight and stored in a desicator for

24 hours before use. It is necessary to have a point of reference for relative humidity as the moisture content of the grafted film in their salt form is very sensitive to atmospheric conditions. Typical results are shown in Table 8-22. The moisture content of the grafted film determined in this way varies from 3-7%. Of course, when the films are equilibrated to atmospheric conditions, the moisture content is higher.

Another method was developed to measure the moisture content. During the determination of potassium by atomic absorption, the film in the salt form has to be dried before ignition. The weight loss during drying is due to moisture. These results are also shown in the table. Agreement between the two methods is satisfactory although the Karl Fisher method should be more accurate.

TABLE 8-22

Moisture Content of Grafted Membranes

Material	Position	% Moisture	Method
P231-46 Beginning	Top	6.78	Karl Fisher
"	Bottom	3.28	" "
Middle	Top	4.03	" "
"	Bottom	4.29	" "
End	Top	3.48	" "
"	Bottom	3.40	" "
WP 231-71	22.8% Graft	6.1%	Drying
	38.6%	7.4%	"
WP 231-67	84.6%	5.8%	"
	102.2%	6.5%	"
	125.7%	5.5%	"
	126.3%	5.9%	"

F. Hull Test(5)

The zinc penetration times were determined using a Hull Test. When zinc is plated out of alkaline solution, the product is either spongy or dendritic. The dendrite in a cell could rapidly grow to the silver plate and short out the cell in the absence of a separator. A significant test for a separator is to determine if it retards the penetration of zinc dendrite. The procedure standardized at this laboratory is as follows:

Size of Cathode Plate: 3 7/8" x 2½"
" Anode Plate 2½" x 2½"

Electrolyte: 45% KOH in a 1 molar ZnO Solution

Current: 1 Ampere

Size of Film: 6" x 5"

Cleaning Steps for Film:
Hot KOH then water wash

I PREPARATION OF ZINC PLATES

The larger plate must have its edges and corners sanded smooth to prevent any punctures or tears in the film.

After the sanding, both plates are washed in a solvent, such as acetone, to remove any surface dirt. The smaller plate is connected to the positive terminal.

II PREPARATION OF FILM FOR TEST USE

A piece of film measuring 6" x 5" should be cut from the desired sample to be tested. Cuttings should be taken from a clean area of the film and should always be handled carefully, by the edges, in order to avoid a puncture or tear.

Because this film is to be used in a basic environment, we must convert it to its basic form. This is done by washing the film in a hot (90° - 95°C.) 5% KOH bath for approximately 25 - 30 minutes. The film is then rinsed in deionized water to remove the KOH. The film is towel blotted until dry.

III FITTING FILM ON PLATE

The prepared piece of film must now be fitted to the larger (3 7/8" x 2½") plate. The film is first folded in half along its length covering the plate evenly. That film extending beyond the sides of the plate is folded backwards and securely taped. That film remaining above the plate is cut, so that it fits tightly around the plate with no excess. This plate is placed in the Hull Test Unit and connected to the negative terminal. The connection must be in contact with the zinc plate, and is therefore, slipped under the film. The connecting clip should clamp onto the cell wall. After this is done, the 45% KOH-ZnO solution is poured to the filling line on the test cell. The current is then passed at 1 ampere. A timer should be used and set at 15 minute intervals. The test for dendrite formation is a visual one with most of the films showing dendrite formation at the closest distance between the plates. The time when the dendrites just penetrate the film is recorded as the failure time.

Results of Hull Test on films with different percent graft are given in Table 8-23. It is clear that as the percent graft decreases, the time to dendrite growth increases. Increasing percent graft brings a decrease in time to dendrite growth as shown in Figure 8-23. Such a relationship parallels that of electrical resistance and percent graft. Obviously if zinc penetration time is the only concern of the separator, then the membrane should have as low a graft as possible. This would give the separator very high electrical resistance which is undesirable. A compromise between Hull Test time and percent graft (or electrical resistance) has to be built in the separator. It is interesting to note that this curve is quite similar to the plot of resistance vs. grafts and indicates that as the graft increases, the dendrite resistance decreases. Further, both curves i.e. Figure 8-20 and Figure 8-23 approximate a figure which has a distinct slope change beyond a graft of 60%. A graft of about 45% would result in a resistance of about 25 milliohm and a zinc dendrite resistance of 2½ hours. A 60 milliohm film would have a zinc dendrite resistance of about 5 hours. Beyond 45% graft the data is scattered but the trend is toward an increased rate of dendrite failure per unit increase in graft. This data indicates that as the resistance decreases below 30 milliohms, the "pore" size probably increases at a faster rate or the effect charge repulsion of the negative carboxylate on zincate flow is drastically altered. This type of thinking is in line with the decrease in charge acting inversily as the square of the distance. Support for this is evident by the parabolic shape of the curve which suggest a inverse square relationship of charge with distance.

TABLE 8-23

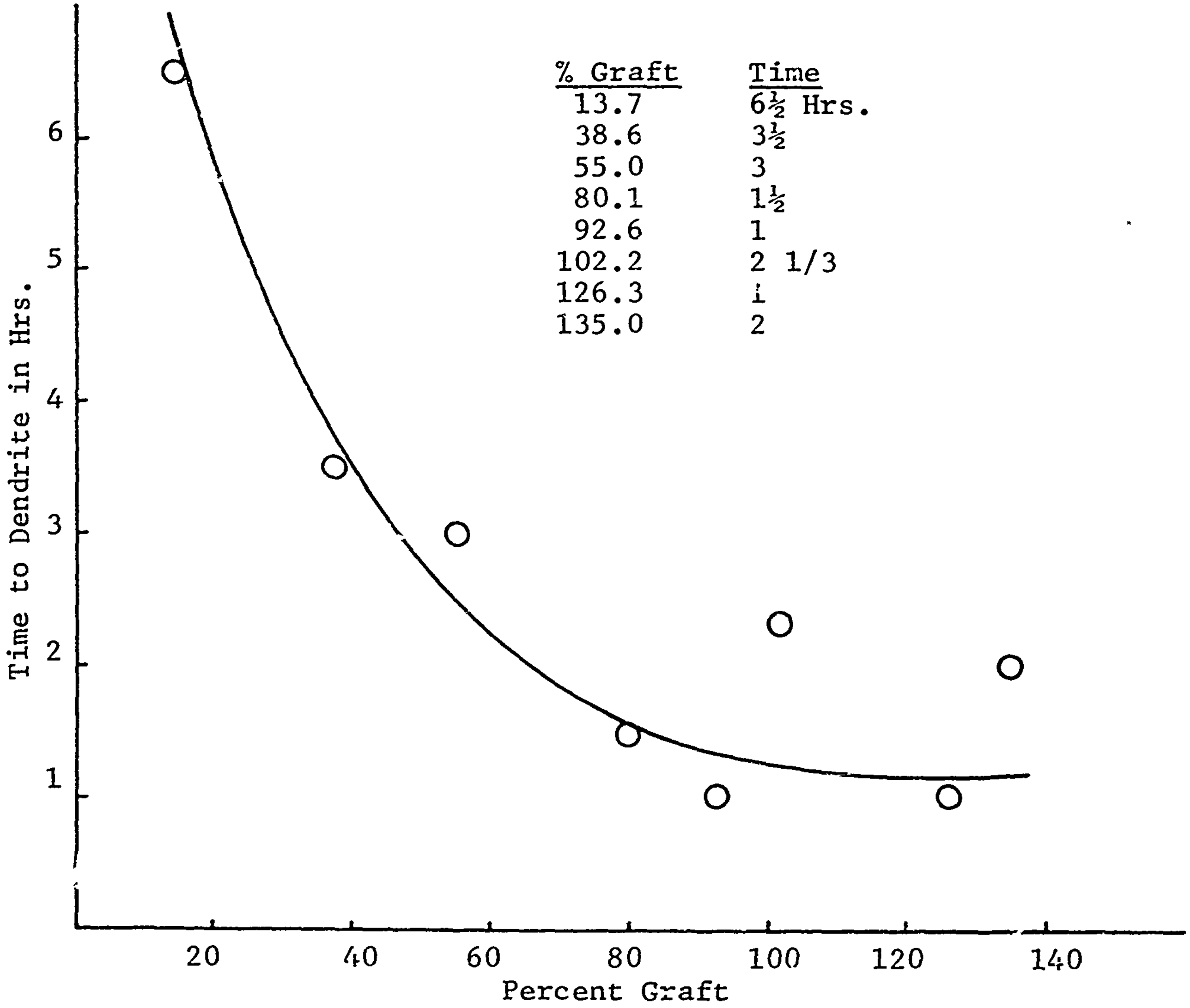
Hull Test on Grafted Membranes

% Graft	40% KOH Resistance (milliohm/in^2)	Time to Dendrite Growth (Hours)	Time$^{(a)}$mil (Hours)
13.7	720	6½	6½
38.6	42	3½	3½
55.0	27	3	3.0
80.1	15	1½	1½
92.6	11	1	1
102.2	21	2 1/3	2 1/3
126.3	14	1	1
135.0	14	2	2
P2291	60 - 100	3 - 5	3 - 5
WP 231-46	Top Beginning Part	2	2
	Bottom " "	2	2
	Top Middle Part	1 4/5	1 4/5
	Bottom " "	1	1
	Top End Part	1	1
	Bottom" "	1 7/10	1 7/10
Pudo 193		1½	1½
Sausage Casing		1 3/4	7/12

(a) Normalize to a dry thickness of 1 mil on a wet thickness basis both the PUDO 193 and Sausage Casing would have even less resistance than Permion on a normalized one mil film.

G. Diffusion Test

The diffusion of zinc and silver ions through the separator is an important characteristic of the separator. Each type of separator has its own characteristic diffusion properties. The diffusion properties characterized



% Graft	Time
13.7	6½ Hrs.
38.6	3½
55.0	3
80.1	1½
92.6	1
102.2	2 1/3
126.3	1
135.0	2

Figure 8-23. Percent Graft vs. Hull Test.

by flux of species through the membrane, has been well established for the cellophane separators. The procedure for determination of diffusion properties of P-2291 is taken from "Battery Separator Screening Methods"(9).

1. ZINC DIFFUSION

This method consists of placing a membrane between two half cells with one side having a zinc rich solution and on the other, a zinc poor solution. The concentration change is sensed by an amalgamated zinc electrode with Hg/HgO as the reference electrode. For every 10-fold change in the concentration of the zincate ion, there is a change of 0.0295 volt in the potential of the zinc-zincate ion couple. It is a potentiometric method. The calibration curve between zincate concentration and zinc potential in 45% KOH is shown in Figure 8-24. Data on zinc diffusion are illustrated in Table 8-24.

The flux value K for P-2291 separator is one order of magnitude less than the cellophane separators, making P-2291 a better retarder for zinc diffusion. The average of 13 measurements in various spots of P-2291 is 1.34 x 10^{-7} mole/in^2-min, while for Pudo 193 it is 2.77 x 10^{-6} and for sausage casing 1.65 x 10^{-6} mole/in^{2}min. The separators also vary in thickness, so that the normalized flux varies correspondingly. If it is assumed that the K values vary linearly with the concentration gardient, then the K values can be reduced to moles/in^2-min for 1 mil thickness.

Separator	Wet Thickness	Found Flux mole/in^2 min	(mole/in^2-min-mil) Reduced Flux
P-2291	1.3	1.34 x 10^{-7}	1.74 x 10^{-7}
Pudo 193	2.0	2.77 x 10^{-6}	5.54 x 10^{-6}
Sausage Casing	6.0	1.65 x 10^{-6}	9.90 x 10^{-6}

TABLE 8-24

Zinc Diffusion Properties of Separators

Membranes		Initial Voltage (volts)	Final Voltage (volts)	Initial Conc. (moles)	Final Conc. (moles)	K mole in^2-min.
First Roll						
P-2291	0 Ft.	1.450	1.439	0.0008	0.0021	1.00×10^{-7}
	50 Ft.	1.445	1.435	0.0012	0.0027	1.37×10^{-7}
	100 Ft.	1.437	1.422	0.0023	0.0077	0.97×10^{-7}
	150 Ft.	1.443	1.428	0.0014	0.0048	1.04×10^{-7}
	200 Ft.	1.438	1.426	0.0022	0.0058	0.88×10^{-7}
	250 Ft.	1.442	1.435	0.0016	0.0027	1.02×10^{-7}
	300 Ft.	1.437	1.427	0.0023	0.0052	2.18×10^{-7}
	350 Ft.	1.439	1.423	0.0020	0.0075	0.95×10^{-7}
Second Roll						
P-2291	0 Ft.	1.465	1.437	0.0003	0.0023	2.15×10^{-7}
	50 Ft.	1.437	1.429	0.0023	0.0049	1.09×10^{-7}
	100 Ft.	1.446	1.440	0.0012	0.0018	2.07×10^{-7}
	150 Ft.	1.452	1.431	0.0007	0.0037	1.29×10^{-7}
	190 Ft.	1.450	1.439	0.0008	0.0020	1.43×10^{-7}
Pudo 193		1.456	1.429	0.0005	0.0045	2.81×10^{-6}
		1.464	1.428	0.0003	0.0048	2.73×10^{-6}
Sausage Casing		1.447	1.438	0.0010	0.0021	1.20×10^{-6}
		1.447	1.430	0.0010	0.0035	2.10×10^{-6}

From Literature:	Thickness	(mole/in^2 min) Found Flux
Cellophane	4 mil	1.59×10^{-6}
Fiber-strengthened Cellulose	5.7 mil	1.02×10^{-6}
Low density PE with acrylic Graft	1.5 mil	0.93×10^{-6}

	(mole/in^2 min/mil) Reduced Flux
Cellophane	6.35×10^{-6}
Fiber-strengthened Cellulose	5.8×10^{-6}
Low density PE with acrylic graft	1.4×10^{-6}

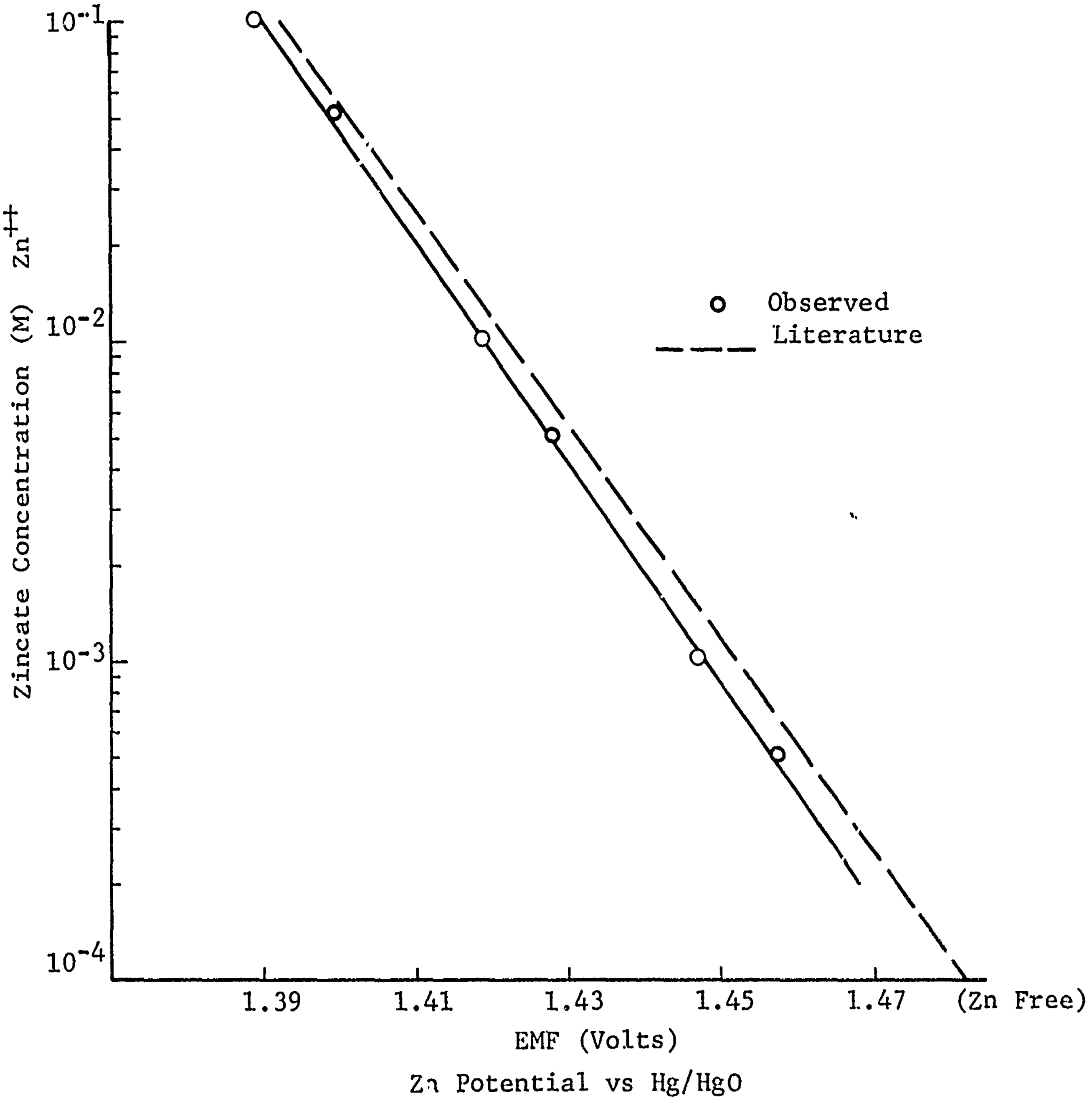


Figure 8-24. Calibration Curve for Zn Concentration and Potential in 45% KOH.

Another method of measuring the diffusion properties of membranes was also developed. Instead of two half cells, a RAI Batch Dialyzer was used, and the zincate ion concentration was determined by atomic absorption. The RAI Batch Dialyzer provides stirring immediately next to the two membrane surfaces, affording precise control over the boundary layer resistance. A unique feature of the RAI dialyzer is its carefully developed calibration which permits correction of the overall permeability for boundary layer resistance, and thus the assessment of the true membrane permeability, in addition to the flux values. The dialyzer is light tight, a condition ideal for the silver diffusion measurement. A photo of the RAI Batch Dialyzer is shown in Figure 8-25. The time-concentration curves for P 2291 and Sausage casing separators are shown in Figure 8-26.

Since the zinc rich side was more concentrated than the zinc poor side, the concentration gradient is essentially constant, and the flux or rate of mass transfer is a characteristic of the membrane. The change in concentration with time represents the slope of the curve.

$$m = \frac{\Delta c}{\Delta t}$$

If the measured volume V of the zinc rich and poor sides does not change, the rate of material transfer through the membrane is

$$\frac{\Delta c}{\Delta t} V$$

Because the area through which the mass change takes place is known, the flux K can be calculated as follows:

$$K = \frac{\Delta c}{\Delta t} \cdot \frac{V}{A}$$

The K values found using the RAI dialyzer are:

Membrane	K
WP 231-46	3.95×10^{-6} mole/in^2 min
Sausage Casing	3.60×10^{-6} mole/in^2 min

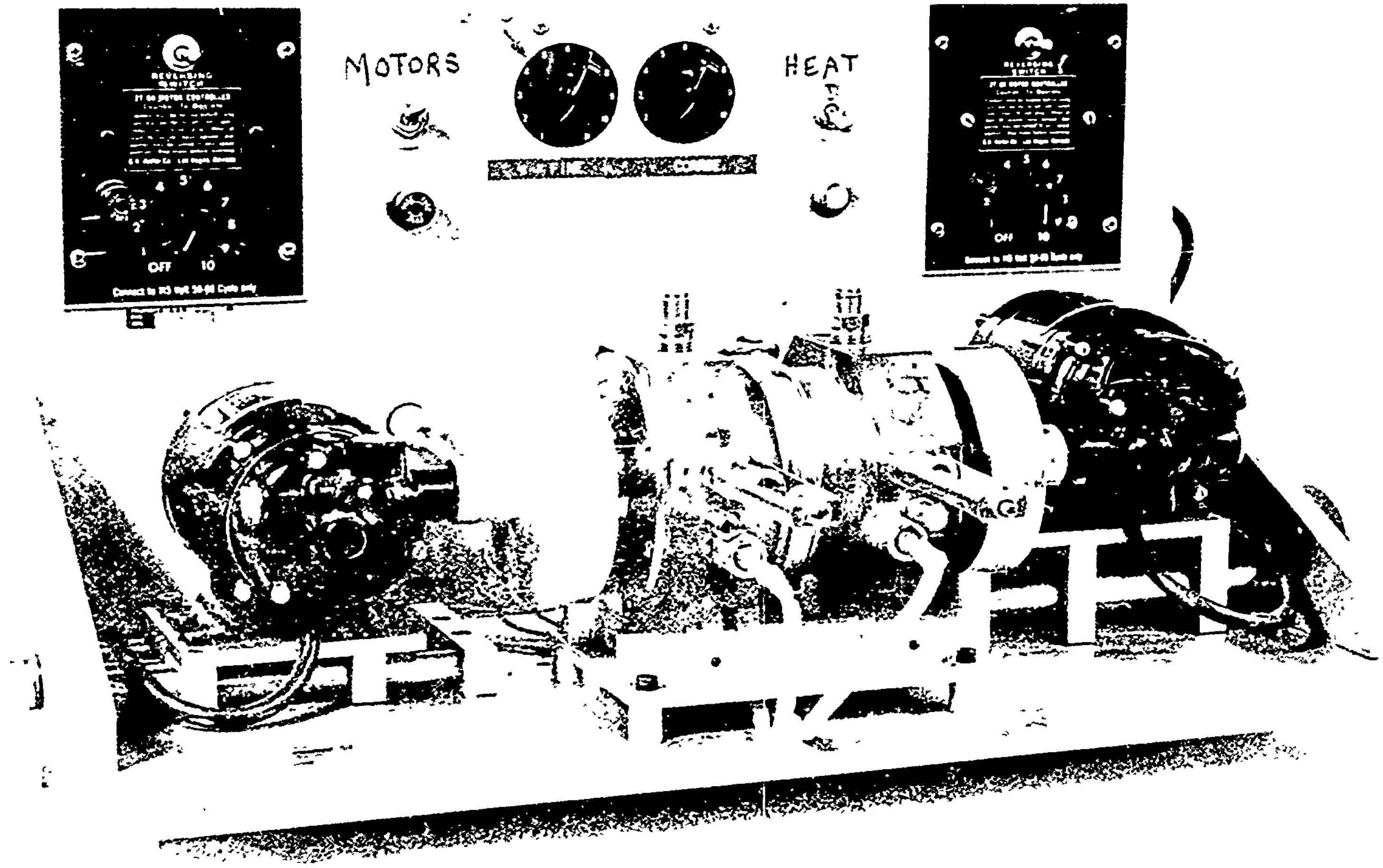


Figure 8-25. The R A I Batch Dialyzer.

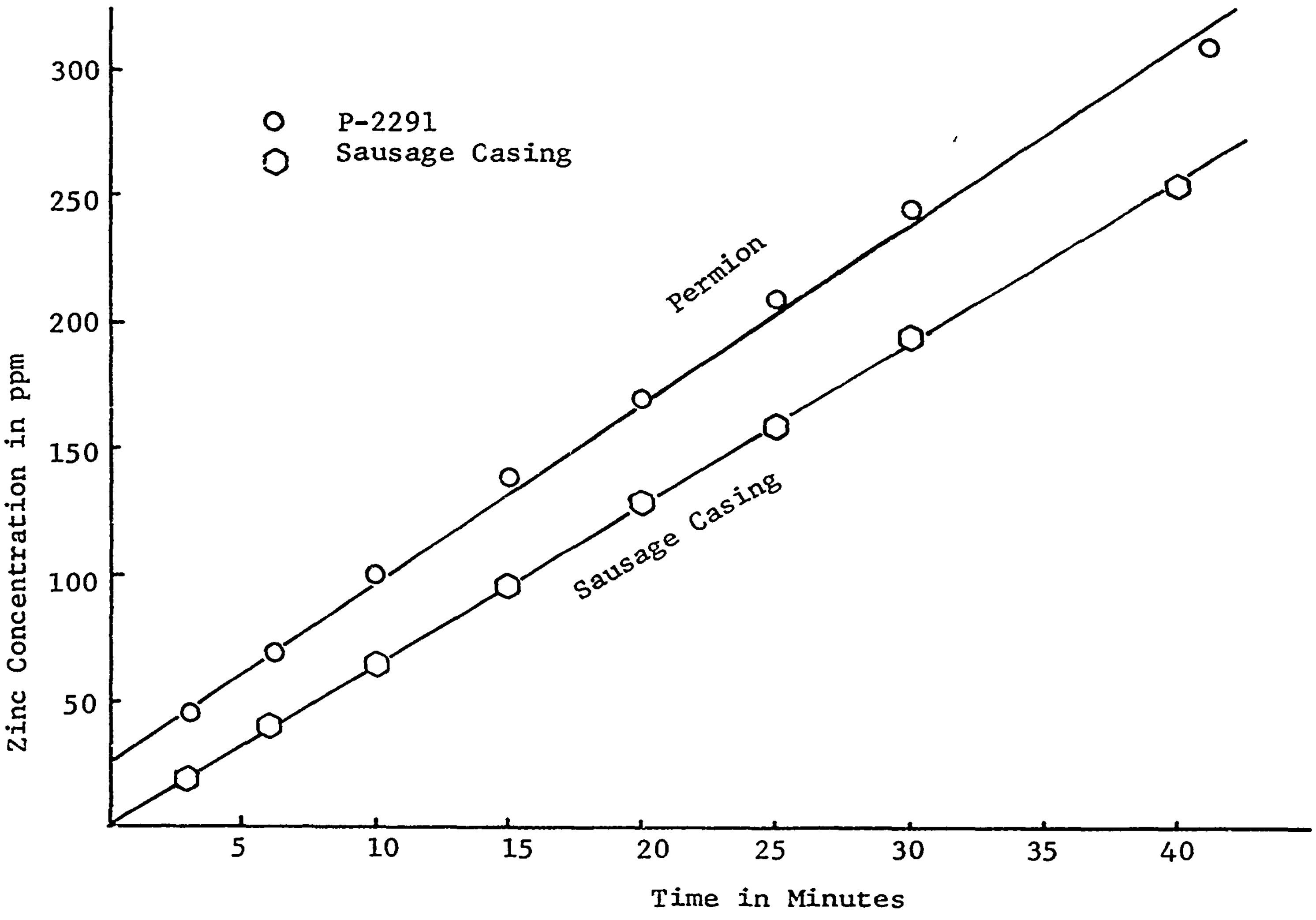


Figure 8-26 Zn Diffusion Through Separators - Zinc Poor Side

It appears that the K values found by this method are larger than those outlined in the "Screening Methods". The larger K values obtained using RAI Batch Dialyzer are probably due to a difference in experimental conditions because of stirring next to the membrane surface at constant speed. In evaluating membrane permeability, the total resistance to mass transfer, R_{OV} as measured by any time-concentration curves, is the sum of three resistances in series, namely the membrane resistance R_m and the resistance of the liquid films on each face of the membrane (R_{F1}, R_{F2}).

$$Rov = R_M + R_{F1} + R_{F2}$$

Since the permeability is related to the resistance by $R = 1/P$, the overall permeability is:

$$1/Pov = 1/P_M + 1/P_{F1} + 1/P_{F_2}$$

Because of the overall permeability 1/Pov contains a liquid film boundary layer resistances, its measured value does not truly characterize the membrane. The actual membrane permeability P_M is the true property. Fortunately, the liquid film resistances are important only for very permeable membranes. In the concentration range, 10^{-6} mole/ in^2 min, the correction is very small. However, it is interesting to calculate the liquid film resistance and the membrane resistance from the measured total resistance. The correlation between the rate of mass transfer and the liquid film mass transfer coefficient was obtained from a modified form of Chilton-Colburn (11) equation. The resistance are listed below:

Membranes	Rov (sec/cm)	$R_{F_1} = R_{F_2}$ (sec/cm)	R_M (sec/cm)	D effective * (cm^2/sec)
WP 231-46	94109	461	93187	0.26×10^{-7}
Sausage Casing	125396	461	124474	0.61×10^{-7}

* D effective is obtained from $P_m t$ where t is the thickness of the membrane.

The effective diffusion coefficient for P 2291 is still less than that of sausage casing, although the flux in this case is larger for P 2291 than the cellophane. The membrane resistance R_M is 93,187 sec/cm for P 2291 while R_M is 124,474 sec/cm for sausage casing. This is the true membrane resistance. They are quite close to the overall resistance Rov since the liquid film resistance at the two surfaces are small. The diffusion coefficient D of zincate ion in KOH has been calculated from polarographic measurements by Dirkse(12). He reported a theoretically value of 5.85×10^{-6} cm^2/sec, independent of the membranes. Our D effective may be close to the experimental reality.

2. SILVER DIFFUSION

Using the same dialyzers, the silver concentration was followed by atomic absorption spectroscopy. It was found that no silver was detected on the silver poor side, indicating that no silver species actually diffused through the membrane. There is a decrease of silver concentration on the rich side. The rate profile is shown in Figure 8 27. When the diffusion cell was opened, there was a silver coating on the membrane surface. The decrease in silver ion can only be attributed to the adsorption/absorption of silver on the membrane surface but not due to diffusion. From the initial slope of Figure 8-27, the rate of silver deposition can be calculated as:

Lander's Dialyzer

Membranes	Poor Side	Rich Side
WP 231-46	Not Detected	Over 90 minutes
Sausage Casing	Not Detected	Over 90 minutes

R A I Dialyzer

Membranes	Poor Side	Rich Side
WP 231-46	Not Detected	$0.19 \times 10^{-6} g/in^2$ hr.
Sausage Casing	Not Detected	$0.14 \times 10^{-6} g/in^2$ hr.

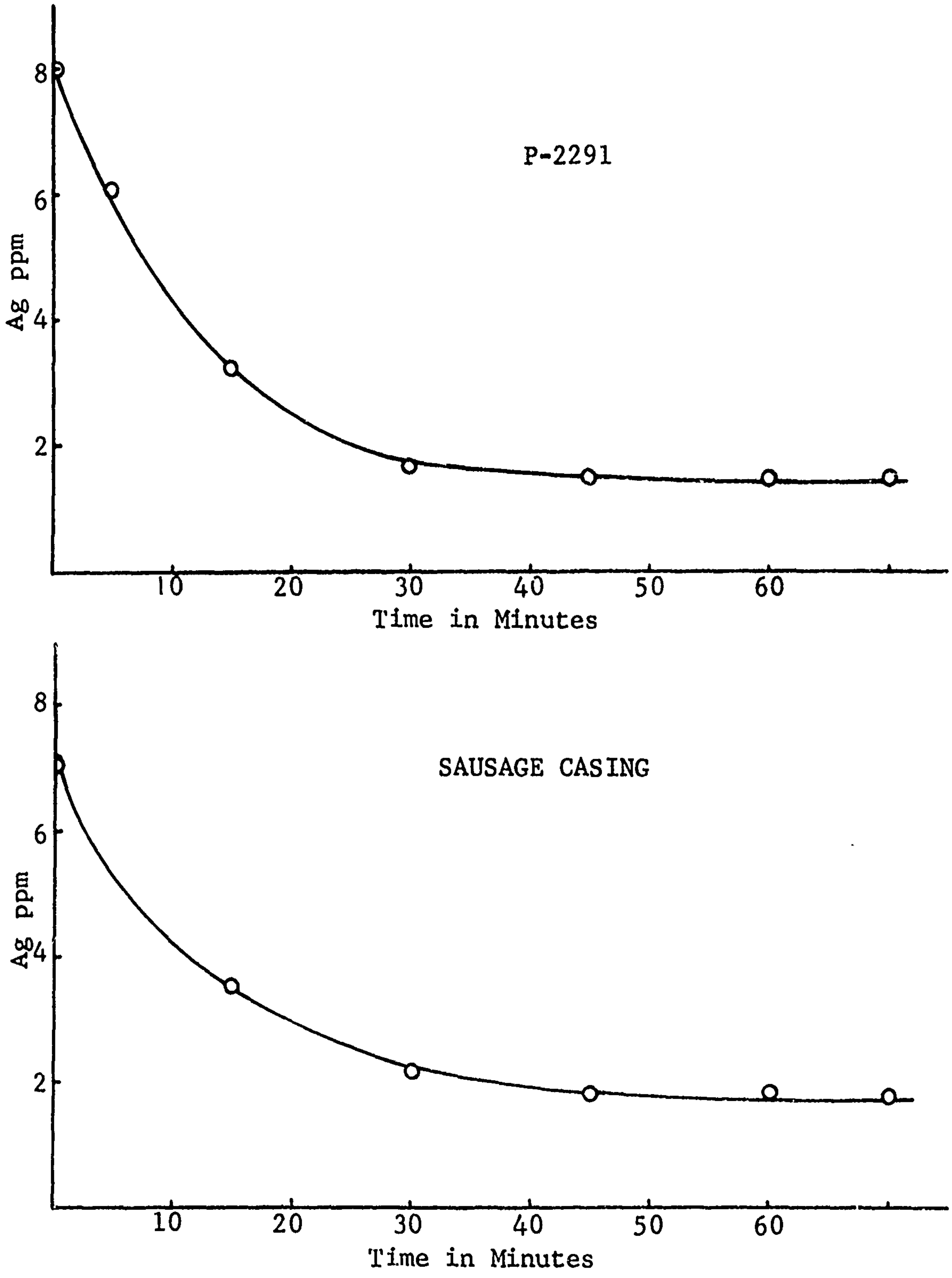


Figure 8-27. Silver Pick-up Through Membranes Silver Rich Side.

The rate of silver pick up by the membrane has also been reported by the method of radioactive tracing in the Battery Separator Screening Methods. For the grafted membrane, the rate is 2.6 x 10^{-6}g/in^2-hr and for the cellophane, it is 11 x 10^{-6}g/in^2 hr. Our results indicate that the rate of silver pick up is about ten times smaller than the value reported in the literature. No silver ion diffusion through the membrane was found. Silver was only found on the membrane surface as a coating. It is not possible to calculate flux value K as in the zinc diffusion case.

H. SWELLING CHARACTERISTIC

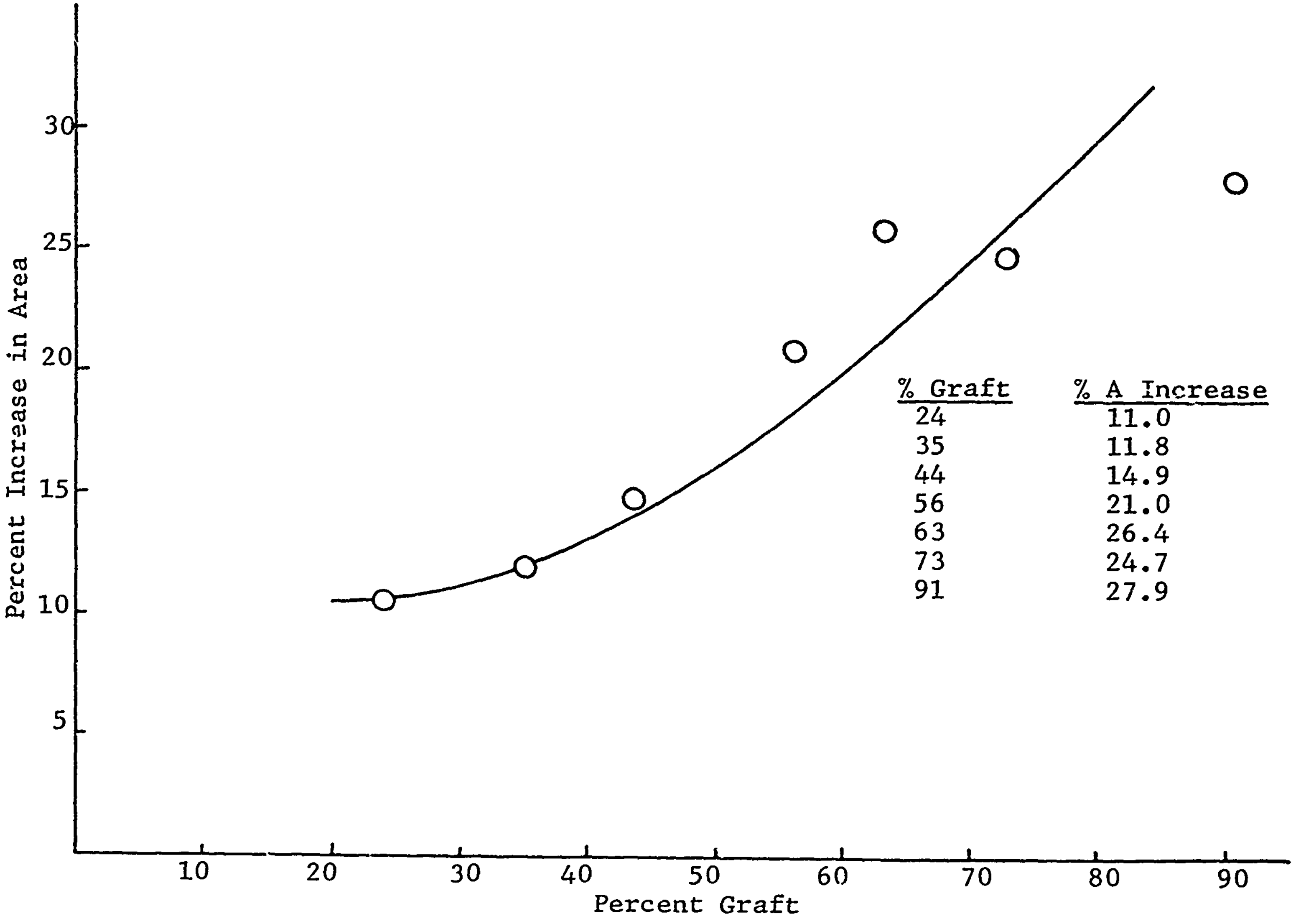
The percent swelling in 45% KOH is an important factor in battery design. In general, the grafted film will swell more (expansion) in dilute KOH than in concentrated KOH. The film was cut into 4½" x 3½" pieces, and measured on a glass plate to the nearest 1/16" with a stainless steel ruler. The film was then submerged in a 45% KOH bath kept at 23 - 24°C for one hour. The film was then measured wet on the glass plate to the nearest 1/16". Results are given in Table 8-25.

TABLE 8-25

Dimensional Changes in 45% KOH

	BEFORE SWELLING			AFTER SWELLING		
% Graft	Length	Width	Thickness	Length	Width	Thickness
24	4.50"	3.50"	1.21 mil	4.68"	3.73"	1.21 mil
35	4.56"	3.56"	1.16 mil	4.79"	3.79"	1.13 mil
44	4.56"	3.56"	1.24 mil	4.87"	3.83"	1.26 mil
56	4.56"	3.56"	1.45 mil	5.02"	3.92"	1.55 mil
63	4.54"	3.54"	1.22 mil	5.08"	4.00"	1.35 mil
73	4.56"	3.54"	1.27 mil	5.06"	3.98"	1.40 mil
91	4.52"	3.60"	1.34 mil	5.10"	4.08"	1.48 mil

The area expansion increases with an increase in percent graft. Such a relationship is shown in Figure 8-28. The increase in area by swelling is approximately linear with percent graft. Figure 8-29 and 8-30 indicate the linear expansion in length and width as a function of percent graft and resistance.



% Graft	% A Increase
24	11.0
35	11.8
44	14.9
56	21.0
63	26.4
73	24.7
91	27.9

Figure 8-28. Area Increase vs Percent Graft in 45° KOH at 24°C.

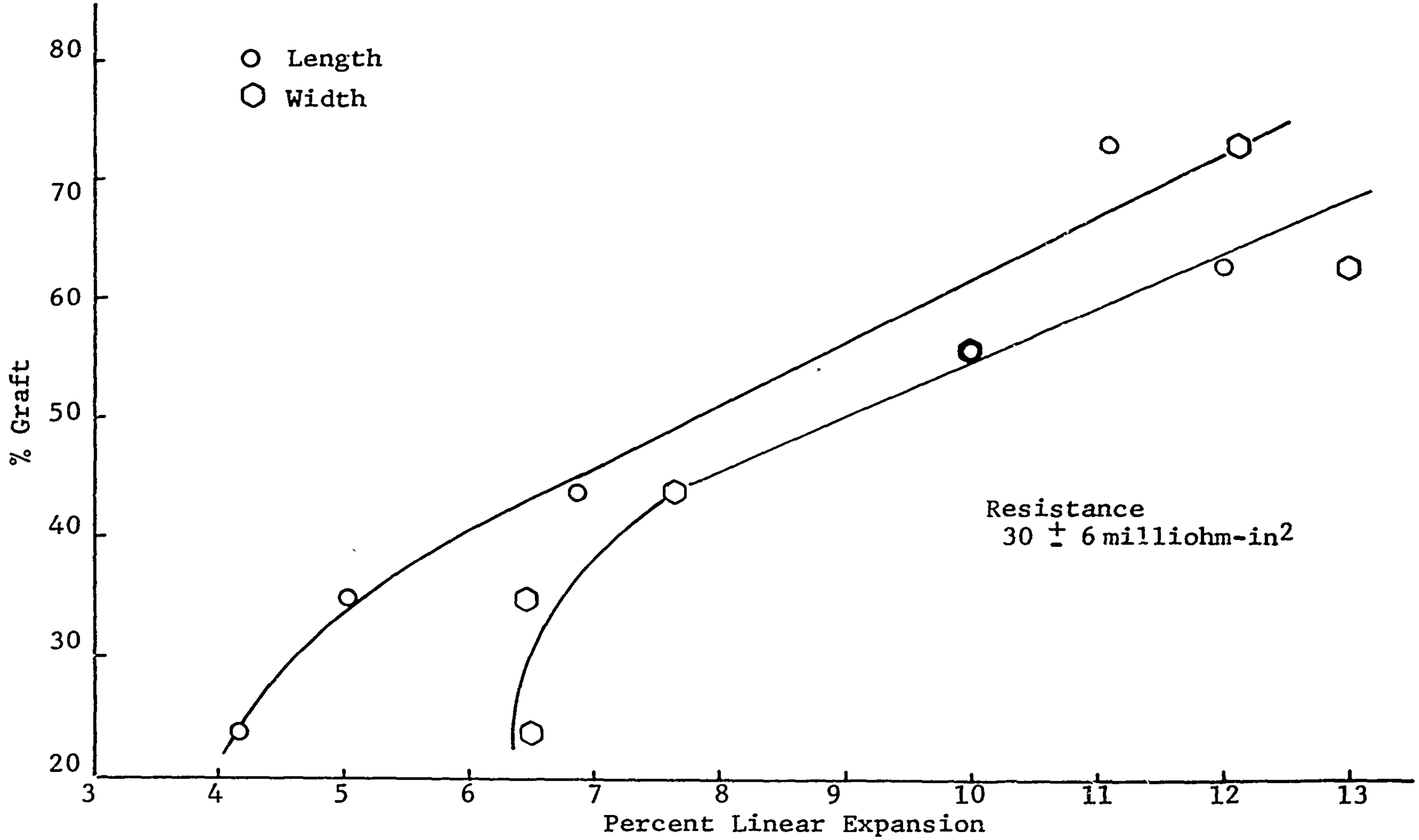


Figure 8-29. Linear Expansion vs Percent Graft

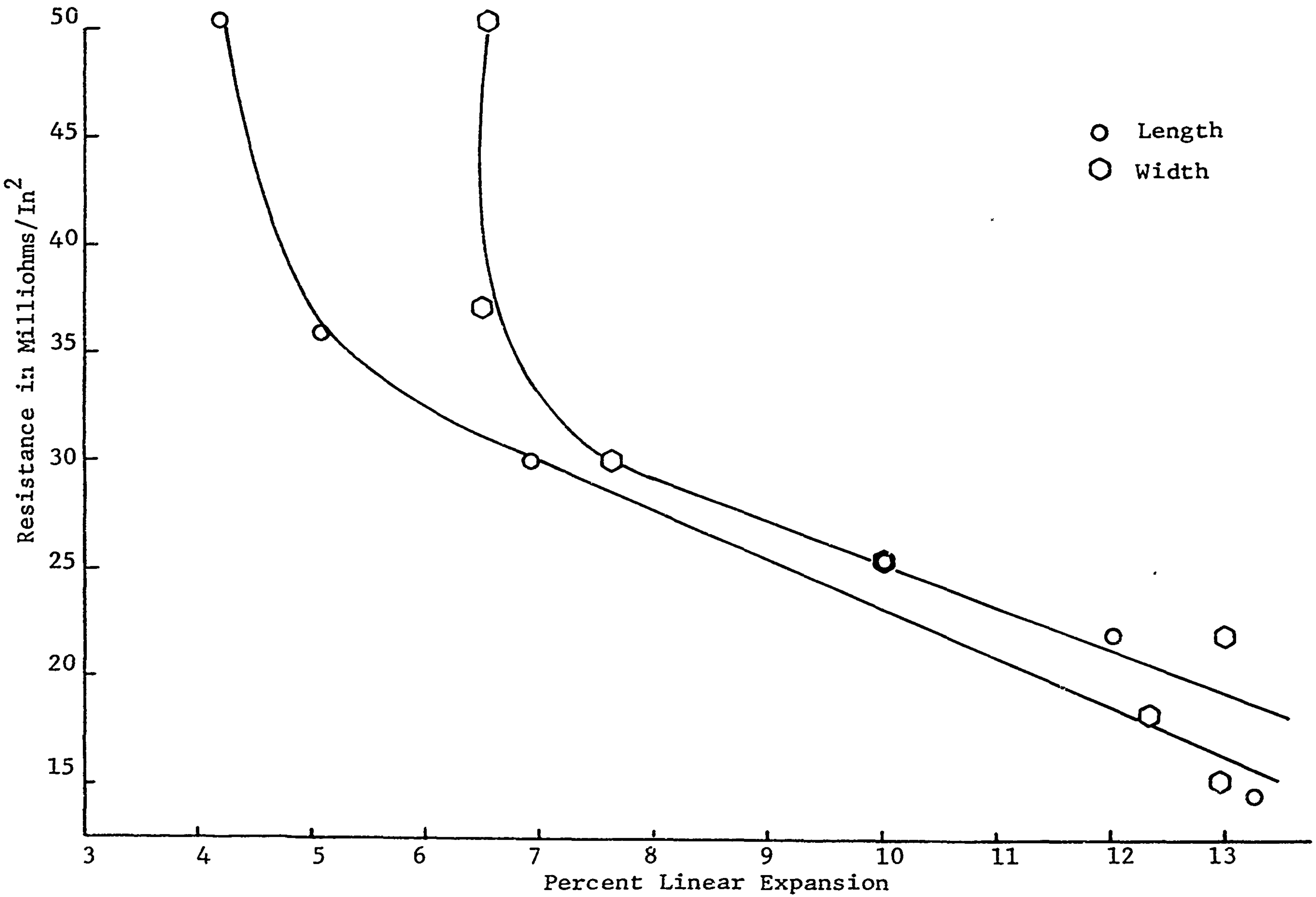


Figure 8-30. Linear Expansion vs Resistance.

I CYCLE TESTING

The ultimate test for the separator is in battery cycle life testing. If the battery separator is to be considered satisfactory, it must give a long cycle life. Cells consisting of three plates, usually two silver plates and one zinc plate (zinc limited) are wrapped with one layer of the separator. Electrolyte 45% KOH is added, and the plates are formed before undergoing discharge and charge cycle testing. The plates were supplied by the Electric Storage Battery Company. The silver plates are supplied as silver metal and zinc plates as zinc oxide. They are formed at 150 ma for about 20 hours.

$$2\,Ag + ZnO \rightleftarrows Ag_2O + Zn$$

The capacities of the cells were determined by discharging across a fixed 2 ohm resistor. Typical data are in Table 8-26. The discharge curves for the cells prepared with P 2291 and Sausage Casing are represented in Figure 8-31 and 8-32 from which the capacities of the cells were calculated to be 1.41 amp-hour and 1.32 amp-hour at a 1.32 volt cut-off. Since the ZnO plate weighs 3.82 grams, or 0.094 gm-equivalent weight, the theoretical capacity is 2.91 amp-hour, based on 1 gm-equivalent weight = 26.8 amp-hour. The efficiency is from 46-50%. This is within the general efficiency range. The cycle consists of 35 minutes of discharge at 1 ampere and 85 minutes charge at 450 ma, corresponding to about 41% depth of discharge and 9% overcharge. In practice, the discharge current falls below 1 ampere near the end of discharge, while the charge current falls below 450 ma near the end of charge. This will be seen in the later section.

A picture of the cycle life tester is shown in Figure 8-33 and a block diagram of the circuits in Figure 8-34. The voltage under load was recorded and a failure was established if the voltage under load is less than a set value. Shorting failure occurs when the open circuit voltage of the cells is zero after it is fully charged. If the open circuit voltage does not change after fully charged, or sometimes it decreases very slowly after a few days, it is regarded as a capacity loss failure. Results of cycle life testing are summarized in Table 8-27.

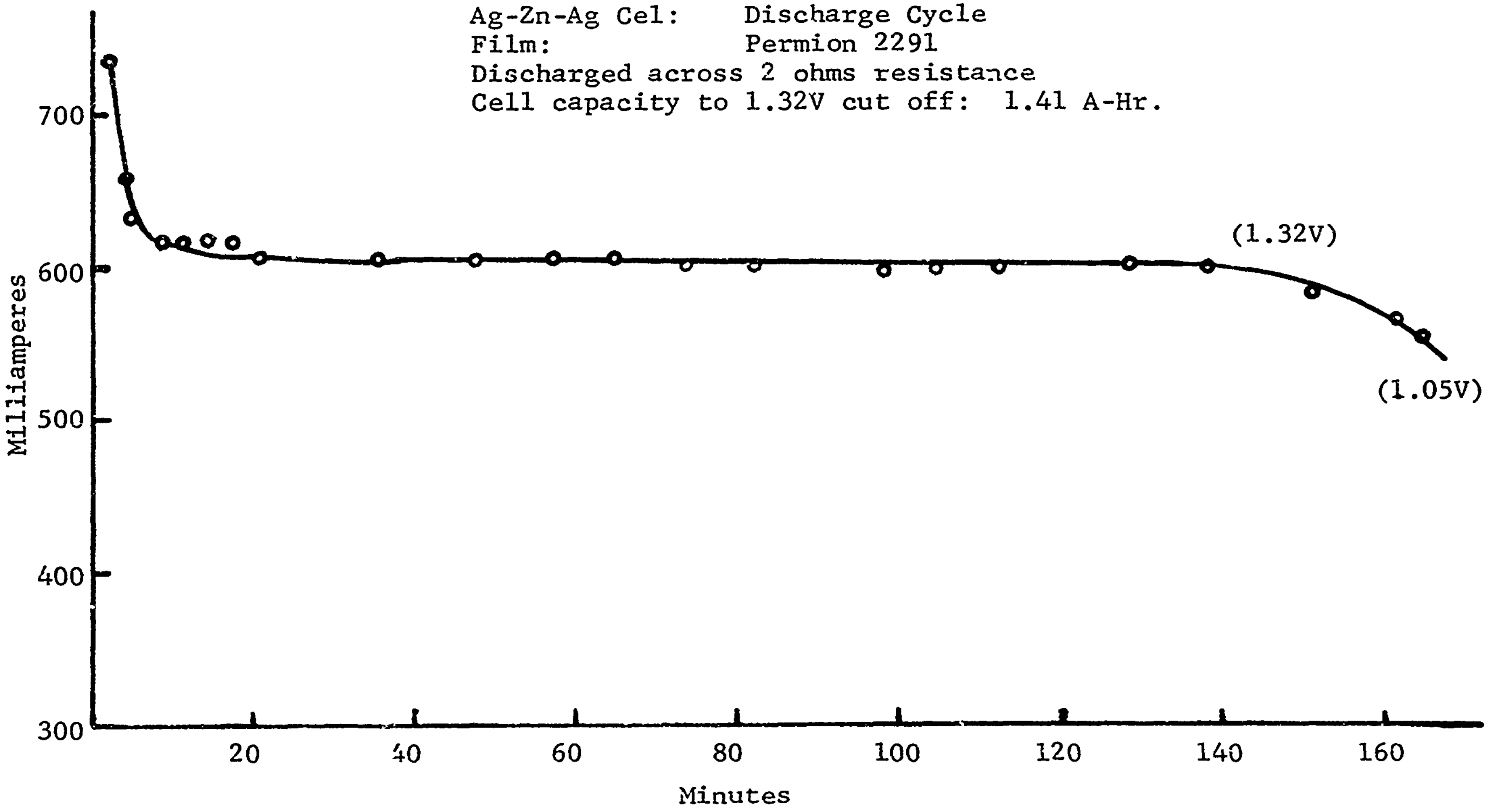


Figure 8-31. Discharge Curve of Three Plate Cell
- Permion 2291.

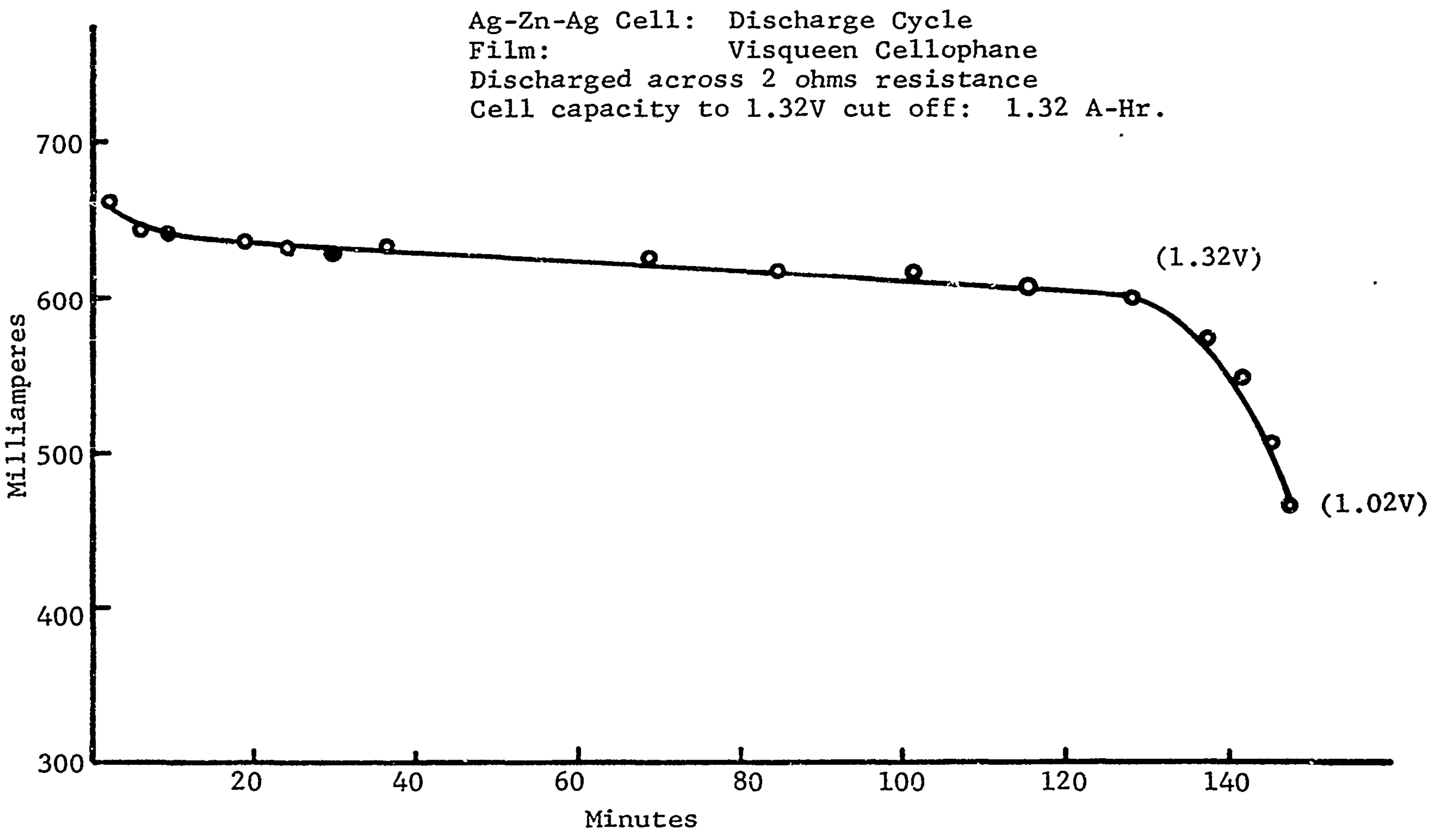


Figure 8-32. Discharge Curve of Three Plate Cell
- Visqueen.

TABLE 8-26

Capacities Measurement of the Three Plate Cells

Time of Discharge	Voltage Under Load Volts	Discharge Current ma	Open Circuit Voltage Volts	Film
8.46	1.40	650	1.86	Permion 2291
8.55	1.40	650		
9.03	1.38	625		
9.08	1.38	625	1.58	
9.17	1.37	625		
9.20	1.36	620	1.58	
9.27	1.36	610		
9.38	1.35	610		
9.45	1.35	610		
10.02	1.34	610	1.57	
10.10	1.33	605		
10.21	1.28	600	1.56	
10.25	1.25	590		
10.29	1.10	540		
10.31	1.00	480		
10.32	0.87	440		
10.34	0.65	330		
1.46	1.65	750	1.90	Visqueen
1.50	1.45	660		
1.54	1.35	620		
1.59	1.35	620		
2.04	1.35	620		
2.11	1.33	610		
2.21	1.33	610	1.59	
2.24	1.33	610		
2.37	1.33	610		
2.43	1.33	610		
2.50	1.33	610		
2.59	1.32	605		
3.08	1.32	605		
3.24	1.31	600		
3.38	1.32	605		
3.53	1.32	605		
4.04	1.32	605		
4.15	1.27	590		
4.27	1.25	570		
4.30	1.23	560		
4.40	1.05	480	1.57	

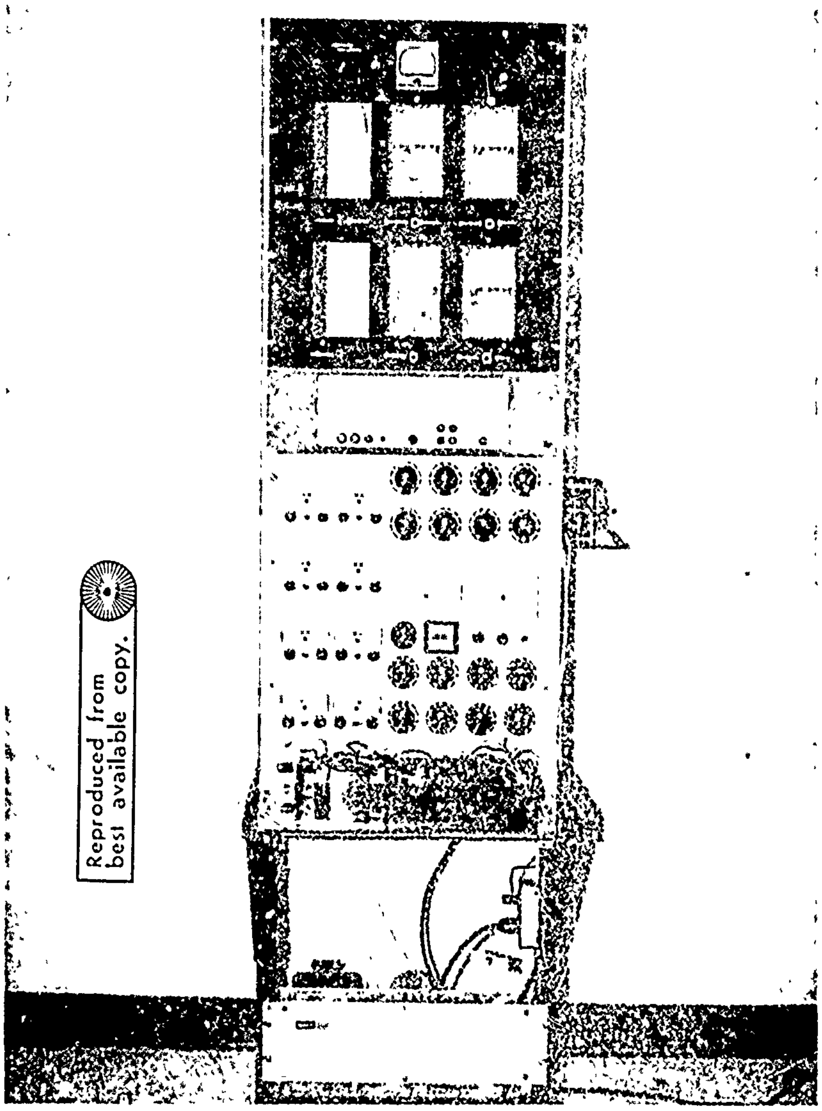


Figure 8-33 Photo of the Cycle Life Tester

The relationship between percent graft and cycle life is dpecited in Figure 8-35. An optimum graft range was found which gave a maximum number of cycles. This range occurs from 38 to 67% and is the initial accepted range of graft for production. Below and above this range, the cycle life of the battery decreases. If the main concern is zinc dendrite penetration resistance in the Hull Test, one should go below this graft range. The present production range represents a compromise between these two extremes as evidenced by the cycle life test. For other applications, low temperature batteries, a low resistance separator is preferable, and a higher graft range may be dictated. On the other hand, a very low drain battery with long shelf life may find a lower graft range preferable. For a high temperature heat-sterilizable battery, a maximum graft range must be set. Too high a graft level would adversely affect a high drain sterilizable battery. The optimum separator for a particular battery varies with the preset battery requirements.

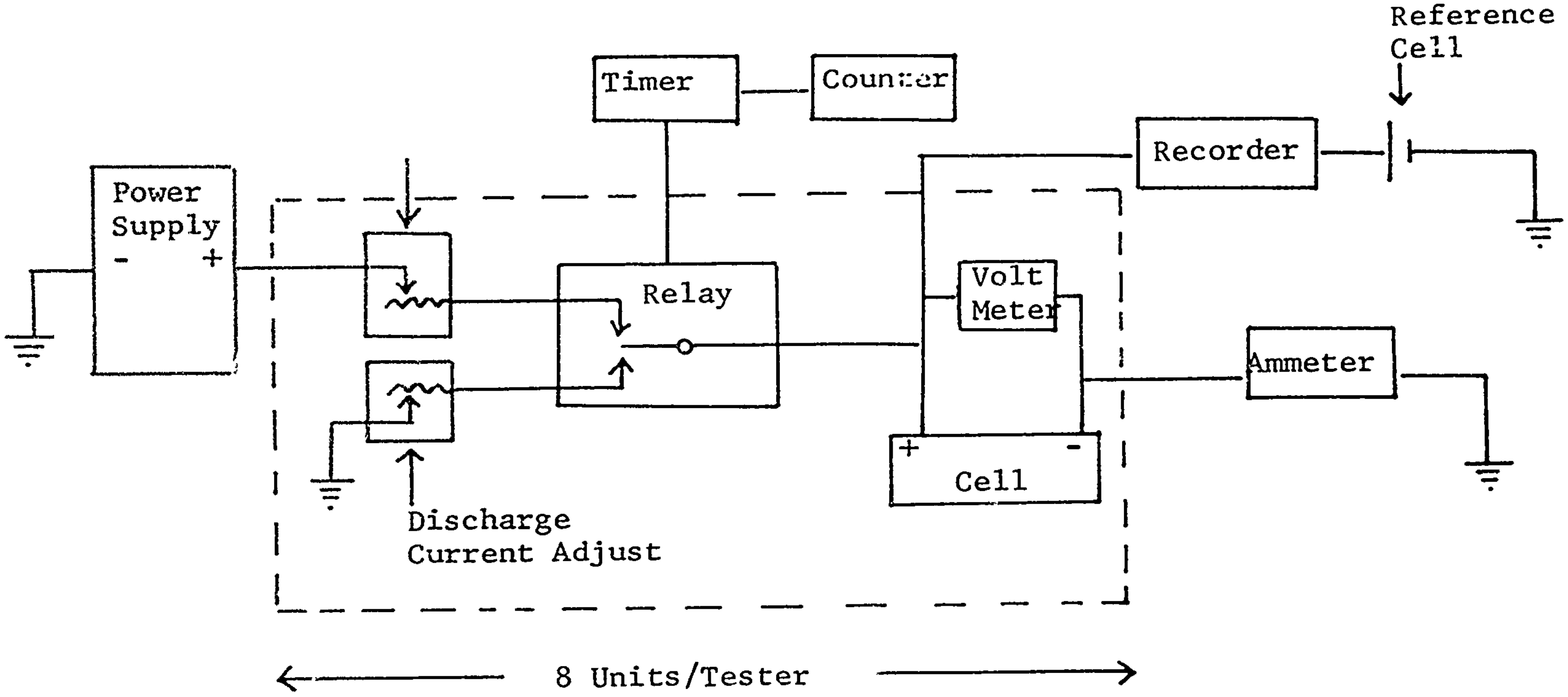


Figure 8-34. Schematic of Cycle Life Tester

TABLE 8-27

Cycle Life Testing in 3-Plate Cells at Room Temperature

Separator	% Graft	Number of Cycles	Average	Failure
P-2291	24	26	42	Capacity Loss (C.L.)
		34		Short (S.)
		65		C.L.
	35	45	45	S.
	38	45	72	C.L.
		59		C.L.
		63		S.
		76		C.L.
		77		C.L.
		90		C.L.
	44	45	61	C.L.
		59		S
		78		C.L.
	55	44	62	C.L.
		58		C.L.
		63		S.
		83		S.
	66	59	69	S.
		78		C.L.
	80	42	43	C.L.
		42		S.
		44		C.L.
	83	24	26	S.
		24		C.L.
		29		C.L.
	117	19	19	S.
		19		S.
Delco Remy P 2291		36	73	S.
		40		C.L.
		54		C.L.
		72		C.L.
		85		C.L.
		100		C.L.
		120		C.L.
		55		C.L.
		61		C.L.
		68		C.L.
		76		C.L.
		111		C.L.

TABLE 8-27 (continued)

Cycle Life Testing in 3-Plate Cells at Room Temperature

Separator	% Graft	Number of Cycles	Average	Failure
Sausage Casing		35	82	S.
		77		C.L.
		80		C.L.
		135		S.
Pudo 193		21	34	S.
		46		C.L.

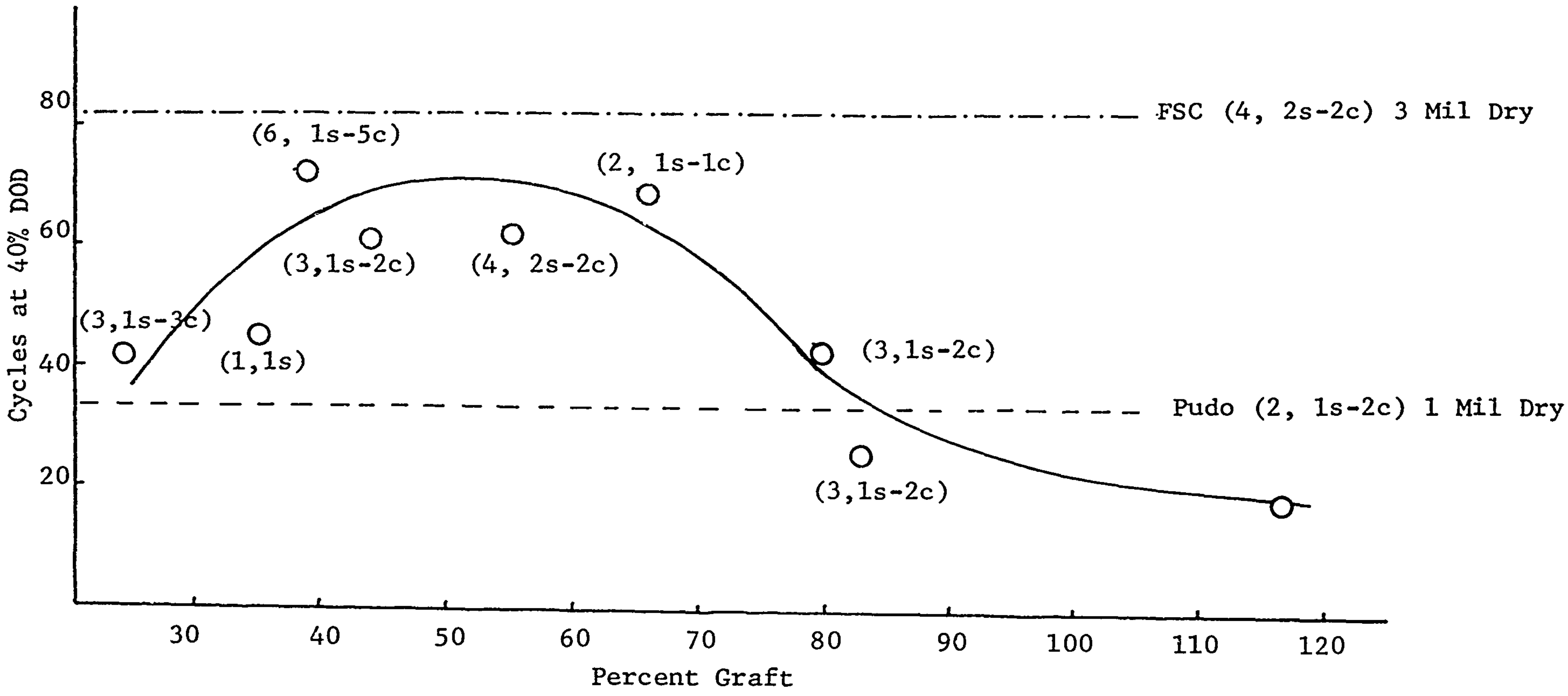


Figure 8-35. Percent Graft vs Cycle Life of 3 Plate Cells.

3.0 FINAL PRODUCT SPECIFICATIONS

Data obtained from the preceding tasks were used to establish the final specifications for incoming material, process control, and final product acceptance. Preliminary specifications have been changed recently to narrow the acceptable resistance and percent graft range. While numerous tests were evaluated, only those of significant importance which are pertinent to quality assurance are incorporated in these final specifications.

3.1 INCOMING RAW MATERIALS

A. Film Resin:

A minimum of three tests is required. These are the molecular weight distribution, the infrared spectrum and density.

$$\frac{\overline{M}w}{\overline{M}n} = 2.7 \pm 0.5$$

I.R. No absorption at 3050 - 3300 CM^{-1}
1650 - 1750 CM^{-1}
800 - 1000 CM^{-1}

Density = 0.922 ± 0.009 g/cc at 23°C

B. Extruded Film:

To insure the absence of foreign material during extrusion four tests are required:

Thickness = 1.0 ± 0.1 mil

I.R. No absorptions at 3050 - 3300 CM^{-1}
1650 - 1750 CM^{-1}
800 - 1000 CM^{-1}

Atomic Absorption: Ash = 0.12 ± 0.03%
Iron $\leq$ 0.012%

Tensile Strength = 3200 ± 500 psi

C. Paper Mesh Interlayer:

Two tests are used one of them is the manufacturer's specifications.

Grade: 28" wide weave, natural Leonet, plain with no drawtapes.

Thickness: Single thread side 53 ± 4 mil
Double thread side 47 ± 6 mil

D. Solvents:

The refractive index and infrared spectrum will be used for all incoming solvents.

Benzene

$N_D^{20} = 1.5005 \pm 0.0007$

I.R. No absorptions at $2800 - 2950\ CM^{-1}$
$1750 - 1650\ CM^{-1}$

Carbon Tetrachloride

$N_D^{20} = 1.4608 \pm 0.0006$

I.R. No absorptions at $4000 - 1600\ CM^{-1}$

E. Monomer:

Three tests are included of which one is a manufacturer's specification.

Methacrylic acid

Grade: Glacial, MEHQ 250 ppm

$N_D^{20} = 1.4311 \pm 0.0006$

Viscosity (Kinematic) = 1.38 ± 0.09 centistokes

3.2 IN-PROCESS TESTING

A. Crosslinking:

The crosslinked film were tested by gel content, its Mc value and infrared Spectrum. In addition, the machine settings must be standardized based on actual dosimetry.

Machine Settings: Voltage = 1 MeV
Current = 9.3 ma
Film Speed = 7.75 ft/minute

Gel Content $\geqq$ 70%

Mc value $\leqq$ 5,000
I.R. no absorption at 1700-1650 cm^{-1}

B. Dosimetry:

The dose rate on a four foot line when the center of the source is 27 inches above the floor is 10,100 r/hr on February 18, 1971. This will decrease with time subject to its half-life of 5.3 years.

Dose rate = 10,100 rads/hr

C. Monomer Solution:

The monomer solution will be tested by refractive index and alkali titration.

Methacrylic acid = 17.5 ± 0.3% by weight
Benzene = 80.2 ± 0.3%
Carbon tetrachloride = 2.3 ± 0.3%

$N_D^{20} = 1.4850 \pm 0.0008$

Titration of M.A. = 17.5 ± 0.3%

D. Equilibrium Swelling Time:

The film is swelled in the grafting solution for at least 24 hours before irradiation.

Swelling Time $\geq$ 24 hours

E. Washing Temperature, Concentration and pH

The grafted film is washed on a line with five tanks. The first two tanks are hot water to wash out homopolymer. The third tank is KOH where the film is converted to the salt form. The fourth and fifth tanks are water to wash out the base.

1st Tank Washing Temperature $\geq$ 90°C
2nd " " " $\geq$ 90°C
3rd " " " $\geq$ 90°C
KOH Concentration = $4.5 \pm 0.5\%$
4th Tank Washing Temperature $\geq$ 90°C
5th " " " $\approx$ 60°C
pH 6.5 $\leq$ 8

3.3 FINAL PRODUCT

The finished grafted membrane is qualified by a minimum of three test, namely: grafted uniformity, electrical resistance and cycle lift. Specification D-H will conform if test A-C meet the specifications indicated. These parameters are dependent on the percent graft, graft uniformity and resistance.

A. Graft Uniformity

The percent graft in the membrane throughout the roll will be from 36.5 to 53.5% by weight.

Percent graft = 44.5 ± 8.5

B. Resistance

The electrical resistance is tested with an A.C. bridge as discussed in Section 2.8 at 40% KOH and room temperature.

Resistance = (30 ± 6 milliohms) in 40% KOH at 25°C

C. Cycle life:

The cycle life is tested in a 3-plate cell (2 silver + 1 zinc plate) at 40% depth of discharge under a two hour regime as described in Section 2.8.

Cycle life $\geqq$ 50 cycles

Other tests are outlined below:

D. Thickness:

The thickness of the grafted membrane conforms to the following:

Thickness = 1.2 ± 0.15 mil

E. Exchange Capacity:

The exchange capacity of the film as tested by equilibrating the acid form in KOH and back titration with HCl is over 3.5 milliequivalent/gram.

Exchange Capacity 2.7 - 3.7 milliequivalent/gram of dry separator

F. Mositure Content:

The mositure content as tested by the Karl Fisher Method when the grafted film is stored in a dessicator is 5%. (Storing under atmospheric conditions gives a changing content,depending on humidity, up to 25%.)

Mositure = 5 ± 2%

G. Hull Test:

The zinc penetration time as described in Section 2.8.

Hull Test 2.5 to 3.7 hours

H. Diffusion Test:

The zinc diffusion is characterized by its flux value (K), but no silver diffusion through the grafted membrane is found as described in Section 2.8. Only deposition on the silver rich surface is detected.

K (for zinc) = $1 \sim 2 \times 10^{-7}$ mole/in^{-2} min.

This is tentative: a new specification must include Diffusion vs % Graft in the graft range 36.5 to 53.5%.

I Swelling Characteristics:

The expansion due to linear swelling in 45% KOH at room temperature will conform to the value obtained from Figure 8-29 and 8-30. Expansion is a function of % graft and resistance. For a membrane with a graft range of 44 ± 8.5% (i.e. 36.5 - 53.5% graft) the swelling is:

Length	5-9%
Width	6-10%

4.0 TEST PROCEDURES

The following test procedures were developed in order to establish specifications throughout the manufacturing process for grafting membranes.

4.1 MOLECULAR WEIGHT DISTRIBUTION

The molecular weight distribution is determined using gel permeation chromatography. Since this equipment is not in house, samples, about five gram in weight, were sent to Waters Associates, Inc., Massachusetts, for analysis. The following conditions were specified and constitute part of the test procedure.

Solvent: 1,2,4 trichlorobenzene
Columns Styragel with contour chain length exclusion value of 10^6, 10^5, 10^4 and 10^3 Å in series
Temperature: 138°C
Flow Rate: 1 cc/minute
Concentration: 0.25% polymer solution

The chromatogram derived could be interpreted by Water Associates, however, we interpreted the curves ourselves. A sample calculation was given in Table 8-1.

4.2 INFRARED SPECTRUM

The infrared spectra have been most useful in detecting contaminants, certain functional groups and structures. The spectrophotometer used here is a Perkin-Elmer I.R. Model 21. Spectra have been obtained under the following conditions:

Gain Setting: 2
Response: 1
Speed: 8
Resolution: 927 Slit Program
Suppression: zero
Scan: 4000 cm^{-1} to 675 cm^{-1}

When the sample is a resin, it is made into a KBr pellet. When the sample is in a thin sheet form, it is taken as is. If the sample is a liquid, the spectrum is taken using an I.R. cell. The procedure for operation is given in the manufacturer's instruction manual. The spectra obtained is compared to a standard known control of Bakelite DFD-0602 resin or film, or to the liquid sample under test. Major peaks are confirmed and deviation from the standard are looked for. In particular, with the film as received or crosslinked, the existence of carbonyl would indicate contamination due to oxidation.

4.3 DENSITY MEASUREMENT

The density of the resin and the extruded film are tested according to ASTM D 1505-60-T. The density gradient column used was equilibrated at 23 ± 0.5°C and then filled with the following liquids, the heaviest first. Care must be taken not to disturb each layer.

Density of Liquid g/cc	Amount cc	Location
0.965	210	Bottom of Column
0.955	10	
0.945	10	
0.935	10	
0.925	10	
0.905	10	
0.895	10	
0.885	120	Top of Column

By means of a small wire screen, the solution in the column was gently stirred using an upward and downward motion only. Calibrated density floats were dropped into the solution. After standing overnight, the floats were read with a cathometer. A linear gradient should result. This is shown in Figure 8-6 which is the calibration curve. Small pieces or resin or film are then cut, and dropped into the column. When the film speciment reaches an equilibrium position, its position is read with the cathometer and its density read from the standard curve.

4.4 THICKNESS

The membrane thickness was measured using a constant weight head gauge, made by the Federal Products Corporation, Rhode Island. The gauge is graduated in 0.0001" and at least 25 readings were taken over a 10 foot section. Data are treated statistically, as shown in Table 8-16. They are expressed as the average error, the standard deviation and the probable error.

4.5 TRACE METAL ANALYSIS

The trace metals present in the resin or film were tested by semi-quantitative emission spectrum by the Schwarzkopf Microanalytical Laboratory, New York. About five grams of the sample were sent. A typical report is given in Table 8-2.

4.6 TENSILE STRENGTH

Tensile strength of the extruded film was tested by ASTM procedure D 638-60T. A table Instron Tensile Tester was employed under the following conditions:

Sample Size: 0.875" x 0.188" x Thickness (t)
Grip Separation: 0.875"
Strain Rate: 0.2"/min.
Chart Speed: 20" min.
Room Temperature: 25°C

The tensile strength at break and the modulus of Elasticity are calculated as:

$$\text{Tensile at Break} = \frac{\text{Break Point Load (lbs.)}}{\text{Nominal Cross Section}(\text{in}^2)} = \frac{F}{A}$$

$$\text{Modulus of Elasticity} = \frac{\text{Nominal Stress}}{\text{Strain}} = \frac{\sigma}{E} = \frac{\sigma}{\Delta l/l_o}$$

Where F is the actual load recorded in the Instron at the breaking point of the sample, A is 0.188 x thickness x 10^3 in^2 and the modulus is the initial slope of the stress-strain curve recorded in the chart paper. l_0 is 0.875" and Δl is the elongation, which is 0.2/20 x L = L/100 where L is distance taken from the chart paper in inches at the point the slope is taken. In taking the initial slope, it is important that the chart speed is a maximum while the strain rate is a minimum so that the elongation can be measured very accurately. The thickness measurement must be accurate since this goes into the nominal cross section area.

4.7 REFRACTIVE INDEX

The refractive index is a valuable physical constant used to characterize organic compounds. The purity of solvents is checked with an Abbe refractometer against a known literature value. It is important that the temperature be constant. The index can be read to 0.0005 division. The temperature coefficient is about 0.0004 per degree depending on the compounds. After putting a drop of solvent on the refracting prism, set the scale at the approximate value expected. Bring the borderline, strongly colored, to the crosshair mark, and compensate the color by adjusting the position of the compensating scale dial. The borderline should be faintly blue on one side and faintly red on the other. Observe the crosshair by focussing the eyepiece to a sharp line and bring it to the intersection by means of the coarse and fine hand controls. Depress the contact switch momentarily and read the index to the fourth place.

4.8 VISCOSITY

The viscosity of a solution is measured with a calibrated Ubbelohde viscometer at 25°C. In the case of a resin, a dilute solution is made with the solvent. The time of flow for each is measured with a stop-watch to the nearest tenth of a second. For large flow time, the specific viscosity η_{sp} of the solution is related by:

$$\eta_{sp} \approx \frac{(t - t_0)}{t_0}$$

Where t is the flow time of the solution and t_o is the flow time of the solvent, the specific viscosity is related to the molecular weight of the polymeric resin through the intrinsic viscosity $[\eta]$ by:

$$\eta_{sp} = [\eta] C + K' [\eta]^2 C^2$$

where C is the resin concentration in grams per 100 ml and K' is a constant.

In the case of a pure liquid like methacrylic acid, it is used as such. After equilibrating at 25°C for 15 minutes, the flow time is measured. The flow time is related to the kinematic viscosity of the liquid by the viscometer constant.

$$\underset{\text{(in centistokes)}}{\text{Kinematic Viscosity}} = \text{Viscometer Constant} \times \underset{\text{(seconds)}}{\text{Flow Time}}$$

4.9 GEL CONTENT

The percent gel after an exhaustive extraction is indicative of the extent of network formation as a result of crosslinking. The crosslinked film was weighed and put into a weighed stainless steel cage. The cage was placed into a 4-oz. jar filled with xylene. The xylene is the extracting solvent and contains 0.1% of phenyl-β-naphthylamine to prevent oxidative degradation of the gel during extraction. The jar was then placed in an oil bath and held at 115-120°C. The solvent was changed daily for two days. The cage was let stand and vacuum dried at 90°C for 24 hours. The cage with the gel was then weighed and the gel content calculated as:

$$\% \text{ gel} = \frac{W_G}{W_o} \times 100$$

where W_G and W_o are the dry weights of the gel and the original film. Typical data are shown in Table 8-7.

4.10 Mc VALUE

The molecular weight between crosslinks can be determined by extraction with a solvent or by hot modulus measurement. In the former methods, Mc is related to q_0 which can be obtained from a sol-dose plot.

$$Mc = \frac{w}{q} \approx \frac{w}{q_0 r}$$

where q_0 is the crosslink density per unit dose, r the dose in megarads and w is the molecular weight of the repeating unit in the polymer. In the latter method, Mc is related to the modulus E of the polymer above its crystalline melting point.

$$E = 3\rho RT/Mc$$

where ρ is the density of the polymer at temperature T, and R is the gas constant. The sol extraction method had been adopted in the subcontract with the Delco-Remy Division of General Motors Corporation. The hot modulus method was used in this program, and the two methods give a fair agreement with each other and provide a valid insight into the crosslinking of the base film.

The hot modulus was measured with a table Instron, equipped with a constant temperature cabinet which was maintained at $140^\circ \pm 2^\circ C$. This is above the melting temperature of low density polyethylene. Samples were cut into 1" x 1" x thickness. The following conditions were used:

Strain Rate	=	0.2 inches/min.
Grip Separation	=	1 inch
Chart Speed	=	12"/min.
Temperature	=	140°C

The modulus E is calculated from the stress-stress curve recorded on the chart paper in psi:

$$E = 132.15 \times \frac{F}{L} \times \frac{1}{t}$$

Where F is the load in grams, L is the distance in inches when the initial slope is drawn and t is the thickness of the film in mils. Mc is calculated from:

$$M_c = \frac{1.38 \times 10^6}{E}$$

Typical data are given in Table 8-8.

4.11 FRICKE DOSIMETERS (RADIATION DOSE MEASUREMENT)

This method measures the absorbed gamma radiation dose by the oxidation of ferrous ion to the ferric ion, and is applicable from 0.2×10^4 to 4×10^4 rads range. No dose rate effect up to 10^7 rads/hr and no energy dependence from 0.1 to 2 MeV range are recorded in the literature. It consists of setting up a calibration curve using known ferric ion solution and reading it from a U.V. Spectrophotometer. The ferric ion is related to the absorbed dose by:

$$\text{Rads} = \text{micromoles of } Fe^{+++} \text{ per liter} \times 60.9$$

Next, a dosimetric solution of ferrous ion is prepared, and is exposed to the gamma radiation. The ferric ion concentration after exposure is read by the spectrophotometer, and the dose read off from the calibration curve.

Standard Ferric Soltuion: A weighed quantity of ferric sulfate was added to 0.4M H_2SO_4 solution to make a concentration of about 0.1M. The mixutre was put in an oven at 90-95°C overnight. After cooling, the exact amount of Fe^{+++} ion was determined by titrating against EDTA with ammonium thiocyanate as the indicator. The end point is from dark red to yellow and pH should be slightly acidic. The stock solution was then diluted to cover a range of 10^{-6} to 10^{-3}M. The optical density of these diluted solutions were read with a Beckman U.V. Spectrophotometer, Model DBG. The slit width was fixed at 0.5mm, the wave length set at 305 mu and 0.4M H_2SO_4 was used as the blank. Temperature should be constant because the extinction coefficient changes about 0.7% per °C. The calibration curve is shown in Figure 8-10.

Dosimetric Solution: A solution of 0.001M in ferrous ammonium sulfate and 0.001M in sodium chloride was prepared with 0.4M sulfuric acid in distilled water. The solution was saturated with oxygen by bubbling oxygen through for 15 minutes. The dosimetric solution should be made fresh each day. If the optical density as read at 305 mu with distilled water as blank was larger than 0.4, the dosimetric soltuion must be discarded.

Exposure: About 5cc of dosimetric solution was placed into a clean ampule, and expose to gamma radiation for a carefully measured length of time. After removal from the radiation field, the optical density should be read using the spectrophotometer on the same day, using un-irradiated ferrous solution as the blank. From the optical density of the irradiated sample, obtain the ferric ion concentration from the calibration curve. The dose divided by the time lapsed gives the dose rate at that point.

4.12 EQUILIBRIUM SWELLING TIME

The crosslinked film was cut into approximately 6" x 8" pieces, and accurately weighed. They were then rolled with the interlayer and put into test tubes filled with the grafting solution, kept at 25 ± 1°C. At various time intervals, the film was taken out, blotted dry with tissue paper, and weighed. This was done at least in duplicate and the weight gain is calculated as the grafting solution swelled into the film.

$$\% \text{ Weight Gain} = \frac{W_t - W_o}{W_o} \times 100$$

where W_t and W_o are the weights at time t and time zero. A typical swelling curve is given in Figure 8-13.

4.13 WASHING TEMPERATURE

The grafted membrane after removal from the film reactor was air dried. A 12" x 12" piece was cut and boiled in water for 10-15 minutes. After cooling, it was put into a 4% KOH beaker and kept at 100°C for three minutes. The membrane was then washed with water, blotted dry and used for electrical resistance and cycle life testing. These are the conditions set for an initial indication of the electrical properties of the grafted membrane.

4.14 GRAFT UNIFORMITY

Eight pieces of crosslinked film, each about 12" x 12" were accurately weighed and rolled into the production film bundle at various roll radii. After grafting, the samples were air-dried. Each was boiled in water for 10-15 minutes. It was then washed with distilled water, dilute hydrochloric acid and distilled water again. The sample was blotted dry and kept in an oven at 60°-70°C for three hours. After cooling in a dessicator, it was weighed and the weight gain recorded. The weight gain is calculated as percent graft:

$$\% \text{ graft} = \frac{W_g - W_o}{W_o}$$

where W_g and W_o are the dry weights of the grafted film in the acid form and the initial weight of the film before grafting. The percent graft is then plotted against the roll radius or footage of the film to obtain a graft distribution curve. This curve is indicative of the graft uniformity for the particular run.

4.15 ELECTRICAL RESISTANCE

The electrical resistance of the grafted membrane is measured in 40% KOH at room temperature. The membrane must be converted into the salt form from the acid form. The film was cut into a strip of two inches by five inches. It was boiled in 4% KOH for three minutes, washed with water and blotted dry.

A.C. Method: The strip of film was positioned into the resistance cell, making sure the film lay flat between the electrodes, and no air bubble was between them. The cell was closed, and clamped using a stainless steel forcept. The switch of the bridge was turned on, and the resistance was adjusted by the fine control until a null in the A.C. Voltmeter was reached. The membrane was removed, and the resistance without the separator was obtained. The difference between these two values gives the resistance of the separator. Typical data are shown in Table 8-17.

D.C. Method: Separator samples were cut to 1¼" x 1¼" and soaked in 40% KOH overnight. The membrane was placed in the center of the resistance cell, and the cell was closed by tightening the wing nuts. The 40% KOH was allowed to flood the cell and fill the wells containing the reference Hg/HgO electrodes through the capillary tubes. A pinch clamp was used to close one of the filling tubes. A current of 20 milliamperes was passed through the cell between the two working cadmium electrodes. The potential drop E across the membrane was determined with the electrometer. Before and after measuring the separator resistance, a run was made without the separator. This is the potential drop E without the membrane. The separator resistance R" is calculated by:

$$R'' = \frac{(E' - E)A}{I}$$

where A is the exposed area ($0.049 in^2$) and I is the current (20 ma). Typical data are shown in Table 8-18.

4.16 CYCLE LIFE

A three plate cell was made with two silver plates and one zinc plate, all supplied by the Electric Storage Battery Company. Separators were cut into 4½" x 5½". The membrane was U folded with the zinc plate in the middle and the two silver plates on the sides, separated by a single layer of membrane. The assembly was slid into a plexiglass cell and shimmed tight with plexiglass shims 2" x 1 7/8" x 3/16". It should be very tightly packed. Then 7cc of 45% KOH was added to the cell and the cell was sealed with parafilm and masking tape. Where the leads of the plates protruded out, it was sealed with paraffin wax.

Cell Formation: Since the silver plates are supplied as metallic silver while the zinc plates are supplied as zinc oxide, they must be formed before cycle life testing is started. A group of eight cells were connected in series, and a charging current of 150 ma was passed through the cells using a D.C. power supply for 20 hours. Late in the program, each cell was formed separately in the cycle life tester itself by bypassing the cycle timer. After disconnecting from the power supply, each cell's open circuit voltage was checked with a voltmeter. If the open circuit voltage was less than 1.8, the cell was re-formed.

Cell Capacity: The theoretical capacity of the cell can be calculated from the weight of the reactants. In the silver oxide-zinc couple,

$$\begin{array}{l} Zn + AgO \rightarrow Ag + ZnO \\ 65.36 \quad 123.9 \end{array}$$

189.27g of reactants yield 2 Faradays or 53.6 ampere-hour capacity. The weight of ZnO in the zinc plate is 3.82g. and the weight of silver in the silver plate is 6.28g. In the 3-plate cell, assuming only half of the silver is used, this gives a total reactant of 10.10g. corresponding to a theoretical capacity of 2.83 ampere-hours. The actual capacity of the cell was found by discharging across a fixed 2-ohm resistor, and summing the product of current and time. Typical data are given in Table 8-26.

Cycle Life: After the cells were fully formed, they were connected to the cycle tester. The cycle consists of 35 minutes of discharge at 1 ampere and 85 minutes of charge at 450 ma, corresponding to about 40% depth of discharge and 9% overcharge. The cut-off voltage during discharge is set at 1 volt while the cut-off voltage during charge is set at 2.05 volts. A cycle is considered "failed" if the voltage under load during discharge is lower than 1 volt. Failure could be due to shorting if the open circuit voltage is zero after the completion of a full charge cycle, or due to capacity loss if the open circuit voltage is not zero. Once every 12 cycles the current and voltage for one complete cycle was recorded. This gives information on the discharge and charge characteristics of the cell.

4.17 EXCHANGE CAPACITY

The exchange capacity of the separator was determined by equilibrating a weighed sample of the separator in the acid form in standardized potassium hydroxide and then back titrating with a known concentration of hydrochloric acid to determine the equivalence of potassium hydroxide consumed. This is assumed to be the exchange equivalent of acid groups present in the separator.

$$\text{Exchange Capacity} = \frac{N_o - N_f \times 1000}{W_s}$$

N_o = original normality of potassium hydroxide
N_f = final normality of potassium hydroxide
W_s = dry weight of membrane sample in acid form

The exchange capacity is given in milliequivalence per gram of the separator. The equilibration period for the separator in the standardized potassium hydroxide was set at twenty-four hours at 25°C.

4.18 MOISTURE CONTENT

The moisture content of the separator is determined by the Karl Fisher titration. A 3" x 3" piece was cut and dried at 40°C overnight. The film was stored in a dessicator for 24 hours. To the titration vessel was added 20cc of anhydrous methanol. Stirring was started, and the whole system was made dry by adding a few drops of the Karl Fisher reagent until the needle in the conductance meter indicated 4-5 (end point). The film was quickly introduced into the titration vessel and stoppered. The amount of Karl Fisher reagent consumed was measured. After the titration, 5 cc of a Karl Fisher Water Standard was added to the vessel, and the amount of reagent consumed was again measured. The water standard was supplied with 1 mg of H_2O per 1 cc so that the amount of the reagent consumed is directly related to the mg of water in the sample. Standardization of the reagent has to be done once daily to eliminate moisture absorption error.

4.19 HULL TEST

The Hull Test was determined under the following conditions:

Size of Cathode Zinc Plate	3 7/8" x 2 1/2"
Anode Zinc Plate	2 1/2" x 2 1/2"
Electrolyte	1 M. ZnO in 45% KOH
Current	1 ampere
Separator	6" x 5" in the salt form

After the cathode and anode plates were cut from a zinc sheet, the edges were sanded to a smooth surface to avoid cutting the separator. After the sanding, both plates are washed in a solvent, such as acetone, to remove any surface dirt. The smaller plate is connected to the positive terminal. The prepared piece of film must now be fitted to the larger (3 7/8" x 2 1/2") plate. The film is first folded in half along its length covering the plate evenly. That film extending beyond the sides of the plate is folded backwards and securely taped. That film remaining above the plate is cut, so that it fits tightly around the plate with no excess. This plate is placed in the Hull Test Unit and connected to the negative terminal. The connection must be in contact with the zinc plate, and is therefore, slipped under the film. The connecting clip should clamp onto the cell wall. After this is done, the 45% KOH-ZnO solution is poured to the filling line on the test cell. The current is then passed at 1 ampere. A timer should be used and set at 15 minute intervals. The test for dendrite formation is a visual one with most of the films showing dendrite formation at the closest distance between the plates. The time when the dendrites just penetrate the film is recorded as the failure time.

4.20 DIFFUSION TEST

The diffusion of zinc and silver were measured according to the techniques outlined in the "Battery Separator Screening Methods," or using the method developed in this program which employs an R A I Batch Dialyzer and Atomic Absorption Spectrophotometer. In reporting the results, the method should be specified although the two methods are comparable.

Zinc Diffusion

The Potentiometric Method: This method uses an amalgamated zinc electrode as the sensing electrode with Hg/HgO as the reference electrode. For every 10-fold change of zincate ion concentration, there is a change of 0.0295 volt in the potential of the zinc-zincate ion couple.

A disc about 3" in diameter was cut from the separator and soaked in 45% KOH overnight. After centering the separator in the plexiglass cell, it was closed by tightening the wing nuts. Stirring in the two half-cells was started when one side of the cell was filled with zinc-free 45% KOH and the other side was filled with the zinc-rich 45% KOH. The two electrodes were clamped in the zinc-free side with nitrogen bubbling through the solution. The voltage was read using a potentiometer as a function of time. Time zero was taken as the time at which the voltage begins to change. A calibration curve is shown in Figure 8-24 and typical diffusion data are given in Table 8-24. The temperature should be constant as possible. The diffusion properties are characterized by the flux value

$$k\,(\text{Moles/in}^2\ \text{min}) = \frac{(C_2 - C_1)(\text{Compartment Volume})}{(t_2 - t_1)(\text{Exposed areas})}$$

In our case, the compartment volume is 250cc and the area is 2.40 in^2. C_2 and C_1 were the zincate concentrations read off from the calibration curve.

<u>The Atomic Absorption Method</u>: This method uses the flame-photometry to measure the zincate ion concentration directly. Again, a calibration of zincate ion and the optical density is required, but can be done easily. The diffusion unit is an R A I Batch Di lyzer which could provide stirring immediately next to the two membrane surfaces, affording precise control over the boundary layer. In addition to the flux value, a true permeability constant is calculable.

A disc about 4" in diameter was cut from the separator and soaked overnight. After placing the soaked membrane in the dialyzer unit, the 45% KOH solutions, zinc poor and zinc rich, were introduced into the half cells simultaneously. Then stirring was dialed to the 5.5 scale which gives a stirring rate of 110 rpm. 2cc of sample was taken from the zinc poor side periodically and the volume adjusted by turning the volume-adjust screw. The zinc concentration was determined by atomic absorption spectrophotometer model 448 by Beckman Instrument,Inc. The conditions were listed below.

Air Pressure = 10.5 psi
Acetylene = 3.8 psi
Slit = 6
Wave Length = 218 mu
Filament Current = 11 ma

A standard solution of zinc was obtained from the same company and diluted to various concentrations. After reading in the spectrophotometer, a calibration was set up. The samples from the zinc poor side were measured. Typical data are shown in

Figure 8-26. The zinc flux is calculated from the slope of the time-concentration curve.

$$K(\text{Mole/in}^2\ \text{min}) = \frac{\Delta C}{\Delta t} \times \frac{0.235 \times 10^{-3}}{65.4 \times 6.49}$$

where $\frac{\Delta C}{\Delta t}$ is the slope, ΔC in ppm and Δt in minutes. The compartment volume is 235cc and 6.49 is the exposed area in in^2.

Silver Diffusion: In the silver diffusion experiment, the concentrations in both the silver rich and silver poor cells were measured by flame photometry. The conditions for silver measurement were as below:

Air Pressure = 10.5 psi
Acetylene = 3.5 psi
Slit = 6
Wave Length = 332.5 mu
Filament Current = 5 ma

A standard solution of silver was supplied by Beckman Instruments, Inc. Calibration curve of silver concentration and optical density was constructed. It was found no silver diffused through into the silver poor cell. Typical data are presented in Figure 8.27.

4.21 SWELLING CHARACTERISTICS IN 45% KOH

From the dry finished membrane, pieces 4 1/2" x 3 1/2" were cut. The film pieces were placed on a smooth glass plate and measured with a stainless ruler to the nearest 1/16". The film pieces were then swelled in a 45% KOH bath kept at 24 ± 1°C for one hour. They were removed with a tweezer and again measured wet on a glass plate. The dimensional change is calculated from :

$$\%\ \text{Area Change} = \frac{A - A_o}{A_o} \times 100$$

where A_o, A are the area of film before and after swelling. The linear changes in length and width are also taken by difference before and after swelling.

5.0 PLANT LAYOUT

5.1 Introduction

The results of this manufacturing process development program has resulted in a number of significant improvements in processing techniques which decrease the investment necessary to manufacture one million square feet of membrane per year. Of particular importance in this regard are:

A. Film can be crosslinked continuously at the rate of thirty feet per minute and the equipment necessary to accomplish this does not require an area of more than 6 feet by 8 feet. The crosslinking can be accomplished economically by renting time at a radiation facility. Therefore, no investment cost for purchase or housing a beta radiation facility on site is necessary. The cost for rental of sufficient time to crosslink 1,000,000 is $30,000/year or 3¢/square foot of crosslink film. The investment cost to house such a facility plus maintenance over the time required to depreciate the facility (20 years) would result in close to 3¢/foot square. This results from $15,000/year operational cost plus depreciation of $15,000 per year over 20 years on a $300,000 installation.

B. The radiation reaction time required to graft the crosslinked film has also been reduced from seven days to two days. This improvement in manufacturing processing will result in considerable savings in labor and equipment necessary to produce one million square feet of grafted film. Three thousand five hundred square feet of film are processed in a single reactor over two days. Therefore, if three reactor cans were available, 10,500 feet of film could be processed per week for each station in the Cobalt 60 vault. Two such stations would be required to process the 1,000,000 feet. If the reaction time required were still seven days, six reaction cans per week would be necessary. This would necessitate design of a large Cobalt 60 facility, six reaction stations, and would result in a significant increase in investment cost.

C. There are two additional improvements which were not made during the contract because of lack of funds and time. These additional improvements include winding of more than 3,500 feet of film onto a single roll and then grafting in reactors which are slightly larger than the vessels currently being used and determination of the radiation conditions which would permit grafting without homopolymer formation. The first improvement would result in decreasing the number of runs necessary to make 1,000,000 square feet from 300 to 250 if the roll size were increased to 4,000 square feet. This should result in savings in labor and material. If the homopolymer could be reduced the washing speed could be increased, resulting in reduced labor. Heating and water costs would also be decreased.

5.2 Space Requirements

The area necessary to house a facility for manufacture of 1,000,000 square feet of film is shown in Figure 5-1. The plant layout projected here is 10,000 square feet and is based on results of current findings. The Cobalt 60 Vault proposed can house four reaction vessels and could be reduced in size. Since the cost saving which would be realized is only about four thousand dollars and since this is amortized over twenty years, it was felt that the small additional cost on one million feet of film (0.02 cents/foot square) warrants the expansion possibility which this size vault offers.

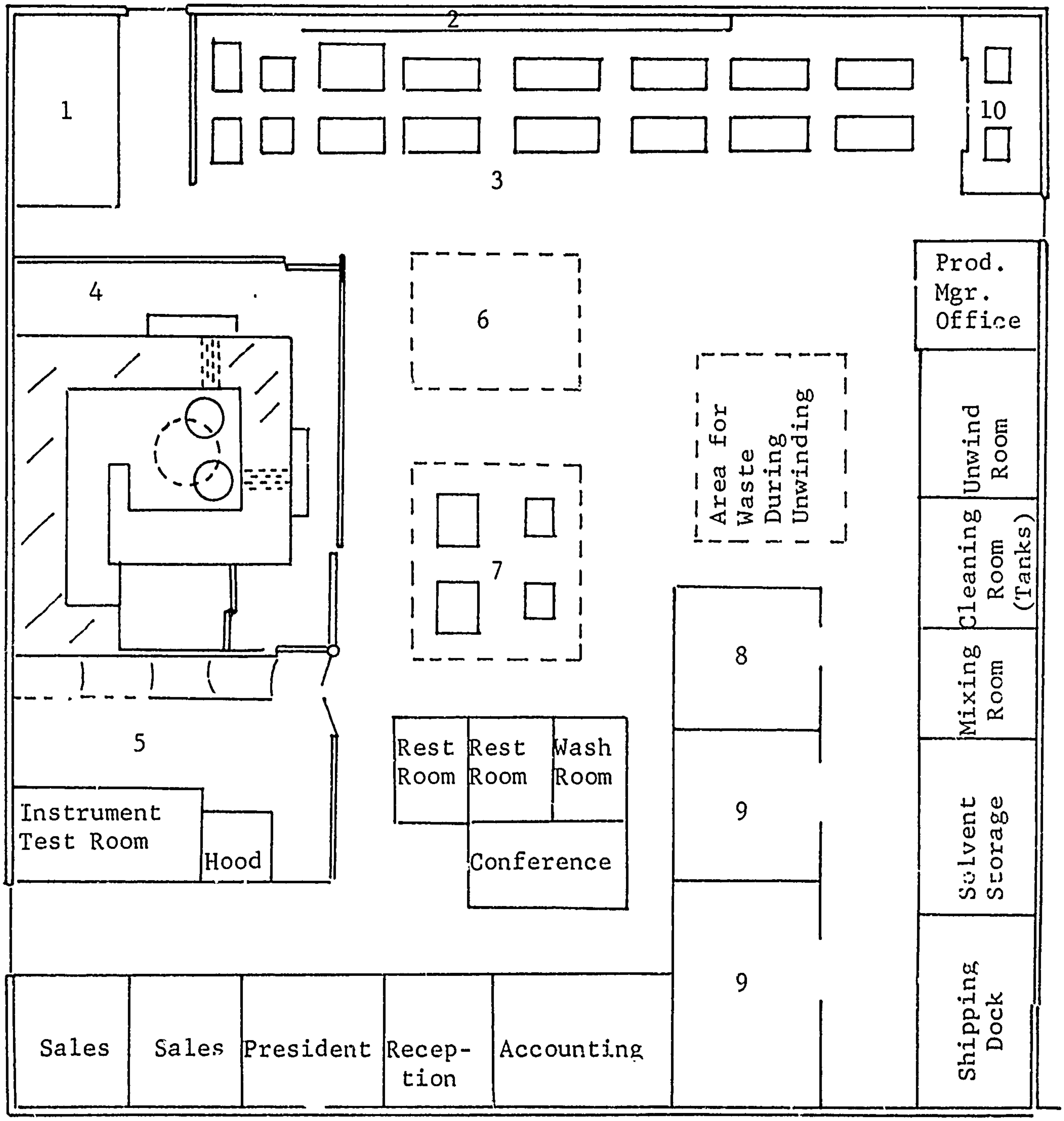
The cost analysis for manufacture of one million square feet of film (given in the next section) projects capital cost based only on a single wash line making the assumption that the washing can be accomplished on a two shift basis. In laying out the plant facility two separate wash lines are shown. The layout provides space for the second wash line although as noted it is not included in the capital cost. The cost for a second wash line with all plumbing, electrical and additional costs for a larger hood area would be about $20,000. This when amortized over 5 years would be $4,000/year or 0.4 cents per foot square. The flexibility offered by having a second line plus the assurance of no down time may warrant this investment.

The laboratory area would house all of the test equipment necessary for quality control. This laboratory would be partitioned and certain pieces of equipment would be kept separate. For example, the constant temperature bath would be kept in the larger laboratory along with the tensile tester, G.P.C., D.C. and A.C. resistance test fixtures, Hull test, moisture test equipment, and atomic absorption unit. In the smaller laboratory the infrared, ultraviolet and cycle tester would be kept. One hood would be necessary for the Atomic Absorption Unit.

A solvent storage room is given in the plant layout. This facility could be decreased in size if a storage tank for benzene were provided. The methacrylic acid monomer would not be stored in tanks since the yearly requirement does not amount to more than 125, 50-gallon drums. The carbon tetrachloride also would be stored in drums.

The special room provided for unwinding rolls is necessary because of the homopolymer which forms and which on unrolling is readily suspended as a fine dust in the air. The mixing room, cleaning room, unwinding room and the room at the beginning of the wash line are all hooded rooms. It is possible to eliminate the need for the room in which the rolls are unwound if the homopolymer could be eliminated.

All cost for renting 10,000 square feet of space and installing all manufacture and test equipment plus general and administrative costs are given in the next section. The projected cost of the film based on these costs is also given.



1. Boiler Room
2. Electrical Controls for Wash Line
3. Wash Lines
4. Radiation Vault & Reactor Stations
5. Quality Test Lab
6. Final Packaging Area
7. Film Winding Area
8. Maintenance
9. Storage (X-Link EQ) Film, Chemicals Interlayer, Etc.
10. Hooded Room With Rolls Feeding to Wash Tanks

Figure 5-6 Preliminary Plant Layout

6.0 COST ANALYSIS FOR MANUFACTURE AND SALE OF ONE MILLION FEET OF SEPARATOR PER YEAR

6.1 INTRODUCTION

The cost which are given make the assumption that a new venture is to be undertaken to construct a facility capable of manufacture, testing and selling one million square feet of separator per year. These costs include direct manufacturing labor, direct material costs, manufacturing expenses -- which is the depreciation on facility--and production equipment and operating, selling and administrative expenses. A summary of these costs is given in Table 6-1.

TABLE 6-1

Cost Analysis Based on Production of
One Million Feet of Permion 2291 Annually

Category	Amount	Per Linear Foot	% of Total Cost
Direct Labor	$104,000	$0.104	25.2%
Direct Material	115,175	0.115	27.9
Manufacturing Expense	91,600	0.092	22.2
Operating Expense			
A. Selling	44,500	0.045	10.8
B. Administrative	57,400	0.057	13.9
TOTALS	$412,675	$0.413	100.0%
Adjusted Costs on Optional Contract Equipment at 5 Yr. Depreciation Value	(9,000)	(0.009)	
Adjusted Costs	$403,675	$0.404	
Estimated Mark-Up 30%	121,103	0.121	
Estimated Selling Price	$524,778	$0.525	

Direct Labor - Schedule I	Man Years	Annual Cost
Production		
Production Foreman	1	$ 10,000
Inspection - Quality Control and Testing - Health Physics	1	10,000
Crosslinking - Preparing Materials-Bundles - Unwind - Cleanup	5	35,000
Washing	6	42,000
Packing - Shipping and Cleanup	1	7,000
Total Direct Labor		$104,000

Direct Material - Schedule II

Film	$ 3,000
Beta Radiation Facility	32,000
Crosslinking - Liquid Nitrogen - Shipping	10,000
Interlayer	15,350
Monomer	15,000
Benzene	15,000
Carbon Tetrachloride	1,875
Cores	750
Potassium Hydroxide	2,000
Safety Equipment (Gloves, Goggles, etc)	500
Nitrogen Gas - Grafting	1,800
Gel Permeation - Outside Cost	1,400
Film for Windup	4,000
Edge Slitting - Outside Cost	7,000
Shipping Supplies	1,000
Testing Supplies - Electrodes - Paper Reagents, etc.	2,500
Freight in and Miscellaneous	2,000
Total Direct Material Costs	$115,175

Manufacturing Expense - Schedule III

Indirect Labor	
Maintenance Labor	$ 9,000
Bookkeeping Labor	4,000
Purchasing	5,000
Rent - 10,000 sq. ft.	20,000
Equipment Repair and Maintenance Contracts	2,000
Insurance	3,000
Labor Expenses - Taxes-Workmen's Compensation-Disability	8,000
Invoicing Supplies	200
Heat, Light and Power & Water	11,000
Employee Benefits	4,000
Depreciation: Pro-rated on 10,000 ft. space	
Plant - Schedule III-A	3,000
Production & Test Equipment - Schedule III-B	16,100
Radiation Badge Costs	300
Other Expenses	1,000
Waste & Rubbish Expense and Cleaning Supplies	1,800
Waste Solvent Disposal	2,200
Production Uniforms - Safety Clothing and Training	1,000
Total Manufacturing Expense	$ 91,600

Schedule of Depreciation and Amortization

	Amount	Depreciation Period	Annual Depreciation
Facility Expenses - Schedule III-A			
Plumbing and Electrical	$15,000	20 Yrs.	
Vault	25,000		
Solvent Room and Hoods	5,000		
Test Laboratory	5,000		
Cobalt Cask	10,000		
Total Facility Expenses	$60,000	20 Yrs.	$3,000
Production and Test Equipment - Schedule III-B			
Production Equipment			
Cobalt 60 Source	8,000	5 Yrs.	
Crosslinking With Auxiliary Equipment	11,000		
Washing Line-Tanks and Drives, Heating	6,000		
Electrical Controls	4,800		
Drying	500		
Pay-Out Stand	600		
Slitting	150		
Steam Boiler-Heat Exchanger	500		
Installation Costs	500		
Wind-Up Stand	500		
Preparing: Roll, Solution and Unwinding Roll			
Wind-Up Stand	600		
Take-Up Drive (Special)	600		
Brake	100		
Explosion Proof Hoist	450		
Drum Handling Equipment Roller	800		
Mixing Pump	450		

	Amount	Depreciation Period	Annual Depreciation
Radiation Reaction			
Reactor: Including Drive Motor, Blow-Out, Transmission, Stainless Pipe, Valves, Connections, Flexible Connectors	$ 6,000	5 Yrs.	
Pumps (Explosion Proof Motors)	1,000		
Temperature Probes	500		
Flowmeters	200		
Heat Exchanges and Heating Solenoid	750		
Temperature Read Out and Recorders	3,000		
Oxygen Analyzer (2)	1,000		
Test and Quality Control Equipment			
Tensile Tester, With Special Low Load Jaws and Heating Box	8,000		
Infrared	4,000		
Ultraviolet	3,500		
Refractometer	1,000		
Constant Temperature Water Bath and Cooling Unit	700		
Thickness Gauge	100		
A.C. Resistance Test	1,000		
D.C. Test Equipment	400		
Ag, Zn Dialyzer	2,000		
Atomic Absorption	3,800		
Cycle Tester (2)	4,000		
Karl Fisher Moisture Tester	350		
Miscellaneous Equipment-Glassware, etc.	1,000		
Miscellaneous Equipment			
Storage Racks	350		
Tables-Shipping, Film Handling	300		
Radiation Detection Equipment	1,000		
Radiation Equipment on Vault	1,000		
Total Production and Testing Equipment	$80,500	5 Yrs.	$16,100

Operating Expenses - Schedule IV

Selling Expenses - A

Division Director (1/2)	$12,500
Labor - Salesman	15,000
Operating	7,000
Fares and Travel	10,000
Total Sales Expense	$44,500

Administrative Expense - B

Executive Office	$ 9,000
Division Director (1/2)	12,500
Secretarial	6,500
Supplies - Postage	1,000
Publications	700
Telephone	2,400
Legal - Licensing	25,000
Personnel	300
Total Administrative Expenses	$57,400

7.0 CONCLUSION

The goals of this manufacturing process contract have been successfully accomplished. Results substantiate the conclusion that one million square feet of separator material with performance equivalent to Permion 2291 and having a lower resistance (30 ± 6 milliohms) can be manufactured with excellent uniformity and reproducibility. Qualification tests necessary to substantiate the uniformity and reproducibility have been standardized.

The economics indicate that the specified material can be sold at a cost of approximately $.50/square foot which was the original goal. In addition to the working capital necessary for inventories, labor and operating costs, a capital investment of $140,500 is required. Fixed facility costs are amortized over twenty years and capital equipment costs amortized over 5 years. It is also assumed that the plant facility is rented at $2/foot square per year.

8.0 RECOMMENDATIONS

The results of this manufacturing contract indicate that the manufacturing procedure currently used can be modified to effect cost savings. This is possible by:

1. Redesign of the reactor container to house 5,000 square feet of film. This was an original goal of the program which was not realized when it became necessary to use a thicker interlayer material. Greater production was sacrificed for product quality. Based on our final results it is recommended that additional work be done to scale up this phase of the production. If a reactor could yield 5,000 square feet of film then the number of reactions necessary to produce 1,000,000 square feet could be reduced to 200/year. This would effect material and labor savings.

2. The grafting parameters should be evaluated with respect to decreasing homopolymer formation during the reaction. As noted one of the runs (#3) conducted during this program resulted in a film with a high graft and no homopolymer. It is believed this was due to bleeding an optimum amount of air into the reaction vessel during the run. This effectively stopped the homopolymer reaction without decreasing the grafting. If the grafting can be accomplished without formation of homopolymer a significant decrease in labor could be realized.

3. Material prepared under this manufacturing contract which had a high percent graft 80% or greater, has a resistance below 20 milliohms. It is proposed that some of these highly grafted materials be evaluated in low temperature battery requirements. Since all cycle testing in this program was with Ag/Zn batteries the quality of the membrane is based on cycle testing in this more stringent environment. Consideration should be given to cycle testing the recommended separator and some of the higher grafted membranes which have lower

resistance in the cold. Though the higher grafted membranes tend to fail earlier in the silver zinc environment, short circuit failing is still not the predominate failure mode. It is conceivable that the higher grafted films may give a decided advantage in certain specific battery requirements. This should be determined.

9.0 REFERENCES

1. D'Agostino, V., Lee, J. and Orban, "Development of Improved Separator Material for the Alkaline Silver Oxide-Zinc Battery", R A I Subcontract D-R164719, AF No. 33(615)-3487, R A I Report No. 407, Final Report August (1968).

2. Trump, et. al., J. Appl. Phys., 21 346 (1950).

3. Charlesby, A., "Atomic Radiation and Polymers", Pergamon Press (1960).

4. Keusch, P., et. al., NASA CR 1384 September (1969).

5. Keusch, P., et. al., "Investigation of Shipping Volume Reduction of Plastic Shapes", Final Report Contract DAAD05-69-C-0092, U. S. Army; R A I Research Corporation Report No. 412, July (1969).

6. Chapiro, A., "Radiation Chemistry of Polymeric Systems" John Wiley & Sons, Inc., New York (1962).

7. Ceresa, R. J., "Block and Graft Copolymers" Butterworth and Company, London (1962).

8. Molan, G. E., editor, "Colloidal and Morphological Behavior of Block and Graft Copolymers", Plenum Press, New York (1971).

9. Wild, L. and Guliana, R., "Gel Permeation Chromatography of Polyethylenes, Effect on Long Chain Branching", U.S.I. Chemical Company (1967).

10. Lander, J. and Cooper, J., "Battery Separator Screening", edited by Cooper and Fleischer.

11. Carton, T. H. and Colburn, A. P., Ind. Eng. Chem., 26, 1183 (1934).

12. Dirske, T. P., Zinc Electrode Kinetics Research Contract No. F33615-70C-1022, Annual Report W.PAFB December 15, 1970.